

NSRDS-NBS 53

U.S. DEPARTMENT OF COMMERCE / National Bureau of Standards



Crystal Structure Transformations in Inorganic Nitrites, Nitrates, and Carbonates



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Foreword

The National Standard Reference Data System provides access to the quantitative data of physical science, critically evaluated and compiled for convenience and readily accessible through a variety of distribution channels. The System was established in 1963 by action of the President's Office of Science and Technology and the Federal Council for Science and Technology, and responsibility to administer it was assigned to the National Bureau of Standards.

NSRDS receives advice and planning assistance from a Review Committee of the National Research Council of the National Academy of Sciences-National Academy of Engineering. A number of Advisory Panels, each concerned with a single technical area, meet regularly to examine major portions of the program, assign relative priorities, and identify specific key problems in need of further attention. For selected specific topics, the Advisory Panels sponsor subpanels which make detailed studies of users' needs, the present state of knowledge, and existing data resources as a basis for recommending one or more data compilation activities. This assembly of advisory services contributes greatly to the guidance of NSRDS activities.

The System now includes a complex of data centers and other activities in academic institutions and other laboratories. Components of the NSRDS produce compilations of critically evaluated data, reviews of the state of quantitative knowledge in specialized areas, and computations of useful functions derived from standard reference data. The centers and projects also establish criteria for evaluation and compilation of data and recommend improvements in experimental techniques. They are normally associated with research in the relevant field.

The technical scope of NSRDS is indicated by the categories of projects active or being planned: nuclear properties, atomic and molecular properties, solid state properties, thermodynamic and transport properties, chemical kinetics, and colloid and surface properties.

Reliable data on the properties of matter and materials is a major foundation of scientific and technical progress. Such important activities as basic scientific research, industrial quality control, development of new materials for building and other technologies, measuring and correcting environmental pollution depend on quality reference data. In NSRDS, the Bureau's responsibility to support American science, industry, and commerce is vitally fulfilled.

Gichard M. Grabert

RICHARD W. ROBERTS, Director

Preface

Many inorganic solids undergo transformations from one crystal structure to another. Studies of these phase transformations are of value in understanding the nature and properties of solids. Recent literature abounds with information on phase transformations of solids and it is often difficult to obtain relevant data or references on the transformation(s) of any specific substance. We, therefore, considered it worthwhile to collect the literature on the phase transformations of various types of inorganic solids and present them in an organized manner. As part of this program, we published monographs on binary halides (NSRDS-NBS-41) and transition metal oxides (NSRDS-NBS-49) some time ago. In this monograph, we have reviewed the important data on the crystal structure transformations of salts of three typical oxyanions, nitrites, nitrates and carbonates. These salts exhibit several types of interesting transformations which have been examined by a variety of techniques. We plan to publish reviews on inorganic sulfates and other solids in the future.

In preparing this monograph, we have surveyed most of the material abstracted up to June 1973 in Chemical Abstracts. We have listed the important references to the published literature after presenting the survey on each solid. In reporting the information on the transformations of a solid, we have indicated the methods employed as well as the important data and conclusions. For each solid, we have given the crystallographic data for the stable phase around room temperature and at atmospheric pressure, making use of the standard data published by NBS whenever possible.

We are thankful to Mr. S. Chattopadhyay for his assistance in the literature survey.

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Crystal Structure Transformations in Inorganic Nitrites, Nitrates, and Carbonates *

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A critical survey of the data describing crystal structure transformations in inorganic nitrites, nitrates and carbonates is compiled. Data on crystallographic, thermodynamic, spectroscopic, electrical, dielectric and other properties are given for each solid. Experimental techniques used to obtain the data are given and comments on the data are included in the tables. The literature is surveyed up to June 1973. References have been selected on the basis of their pertinence to the data cited.

Key words: Nitrites, nitrates, carbonates, crystal structure transformation, phase transformation, x-ray diffraction data.

Introduction

The area of phase transformations in inorganic solids has been very active in recent years and the subject has been reviewed recently by Ubbelohde [1] ¹ and Rao [2, 3]. The general features of crystal structure transformations were described briefly in an earlier NSRDS-NBS monograph from this laboratory [4]. In this monograph we shall confine our attention to the crystal structure transformations in inorganic nitrites, nitrates and carbonates. We have chosen these systems as our first set of typical oxyanion salts in view of their interesting properties and transformations and also because the reviews of the thermal decompositions of these salts have been recently published by the National Bureau of Standards [5, 6].

All the three oxyanions, nitrite, nitrate, and carbonate, are sp^2 hybridized with bond angles close to 120°. The N—O distance in ionic nitrites and nitrates is close to 1.2 Å and the C—O distance in carbonates is 1.3 Å. In some of the salts, these anions form fairly strong covalent bonds particularly with the transition metals.

Inorganic nitrites, nitrates and carbonates show a variety of interesting properties of particular interest to the subject of this review. Thus, NaNO₂ exhibits a well-characterized ferroelectric transition near 438 K. NaNO₃ undergoes an order-disorder phase transition associated with the rotation of the nitrate ion. Many other ionic nitrates also exhibit transitions determined by the orientation of NO₃ ions. RbNO₃, NH₄NO₃, and TlNO₃ undergo several transitions and the different phases are structurally related. KNO₃ transforms from the orthorhombic aragonite phase to the rhombohedral calcite phase near 403 K, but on cooling, the calcite phase reverts back to the aragonite phase through an intermediate ferroelectric phase. CaCO₃ with a critical radius ratio of 0.67 exists as aragonite with a cation coordination of 9 or as calcite with a coordination of 6. The aragonite-calcite transformation proceeds by a reconstructive mechanism and such transitions are also found in nitrates. While aragonite transforms to calcite on heating, the latter reverts back to aragonite only under pressure. Impurities affect phase transitions of several of the oxyanion salts. Under high pressures, many of these oxyanion salts exhibit new phases of interest. We shall now systematically review the phase transitions of nitrites, nitrates and carbonates of the various elements.

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^{*}Supported by Project G-77 of the National Bureau of Standards under the Special International Programs.

¹ Figures in brackets indicate literature references at the end of each section.

- [5] Stern, K. H., and Weise, E. L., High Temperature Properties and Decomposition of Inorganic Salts, Part 2, Carbonates, NSRDS-NBS-30, National Bureau of Standards, November 1969.
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Units, Symbols, and Abbreviations

- $P = Pressure; 1 \text{ atm.}, (\sim 1 \text{ bar}) = 101325 \text{ Nm}^{-2} = 1013250 \text{ dyn cm}^{-2}$
- T = Temperature in kelvins
- $R = \text{Gas constant} = 8.3143 \text{ J mol}^{-1} \text{ deg}^{-1} = 1.98717 \text{ cal mol}^{-1} \text{ deg}^{-1}$
- J = Joule
- C = Coulomb
- Hz = Hertz (cycle/second)
- V = Volt
- cal = Thermochemical calorie = 4.1840 J
- $T_{\rm t}$ = Transformation temperature
- ΔT = Thermal hysteresis in a reversible transformation
- $\Delta H_{\rm tr} = {\rm Enthalpy\ change\ accompanying\ the\ transformation}$
- $\Delta S_{\rm tr} = Entropy$ change accompanying the transformation
- ΔV *=Entropy change accompanying the transformation
- $T_{\rm c}$ = Curie Temperature
- $T_{\rm N}$ = Néel temperature
- C_p = Heat capacity at constant pressure
- $C_{\rm m}$ = Magnetic heat capacity
- σ = Electrical conductivity
- ρ = Density (in grams per cm³)
- ϵ = Dielectric constant
- tan δ = Dissipation factor
- $P_{\rm s}$ = Spontaneous polarization
- $E_{\rm c}$ = Coercive field
- $E_{\rm a}$ = Energy of activation
- ΔG = Gibb's free energy change
- χ = Magnetic susceptibility
- τ = Relaxation time
- Z = Number of molecules per unit cell
- IR = Infrared
- UV = Ultraviolet
- DTA = Differential thermal analysis
- NMR= Nuclear magnetic resonance
- NQR = Nuclear quadrupole resonance
- ESR = Electron spin resonance.

1. Nitrites

The nitrites of only the alkali metals (especially Na and K) have been extensively studied and these undergo phase transformations. The following is an account of the available information regarding the phase transitions of inorganic nitrites.

1.1. Alkali Metal Nitrites

The transformation temperature, melting point, dissociation point, and the heat of transition of alkali metal nitrites are given below [1-3]:

i ransitions in aikan metai nitrite	Transitions	in	alkali	metal	nitrite
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	<i>T</i> _t , K	Melting point, K	Dissociation point, K	$\Delta H_{\rm tr},$ cal mol ⁻¹
LiNO ₂	367	493	503	_
NaNO ₂	439	555	703	250
KNO ₂	320	711	753	120 ± 30
RbNO_2	348	695	793	500 ± 50
CsNO ₂	393	673	783	1100 ± 100

The transformation temperature, T_t , does not show any systematic trend. The transformations in LiNO₂, RbNO₂, and CsNO₂ have not been studied in detail, but a number of workers have investigated the transformation in NaNO₂ and KNO₂ by a variety of techniques.

Lithium Nitrite, LiNO₂ (No crystal data seem to be available).

Protsenko and coworkers [3] have reported a phase transformation in lithium nitrite at 367 K. The transformation has been characterized by the anomaly in the DTA and electrical conductivity measurements.

Sodium Nitrite, NaNO₂, orthorhombic (bodycentered), C_{2v}^{20} -Im2m, z = 2, a = 3.570 Å, b = 5.578 Å, c = 5.390 Å at 299 K.

Sodium nitrite was found to be ferroelectric a number of years after the discovery of its phase transition and the literature on the ferroelectric transition of NaNO₂ up to 1962 has been reviewed by Jona and Shirane [3a]. Ferroelectricity in this compound was predicted by Zheludev and Sonin [4] in 1957 from the changes in point group symmetry due to the ferroelectric phase transition and was independently observed by Sawada et al. [5]. During the past decade, this solid has attracted considerable attention which has led to numerous investigations of its various physical properties such as dielectric constant [6-10], domain structure [11-13], specific heat [14-16], thermal expansion [14, 16-18], thermal conductivity [19], electrical resistivity [20], NMR [21], x-ray diffraction [12, 17, 22, 23], and optical properties [24-27].

Sodium nitrite at normal temperature and pressure has a body-centered orthorhombic unit cell. It is ferroelectric with the spontaneous polarization parallel to the *b*-axis and undergoes a first order transformation to the paraelectric phase around 438 K. Between the ferroelectric (III) and paraelectric (I) phases, a sinusoidal antiferroelectric phase (II) has been reported to exist over the narrow temperature range of 436.8-438 K [10, 10a, 15, 16, 18, 21, 28].

In the ferroelectric phase, the $NO_{\overline{2}}$ ions are parallel in the *a*-planes; the ordering parameter of the NO_2^- ions in the *a*-plane changes sinusoidally along the *a*-axis with a period of about eight layers [28]. Sawada et al. [29] have studied the domain reversal of NaNO₂ and discussed the "Himidashi" (bulging out) phenomenon peculiar to this solid caused by the variation of spontaneous polarization (P_s) and the coercive field (E_c) with the size of the electrode. Recently, Flügge and Meyenn [29a] have studied the theoretical aspects of the order-disorder transition in NaNO₂ in which a two sublattice model of interacting dipoles is treated in a molecular field approximation to describe the ferro- and paraelectric properties of NaNO₂. Polarization values thus calculated, are found to be in good agreement with experiment for the narrow antiferroelectric domain not resolved by the model. Yamada and Yamada [29b] had pointed out earlier that the long-range, dipole-dipole type interaction plays the important role to initiate the phase transitions in sodium nitrite.

In addition to the transitions, III \rightarrow II and II \rightarrow I, some anomalies at 375, 451, and 488 K have also been reported [17, 18, 30]. These anomalies are believed to be related to anisotropic vibrorotatory states of the NO₂ ions.

Gesi [31] has reported a new phase transformation (III-IV) in ferroelectric NaNO₂ at 178 K from precise measurements of thermal expansion and low frequency dielectric constant at normal pressure. Phase IV is a high pressure phase existing at 8 kbar and room temperature and is described in detail later in this section. This III-IV transition did not show any thermal hysteresis and is of second order since no discontinuous change was found either in dielectric constant or volume thermal expansion measurements.

High Pressure Transformations: Bridgman [32] detected a high pressure transition, probably of the second order, as a break in the slope of the compression curve of the solid. This transition was also observed optically by Lippincott et al. [33] in their high pressure anvil device. They measured the bending vibration frequency ν_2 of NO₂ in NaNO₂ at high pressure and found an abrupt change in ν_2 from 825 cm⁻¹ at atmospheric pressure to 855 cm⁻¹ after the III-IV transition at 14.5 kbar. This indicates a change in the electronic structure (or the shape of the NO_2 ion) during the III-IV transition. Rapoport [34] has determined the phase diagram of NaNO₂ up to 40 kbar and from room temperature to 773 K. The phase diagram consists of five solid phases abbreviated as I, II, III, IV, and V. The I, II, and III phases are the paraelectric, antiferroelectric, and ferroelectric phases, respectively. Phase IV is identical to the high pressure phase described by Bridgman [32] and is the same found by Gesi [31] below 178 K. Phase V is another high pressure phase which exists just below the melting point above 10 kbar. Rapoport has indicated that the extrapolation of III-IV phase boundary to atmospheric pressure gives a temperature of 168 K. The problem whether the room-temperature phase III transforms to the high pressure phase IV at atmospheric pressure or not is interesting. The ferroelectric Curie point, $T_{\rm c}$, (III-II phase transition) and the Neel point, $T_{\rm N}$ (I–II phase transition) were detected by DTA up to 40 kbar. These results were found to agree well with those of Gesi [31].

Measurement technique	Observations	Remarks	References
X-ray diffraction	<i>T</i> ₁ , 436 K	Ferroelectric NaNO ₂ crystal transforms through the first order transition to an antiferroelectric phase with a sinusoidal modulation of the moment in which the antiferroelectric order is partially attained. The system transforms to a paraelectric phase at a higher temperature. The suc- cessive appearance of these phases, the order of transition, the temperature de- pendence of the order parameter and the anomalous volume expansion are ex- plained by a thermodynamic calculation on the basis of a molecular field approxi- mation.	[28].
X-ray investigation of the dis- ordered structure of NaNO ₂ near T _c (~ 433 K).		 The observed diffuse scattering, the satellites and the plate-like diffuse scattering normal to the b-axis around them can be interpreted on the basis of a disordered arrangement of two kinds of structural units. The atomic positions in each structural unit were determined from the relative intensity of the Bragg reflections and that of the satellites. The structure factors and the corresponding Fourier synthesis were also calculated. It is concluded that at 423 K, about 15 percent of the NO₂ groups are in their centrosymmetric positions. 	[23, 35].
Differential Thermal Analysis	<i>T.</i> 433–435 K		[37].
Differential scanning calo- rimetry.	Enthalpy of phase transition, $\Delta H_{\rm tr}$, 299 ± 33 cal mol ⁻¹ .		[38].
Specific heat measure- ments in an adiabatic calorimeter.	The specific heat starts to increase anoma- lously at 373 K. At 436 K, there is a sharp peak in the curve. At 437 K a small peak appears after which the specific heat decreases gradually with increasing temperature up to 453 K.	The first anomaly corresponds to the first order ferroelectric to antiferroelectric phase transition, while the second anomaly is regarded to be due to an antiferroelectric-paraelectric phase tran- sition.	[15].
Thermal conductivity in the range 343-463 K along <i>a</i> , <i>b</i> , and <i>c</i> axes.	Thermal conductivities in the b and a directions show a gradual decrease on heating over a wide temperature range of 50 K below the transition. This decrease is due to an additional thermal resistivity. No anomaly is found in the temperature dependence of thermal conductivity in the c-direction.	A tentative model of the order-disorder arrangement of the $NO_{\overline{z}}$ ions is pro- posed to account for the origin of the additive thermal resistivity in which uneven interatomic forces, due to the disordered as scattering centers of pho- nons.	[19].
Thermal expansion and di- electric studies.	A new phase transformation at 178 K in NaNO ₂ (ferroelectric phase) is indi- cated by slight break in these properties both in dielectric constant versus temp. and thermal expansion versus tempera- ture curves.	The transition is believed to be the III-IV transition in which the ferroelectric NaNO ₂ transforms to the high pressure phase which exists above 8 kbar at 298 K.	[31].

 $NaNO_2 - Continued$

Measurement technique	Observations	Remarks	References
Dielectric Studies, in dc bias fields up to 3.5 kV cm ⁻¹ at 436–437 K.	The temperature range studied is between T_c (Curie Temperature) and T_N (Neel Temperature).	It is difficult to conclude whether the ferro- electric phase to sinusoidal phase transi- tion becomes first order with increasing bias fields. The sinusoidal state narrows gradually and disappears at ~ 2.6 kV cm ^{-1.}	[39].
Dielectric and pyroelectric measurements (ϵ meas- ured along the ferro- electric <i>b</i> axis.	ϵ_b shows a distinct anomaly at T_c and obeys Curie-Weiss law, below and above T_c . The ratio of the Curie constants was found to be 9.6:1.		[6].
Experimental (dielectric con- stant, pyroelectric current etc) and theoretical studies.	ϵ shows a peak at 437.2 K while heating and 435.6 K while cooling. Dielectric dispersion exists in all axial directions $P_s \sim 8.6 \ \mu C \ cm^{-2}$ estimated from pyro- electric current measurements, at room temperature.	Ferroelectricity in NaNO ₂ is discussed phenomenologically taking account of the electrocaloric effect. It is concluded that the transition in NaNO ₂ is a first order one and that the main contribu- tion to the spontaneous polarization comes from the relative displacement between Na ⁺ and NO ₂ ions. Also the ferroelectric NaNO ₂ is half-way between an ionic and a molecular crystal.	[9].
Electrical conductivity (poly- crystalline pellet).	The conductivity-temperature curves showed discontinuities or change in slope at or near the transformation tempera- ture.	·	[40].
Infrared Spectra	Transitions are associated with changes in vibration frequency. NaNO ₂ exhibits changes of all the parameters of the Urbach equation.	Transition in ferroelectric crystals can be correlated with dynamic theories of the crystal lattice of NaNO ₂ .	[41].
Raman Spectra range: 303– 451 K.	Raman lines show marked changes near the transition points.	A group theoretical treatment of the vibra- tional spectrum of the NaNO ₂ crystal is presented for the low and high tempera- ture modifications of NaNO ₂ .	[42].
Range: 313-493 K	The temperature dependence of frequen- cies of bands at 119, 153, and 220 cm ⁻¹ shows an abnormal decrease in the fre- quency of the dipole vibration at 153 cm ⁻¹ .	The decrease in the dipole vibration fre- quency has been discussed on the basis of the Ginzburg-Anderson-Cochran theory.	[43].
Range: 323-455 K	Spontaneous polarization disappears above the λ-point.	The disappearance of P_s has been explained partially by reorientation of some NO ₂ ⁻ groups as a result of their rotation by 180° around the axis parallel to the line joining O-atoms. The forms of normal vibrations are considered on the basis of symmetry coordinates and the intensity of lines. Recent studies [45a], however rule out any major difference between the low and high	[44, 45].
		temperature spectra. It seems that crys- tal symmetry is not changed during the transformation.	
Ultraviolet Absorption spectra.	A gradual shift of absorption bands is found to accompany thermal expansion of the crystal. An abrupt change in the absorp- tion spectrum is observed at transforma- tion points. $T_t \sim 313-323$ K (II \rightarrow I) (marked hysteresis).	These two effects of temperature seem to be correlated. In cases where crystal struc- tures are known, shifts in absorption max- ima due to changes in temperature have been interpreted in relation to changes in the cation-anion distances.	[26].

Measurement technique	Observations	Remarks	References
Neutron diffraction	$T_{\rm t} \sim 438 { m ~K}$	The larger increase in μ_x than in μ_y' (μ = root-mean-square amplitude) for the N- atom might indicate the expected rotation about (001). μ of motion for O-atoms are ambiguous.	[46].
Nuclear relaxation	A peak is observed in the Na ²³ nuclear relaxation rates, at the ferroelectric transition.	This effect is explained on the basis of the theory of the transition in terms of lattice dynamics. It is argued that nuclear-spin- phonon relaxation can be a powerful tool of investigation for a ferroelectric tran- sition.	[47].
Nuclear quadrupole resonance.	N ¹⁴ NQR lines have been observed in the ferroelectric-phase of NaNO ₂ and the change of NQR frequencies with τ be- tween 77 and 437 K has been investi- gated. The NQR frequency seems to begin to deviate from the rigid molecule vibration model around III-IV transi- tion.	The results can be explained by an order- disorder model where the NO ₂ ions are flipping between two equilibrium sites. Disappearance of ferroelectricity can be attributed to the onset of rotation of NO ₂ ions above T_t (473 K).	[48, 49].
Effect of hydrostatic pressure on T_c and T_N up to 10 kbar.	Both T_c and T_N increase with increasing pressure.	The experimental results could be fairly explained on the basis of a phenomeno- logical model developed by Gesi. The model includes a three dimensional lat- tice strain and accounts for the dielectric constant variation in a bias field.	[50, 51].

Potassium Nitrite, KNO_2 , rhombohedral, $R\overline{3}m$, Z = 1, a = 4.455 Å, $\alpha = 68°58'$ at 298 K (54).

The room-temperature structure of KNO₂ was first considered to have monoclinic symmetry (space group C_s^3 -Am) [52], but recent studies [52a-54] have established the structure to be rhombohedral with a centrosymmetric space group R3m. The unit-cell parameters for a disordered, rhombohedral, room temperature phase according to Solbakk and Strømme [53] are: a=b=5.011 Å, c = 10.153 Å with Z = 3. The crystal structure of KNO₂ at low temperatures (253 K) has monoclinic symmetry, space group, P2₁/c, and the unit cell parameters $a = 4.16 \pm 0.02$ Å, $b = 962 \pm 0.05$ Å, $c = 6.19 \pm 0.03$ Å, $\beta = 113 \pm 1^\circ$, Z = 4. Above 313 K, KNO₂ is cubic (Fm3m), with a = 6.66 Å, Z = 4 at 318 K (53).

Three transformations are known in KNO₂. Denoting the various phases as I, II, and III, the transformations can be described as follows (55):

$$III \xrightarrow{260 \text{ K}} II \xrightarrow{313 \text{ K}} I$$

(monoclinic) (rhombohedral) (cubic)

Another transition is reported at 343 K by Tanisaki and Ishimatsu [54] who also report an appreciable dielectric anomaly at ~ 230 K. Ray and Ogg [56] report $\Delta H_{\rm tr} \sim 1200 \pm 200$ cal mol⁻¹ for the transition at 260 K. The nature of the transition around 313 K has been controversial and was considered to be a ferroelectric-paraelectric transformation by Rao and Rao [57]. Recently, Mansingh, and Smith [55] in their studies of dielectric constant and electrical conductivity have concluded that there is no ferroelectric phase in KNO₂ up to its melting point. At 313 K, there is only a crystal structure change from the rhombohedral to the cubic form. This has also been supported by the assignment of a centrosymmetric (R3m) space group to KNO₂ by Solbakk and Strømme [53]. Above 319 K, KNO₂ has the cubic NaCl structure with a = 6.71 Å [56]. Doucet and coworkers [58] have reported a hitherto unknown transition in KNO₂ at ~ 402 K from x-ray and dielectric constant measurements.

High Pressure Transformations: Bridgman [59] reported a high pressure transition in potassium nitrite. He however, used a rather impure sample (~ 89% purity). High pressure transitions at 260 K and 320 K have been reported by Ray and Ogg [56] and Hazlewood et al. [60], respectively. A continuous transformation starting at about 638 K has also been observed. Rapoport [34] and Clark and Rapoport [61] showed the phase diagram of KNO_2 to consist of the six solid phases given below:

Phase diagram of KNO2

Phase	Crystal structure	Range of stability
I	Cubic, NaCl type	Above 323 K and below 10 kbar.
II	Cubic, distorted NaCl type.	Below 323 K and 8 kbar.
III	(metastable phase)	Below 273 K and 8 kbar.
IV	Cubic, distorted CsCl type.	Above 273 K and 10 kbar.
V	Cubic, CsCl type	Above 345 K and 10 kbar.
VI		Around 373 K and \sim 35 kbar.

The I-II and IV-V phase boundaries determined by DTA were found to rise very slowly with pressure. The II-IV, I-IV and I-V boundaries were determined by the volume discontinuity method. In this work two new high pressure phases, V and VI, were discovered. The melting curve of KNO₂ exhibited a maximum at 7.0 kbar and 739 K, and meets the I-V boundary at a triple point at 15.2 kbar and 686 K and then increases steeply with pressure. Clark and Rapoport [61] report the pressure dependence of KNO₂ (III-II) transition by DTA in a pistoncylinder device [62-65]. They used a 97.5 percent pure sample after two recrystallizations. The III-II transition was found to be from a completely ordered (NaCl like) phase to a partially disordered phase, whereas the II-I transition is from a partially disordered phase to a completely disordered NaCl phase [61]. Larionov and Livshits [66] have studied the polymorphic transformation (III-IV) at 15 kbar and 77-488 K and described the phase diagrams showing the relative disposition of the various phases.

Rubidium Nitrite, RbNO₂.

RbNO₂ is reported to undergo an endothermic phase transformation at ~ 348 K with $\Delta H_{\rm tr} = 500 \pm 50$ cal mol^{-1} [1]. The DTA and electrical conductivity studies of Natarajan and Hovi [70] indicate an anomaly in the temperature range 340-390 K due to the phase transformation. Richter and Pistorius [69] have investigated the crystal structure and the pressure transformations of RbNO₂. According to them, RbNO₂ (phase I) at ambient conditions is cubic (space group $O_b^5 - Fm3m$, with a = 6.934 Å). It transforms at ~ 261 K to monoclinic RbNO₂ (phase II) with a=8.904 Å, b = 4.828 Å, c = 8.185 Å, $\beta = 115.7^{\circ}$ (determined at 271 K). RbNO₂ (II) appears to be ordered, whereas $RbNO_2$ (I) has a configuration entropy of Rln 32. The II/I transition line terminates at 0.3 kbar with appearance of RbNO₂ (phase III), a phase 17.3 percent denser than RbNO₂ (I). The II/III transition pressure increases with decreasing temperature to a triple point at 1.2 kbar, 208 K where a further dense phase IV appears. The II/IV transition pressure rises slightly with decreasing pressure. The melting curve of phase I passes through a maximum at 2.2 kbar, 663 K and is terminated at the III/I/liquid triple point at 5.2 kbar, 655 K. The melting curve of phase III rises with pressure.

Cesium Nitrite, CsNO₂, cubic, O_h¹-Pm3m, $a = 4.34 \pm 0.02$ Å at ambient conditions [2].

Cesium nitrite seems to undergo an endothermic transformation at 393 ± 10 K with $\Delta H_{tr} = 1100 \pm 100$ cal mol⁻¹ [1]. Protsenko and Kolomin [71] reported two phase transformations in CsNO₂ at 175 K and 353 K, respectively. The DTA and electrical conductivity studies by Natarajan and Hovi [70] indicate a thermal anomaly in 350-380 K temperature range, which they attribute to a phase transition. Richter and Pistorius [69] have reported CsNO₂ (phase I) to undergo a transformation at 179 K to a rhombohedral CsNO₂ (phase II, space group: $D_{3d}^5 - R\overline{3}m$ with a = 4.307 Å, $\alpha = 87^{\circ}22'$). The II/I transition line is found to rise with pressure with an initial slope of 4.9 K/kbar.

Measurement technique	Observations	Remarks	References
X-ray diffraction	A new anomaly in dielectric constant is reported at 230 K. The cubic phase also appears just above 313 K. ΔV is very small during the 313 K transformation. The <i>a</i> -axis decreases while <i>c</i> increases at this point.	The absence of any superlattice reflections indicates some kind of disordered arrange- ment of the NO ₂ groups. Ferroelectricity or antiferroelectricity is possible only be- low the room temperature.	[53, 54].
	After a thermal cycle traversing the trans- formation temperature to the high temp. form I, a single crystal of KNO ₂ in phase II is converted into a hybrid crystal com- posed of domains of structure II in spe- cific orientations. Detailed interpretation of some oscillation photographs of such a hybrid crystal in terms of composite re- ciprocal lattice demonstrates that the do- main orientations are related by the point group symmetry m3.	It is concluded that form I must have a cubic structure. Consideration of the atomic dis- placements involved in the $II \rightleftharpoons I$ trans- formation show these to be consistent with a NaCl structure for form I; and also the lower cubic symmetry controlling domain orientations arises because of the physi- cal requirement for the domains to coexist within the envelope of a 'single' crystal.	[68]
Differential thermal analysis	KNO ₂ undergoes a transition around 313 K $\Delta H_{\rm tr} \sim 120 \pm 30$ cal mol ⁻¹ ($\Delta T \sim 6$ K).	The observation was supported by studies of the temperature dependent infrared spectrum and a dielectric constant ex- hibiting around 313 K. Electrical conduc- tivity also shows a slight break at 313 K. Protsenko et al. (3) report the phase trans- formation at 320 K.	[57, 69].
Differential Scanning Calo- rimetry.	$\Delta H_{\rm tr} = 199 \pm 2 {\rm cal \ mol^{-1}}$	· · · · · · · · · · · · · · · · · · ·	[38].
Spectroscopic, dielectric con- stant, and electrical con- ductivity measurements.	$T_{\rm c} \sim 313 \text{ K}$ $P_{\rm s} = 2.8 \ \mu \text{C cm}^{-2},$ $E_{\rm c} = 160 \text{V cm}^{-1} \text{ at } 298 \text{ K}$	Anomalies seen in $\epsilon(T)$ and $\sigma(T)$ plots	[3, 57, 69].
Dielectric constant and elec- trical conductivity.	Two clear transitions at ~ 260 K and 313 K are shown by anomalies in $\epsilon(T)$ and $\sigma(T)$ plots. The room temperature phase is rhombohedral with R3c symmetry.	The magnitude of dielectric anomaly does not suggest a ferroelectric-paraelectric transition in KNO ₂ at 313 K.	[55].
	A new transition from orthorhombic (D_{2h}^{16} - aragonite type at 298 K) to a trigonal (close to D_{3d}^{6} -calcite type) structure is indicated by dielectric constant anomaly and loss studies. $T_{t} \sim 402$ K.	The transformation was not reversible and showed hysteresis.	[58].

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1.2. Alkaline Earth Metal Nitrites

(No crystallographic data seem to be available)

Polymorphic transformations in the nitrites of calcium, strontium, and barium have been reported from the anomalies in differential thermal analysis curves [1, 2] and electrical conductivity measurements [3]. Detailed studies, however, have not been carried out. The transformation temperatures for these nitrites are given below:

Nitrite	T _t ,	K
Calcium	539,	633
Strontium	458,	547
Barium	476,	503

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1.3. Thallium Nitrite, TINO₂

(No crystallographic data seem to be available)

Differential thermal analysis studies by Protsenko and Brykova [1] show a polymorphic transformation in TlNO₂ at 442 K. Earlier, Cuttica [2] reported the transformation temperature to be 404 K. Detailed studies, however, have not been made.

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2. Nitrates

Nitrates of many of the elements undergo phase transformations. Among these, alkali-metal nitrates and ammonium nitrate have been investigated extensively. Thermal as well as pressure transformations of nitrates have been studied by observing changes in crystallographic, thermodynamic, electrical, dielectric, magnetic and optical properties. We shall review these phase transitions of nitrates following the position of the element in the periodic table.

2.1. Nitric Acid, HNO₃

A single crystal of HNO_3 in equilibrium with its own liquid grown at a pressure of about 4 kbar has been found to exhibit a transition at room temperature and 8 kbar [1].

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2.2. Alkali Metal Nitrates

As mentioned earlier, phase transformations of alkali metal nitrates have been studied in great detail and the subject has been reviewed by a few authors [1-3]. The orthorhombic-trigonal transformations in NaNO₃ and KNO₃, and the hexagonalcubic transformations in RbNO₃ and CsNO₃ are well characterized. In this section, we shall examine the data on each of the alkali metal nitrates and provide the information in a tabular manner.

Lithium Nitrate, LiNO₃, rhombohedral (calcite type), $D_{3d}^{e} - R\overline{3}c$, Z = 6 (for hexagonal cell) and 2 (for rhombohedral cell), a = 4.692 Å, c = 15.22 Å at 298 K.

The crystal structure of LiNO₃ was reported to be calcite type by Zachariasen [4]. The unit cell dimensions were later confirmed by Swanson et al. [5] at the National Buleau of Standards. There is no evidence for changes in the thermodynamic properties like specific heat and specific volume of LiNO₃ between room temperature and the melting point [6]. A study of the temperature variation of the electronic spectrum of LiNO3 by Rhodes and Ubbelohde [7] shows that there is discontinuity in the absorption coefficient indicating a transformation. McLaren [1] concludes that if this is any indication of a transformation in LiNO3, it could only be due to orientational disorder as in NaNO₃ (above ~ 458 K) or in NH₄NO₃ (in phase II). Fermor and Kjekshus [8] have measured the electrical resistivity and dielectric constant of LiNO₃ from 203 K to the melting point and report a transformation at 263 K, besides another anomaly at 503 K. Morabin et al. [9] have found the dielectric constant to increase linearly with temperature up to 483 K then followed by a faster rate of increase.

Sodium Nitrate, NaNO₃, rhombohedral, $D_{3d}^6 - R\overline{3}c$,

Z = 6 (for hexagonal cell and 2 (for rhombohedral cell), a = 5.0696 Å, c = 16.829 Å at 298 K.

The structure of NaNO₃ was determined by Wyckoff [10] and the unit cell dimensions for the rhombohedral (calcite type) cell are a = 6.3247 Å and $\alpha = 47°16'$ at 296 K. Sodium nitrate has been found to undergo a phase transition from phase II, ordered rhombohedral phase (calcite type), to I, a disordered rhombohedral phase, around 548.5 K (1). Kracek et al. [10a] observed marked changes in the intensities of the x-ray reflections from some of the planes on heating NaNO₃ above ~488 K. They attributed this to the rotation of the NO₃ ions about the trigonal axis. The investigations of Ketelaar and Strijk [11] also show that the transition is caused by internal rotation of the NO₃ groups in the crystal. The most probable mode of rotation is that about an axis through the N-atom and perpendicular to the plane of the NO₃ group. Recently, Terauchi and Yamada [11a] have studied by x-ray scattering the phase transition of sodium nitrate crystal associated with the ordering of the orientation of NO_3^- ions. They have analysed the results on a microscopic basis and have concluded that the pair interactions between NO_3^- ions play an important role during the phase transition.

Anomaly in thermal expansion, DTA and heat capacity measurements were employed to study the transformation in NaNO₃ [12]. Around 548 K, dc electrical conductivity also shows a change in the slope [13]. Protsenko et al. [14] found NaNO₃ to be piezoelectric in the direction of the *b*-axis with a Curie point at 537 K. The dielectric constant had a sharp maximum in the vicinity of 437 K where the value is more than 100 times higher than that at room temperature. Dilatometric measurements showed the coefficient of linear expansion to be 10^{-4} per degree. Rhodes and Ubbelohde [7] noticed that the high energy absorption peak in the electronic spectrum of NaNO3 shifted to lower wavelengths above \sim 548 K. Raman spectrum due to the internal vibrations of NO_3^- ions was studied by Chisler [15] to investigate the transition in NaNO₃. Earlier spectroscopic studies have shown that NO_3^- does not freely rotate above the transition temperature. High Pressure Transformations: Polymorphic transformations at high pressure in alkali metal nitrates were investigated by Bridgman [16] up to 100 kbar. Jamieson and Lawson [17] made some preliminary but unsuccessful attempts to determine the crystal structure of the high pressure form of NaNO₃. Rapoport [18] showed that the pressure dependence of the transition in NaNO3 could be described by the equation, $t=275+6.076p-0.038475p^2$, where t is temperature in degree centigrade and p is pressure in kbar.

NaNO₃

Measurement technique	Observations	Remarks	References
X-ray diffraction	A gradual transition (II \rightleftharpoons I) occurs by the formation of nuclei in the crystal matrix and their subsequent growth. Lattice constants for the two forms both of which have rhombohedral unit cell are: II $a=6.32$ Å, $\alpha=47^{\circ}14'$ at 298 K I $a=6.56$ Å, $\alpha=45^{\circ}35'$ at 553 K.	The transition depends upon the number of nucleating centers. At high temperatures, the nitrate groups seem to be statistically distributed between two twofold dis- torted, non-equivalent sets of position in rhomhedral unit cell.	[10a, 19– 21].
Diffuse x-ray Scattering		The observed ellipsoidal distribution of critical diffuse scattering in the re- ciprocal space has been explained by taking the pair interactions up to second nearest neighbours.	[11a].
		The temperature-dependence of critical scattering gives a reasonable agreement with theoretical values in random phase approximation in the temperature range of $T>T_c+4.5$ K.	
		Both the temperature-dependence of long range order parameter and of anomalous lattice expansion can be satisfactorily explained by taking the strain de- pendence of pair interaction energy into account.	

NaNO₃-Continued

Measurement technique	Observations	Remarks	References
	T _t ~ 548 K	Values of elasticity constants were deduced from intensity data and compared with elastic constants obtained by ultrasonic measurements. The diffuse maxima are believed to be a result of group-disorder. The maxima show strong angular depend- ence which is incompatible with the rota- tional model. The data fit a twofold dis- order model for the nitrate groups pro- vided that the positions have an aragonite type coordination with the surrounding Na atoms, rather than the calcite coordi- nation found in the ordered structure.	[22, 23].
High pressure X-ray up to ~ 85 kbar.	Anomalous line intensity changes near 45 kbar are shown to be due to a transi- tion from R3c to R3c space group without any change in volume.	The data suggest a higher order transition in which the nitrate groups in alternate layers along the trigonal axis rotate in opposite directions under pressure, and the nitrogen position is no longer planar with oxygen atoms. The atomic configura- tion suggests a ferroelectric phase and dielectric measurements indicate an anomaly at the transition point.	[24].
DTA and calorimetric meas- urements).	The specific heat curve shows a break begin- ning around 443 K and reaching a peak around $T_{\rm t}$. $T_{\rm t}$ = 549 K. $\Delta H_{\rm tr}$ = 1030 ± 90 cal mol ^{-1.}	The behaviour of NaNO ₃ has been discussed in terms of free rotation of nitrate ions. The transition is due to the transfer of $NO_{\overline{3}}$ from an ordered state to a dis- ordered state.	[6, 25–29a].
Thermal conductivity, spe- cific heat, thermal diffu- sivity, elasticity.	The abrupt change in thermal diffusivity is influenced by the abrupt change in the elastic constant S_{33} .	It is possible that above T_t the NO ₃ groups may be rotated by 180° about the trigonal axis by means of lattice vibration.	[12, 27, 30].
	An impurity like calcium causes a decrease in the values of thermal characteristics of NaNO ₃ near T_{t} . The decrease is pro- portional to the increase in calcium- concentration.	Thermal conductivity changes have been explained by the presence of an order- disorder scattering mechanism.	[30a].
Thermal expansion	A gradual transition ending to a peak value of coefficient of expansion at T _t followed by a rapid decrease to a normal value.	The transition occurring between 423 and 551 K is more marked along the <i>c</i> -axis than along the <i>a</i> -axis. The coefficients of thermal expansion increase monotonically with temperature up to the melting point.	[12, 27, 31–32a].
Differential thermal analysis (up to 40 kbar).	The effect of pressure on the gradual transition in NaNO ₃ can be expressed by the equation. $T=275+6.076p-0.038475p^2$. T=temp (K), p = pressure (kbar).		[18].
Permittivity measurements at 100 kHz.	Anisotropy is observed and unusual in- crease is seen in the (111) direction at 453 K and in the <i>a</i> -direction at 493 K. At this temperature, orientational polariza- tion begins. At 548 K, the fixed position of NO_3^- ions does not exist and permit- tivity again decreases.	Thermal properties like thermal con- ductivity and thermal diffusivity behave in a similar manner.	[33].

NaNO₃-Continued

Measurement technique	Observations	Remarks	References
Dielectric constant and resis- tivity measurements (from room temperature to melt- ing point).	At transition temperature maxima is observed in ϵ - T curve.		[9, 24, 34].
Electrical conductivity meas- urements.	Conductivity-temperature curves show discontinuities or changes in slope near the transformation temperature.		[13].
Infrared absorption spectra at different temperatures.	Assignments of the bands in the region, 3000-5000 cm ⁻¹ are made as librational combinations with vibrational bands. These bands persist in the temperature range between the IInd order transition and melting point, and disappear in the spectrum of the melt.	The thermal behaviour observed com- pletely eliminates the hypothesis of free rotation of NO_3^- ions above the λ -point. The crystal structure above 548 K is disordered.	[35].
Raman Scattering	The intensity of the NaNO ₃ , 1385 cm ⁻¹ (ν_3) band in the range of 483–553 K increased rapidly ($T_t = 549$ K).	The strong asymmetric broadening of the line is attributed to the superposition of bands due to scattering by bound and quasi-free anions.	[15].
Ultrasonic and IR studies	<i>T</i> _t ~ 549.7 K	 The results are interpreted on the basis that the 'frozen' elastic constant varies smoothly and monotonically with temperature throughout the transition region. The intensity of the totally symmetric vibration ν₁, forbidden in the ordered but allowed, and weakly present, in the disordered phase, shows no sharp change in passing through the transition. This is consistent with the notion that short range order changes slowly with temperature in the transition region. 	[36, 37]
	Strong frequency dependent ultrasonic attenuation is observed at temperatures immediately below and above the λ-point.		
Garland relations applied to the λ-change in NaNO ₃ .	The transition is essentially one dimension- al; most anomalies in properties do show up only in the <i>c</i> -direction.		[38].

Potassium Nitrate, KNO₃, orthorhombic, D_{2h}^{16} -Pmcn, Z = 4, a = 5.414 Å, b = 9.164 Å, c = 6.431 Å at 299 K.

Potassium nitrate, form II (aragonite type), is the stable phase at 299 K and atmospheric pressure, and changes to form I (calcite type) at 403 K. On cooling, KNO₃ transforms from phase I to a new phase III at 397 K and from phase III to phase II at 383 K. The transformation in KNO₃ can be shown as follows [39].



Fischmeister [39a] gave the unit cell dimensions for KNO₃ form I at 425 K as a = 5.42 Å and c = 19.41Å which are in good agreement with the parameters reported by Tahvonen [39b]. This hexagonal cell contains 12 molecules. On heating, the unit cell of form I expands anisotropically, the marked expansion being along the *c*-axis (normal to the plane of anions). The expansion along the *a*-axis is slightly negative. This suggests that the linear vibration of NO₃⁻ is a more plausible form of disorder than the rotation in the plane about the N-atom. Form III has been reported to be ferroelectric [40] and is rhombohedral with a=5.43 Å, c=9.112 Å and space group C_{3v}⁵-R3m at 388 K. Leonhardt and Borchert [41] as well as Kennedy et al. [42] have studied the phase changes in single crystals of KNO_3 by x-rays.

Kracek [43] studied both moist and dry polycrystalline KNO₃ by DTA and observed an endothermic transition in the moist sample beginning around 403 K. On cooling, the sample gave an exothermic DTA peak beginning at 399 K. The forms above and below 400 K are I and II, respectively. The behaviour of the dry sample, however, was different, at least while cooling, where two exothermic peaks at 397 K and 382 K were noticed. The form stable in this temperature range is III. Oja [28] reports the II \rightarrow I transformation at ~ 402.5 K from calorimetric studies.

Conductance studies on compressed polycrystalline pellets of KNO₃ were made by McLaren [1] who found the II \rightarrow I transformation to occur at 399 K. The transitions were indicated by anomalous change in conductivity with increasing temperature [44]. Meinnel and Clinet [45] in their dielectric constant measurements found a sharp increase at ~ 400 K while heating and two distinct anomalies at ~ 380 K and ~ 368 K, while cooling.

Sawada et al. [40] showed that KNO_3 -III is ferroelectric. The nature of ferroelectricity has been examined by Chen and Chernow [46], who measured the unit cell parameters of KNO_3 single crystals in the temperature region of the ferroelectric transition. The changes in the cell parameters as the crystal undergoes paraelectric to ferroelectric transition (I \rightarrow III) have been interpreted as being due to the electrostriction effect.

Ferroelectricity in KNO₃ is due to the ordering of permanent dipoles. The permanent dipole in the paraelectric phase is believed to be due to the displacement of the nitrate ion from the center of the unit cell. The amplitude of this oscillation is 0.4 Å along the *c*-axis. If we consider, instead, that the structure is a disordered array of nitrate ions displaced from the center of the unit cell, the dipole moment per unit cell would be ~ 9.8 μ c cm⁻². This is very close to the value of spontaneous polarization in KNO₃. A double potential along the *c*-axis is considered to be a good model for explaining the NO₃ ion displacement. A statistical theory based on this model and on the assumption of a lattice dependent internal field explains the origin of the electrostriction effect and observed anomalies at the ferroelectric transition. The statistical theory is related to Devonshire's thermodynamic theory of ferroelectric transition and good agreement is obtained between the theoretically predicted and experimentally determined coefficients of Devonshire's free energy. Balkanski and Teng [47] reported a normal vibration analysis of all the three phases of KNO₃ and found a close correspondence between normal modes of different phases. They also report a complete KNO₃ phase transition cycle in Raman Scattering. On heating, all the ionic and rotational modes in phase II were found to vanish abruptly at 403 K suggesting that the transition II \rightarrow I is of a rather sudden nature. A notable and continuous broadening of the rotational mode at 83 cm⁻¹ was also observed near $T_{\rm t}$. Between 383 and 373 K, on cooling, the spectra suggest that the limits between phase III and II may be less precise and that the III→II phase transition probably occurs more gradually than the other phase transition.

High Pressure Transformations: The phase diagram of KNO₃ reported by Bridgman [48] in the pressure range 0-12 kbar up to 473 K, revealed two rhombohedral (I and III) and two orthorhombic (II and IV) phases. The polymorphs III and IV are the high pressure forms. KNO₃-III, however, could be attained metastably at atmospheric pressure and its crystal structure was reported by Barth [49] as rhombohedral with Z = 1 with the NO₃ ion displaced some six percent above the cell center. Davis and Adams [50] studied the kinetics of the phase transformations $I \rightleftharpoons II$ and $II \rightleftharpoons III$ at high pressures in detail. Rapoport and Kennedy [51] have examined the high pressure transformations in KNO₃ up to 40 kbar and 873 K employing DTA. They found as many as seven polymorphs, phases V, VI, and VII being entirely new. The phase diagram of KNO₃ above 15 kbar was found to closely resemble that of RbNO₃, CsNO₃ or TlNO₃ and it is suggested that KNO₃ VII encountered at 30 kbar is structurally similar to the phases found by Bridgman [52] in RbNO₃ at 24 kbar and in CsNO₃ at 27 kbar.

Measurement technique	Observations	Remarks	References
X-ray diffraction	T_t =401 K for orthorhombic to rhoml hedral transformation. While cooling. t solid obtains a mosaic character at 396 and at 386 K changes to a finely divid material.	o- The changes at 396 K and 386 K are due to the I-III and III-II transformations in K KNO ₃ . Crystals of the high temperature phase grow rhythmically from the low temperature phase to form discrete and easily identifiable layers	[41, 42, 53–55].
	Single crystals preserve their nature wi very slow heating rates. The (110) pla of the calcite-type crystal parallels t (010) plane of the original aragonite-ty crystal. An incubation period averagi 4.1 minutes exists for the transformation Structural transformations are co pletely reversible. The volume change the phase boundary is 0.71 percent.	The c-axes of the two structures are not parallel but differ by 26° both lying in the plane common to the two structures. In moist crystals, the b-axis shows a marked persistence with respect to original b-axis. The a and c axes often undergo rotation about the original direction of the b-axis. The direction of none of the original axes persists in rigorously dried crystals.	
	A new transition at 213 K was four showing marked hysteresis effects.	d, From the new phase, the material slowly transformed to the stable, normal II phase at 299 K.	[56].
High Pressure x-ray dif- fraction.	The structural information for the hig pressure phases III and IV are as follow Pressure. Temp., Structural Phase kbar K information	h s: n	[48, 50, 57, 58].
	III 2.5 406 Hexagona pseudo-ce Z = 6, $a = 5.44_0 A$ c = 17.51	l II. Å	
	$(\Delta V \sim 0.036 \text{ cm}^3 \text{g}^{-1} \text{ at } 410 \text{ K and } 0.5 \text{ kbar}$ IV 3.0 298 Ortho- rhombic Z = 10 spa group P _{mr} (for K ⁺ ion a = 11.048 b = 8.367 c = 7.402	 Rate studies on the transition KNO₃ II = IV showed an overall approach to first order kinetics but in detail. reveal several growth stages. The transitions are only partially manifested by an uneven change in the pressure. The change was found gradual, in many cases. over a temp. interval, and the pressure curve before and after 	•
	Several diffraction patterns of the tran tions I-II and III-II revealed preferre orientation of grains in the resultir aragonite type phase. Cell parameter of KNO ₃ -I and KNO ₃ -III (both mod fied calcite structures) taken in the stability fields show a marked reduction in the <i>c</i> -axis length going from phase-I phase-III with increasing pressure constant temperature.	rectilinear. In such cases the intersec- tion of these two rectilinear portions give the transition point. s i- ir n o tt	
Differential Thermal Analy- sis.	$\begin{array}{c c} \Delta H_{\rm tr}. \ {\rm cal \ mol^{-1}} \\ \hline {\rm Transition} & ({\rm approx.}) \\ \hline {\rm II} \rightarrow {\rm I} & 1200 & 100 \\ {\rm I} \rightleftharpoons {\rm III} & 820 & - \\ {\rm III} \rightleftharpoons {\rm II} & 820 & - \end{array}$	The thermal hysteresis. (ΔT). is linearly related to the differences in volume of the transforming and the transformed phases.	[25, 59–60a]

Measurement technique		Observations		Remarks	References
Particle size effects in the II→I transition by DTA.	Particle size μ(micron) 5.5 49.5 115.0 137.0	<i>T</i> _t , K 413 413 406 403	ΔH _{tr} , cal mol ⁻¹ 1450 1200 1000 1050	$T_{\rm t}$ decreases with the particle size while $\Delta H_{\rm tr}$ also shows a progressive decrease. These effects are related to non-attainment of thermodynamic equilibrium and surface energy factors. Effect of heating rates on $T_{\rm t}$ is also discussed.	[61].
Thermal analysis and dila- tometry, up to 300 Mbar.	$T_{t} \text{ for II} \rightarrow I \text{ ch}$ At 50 Mban II \rightarrow I trans 0.0087 cm ³ Mbar $\Delta V =$	nange is affecte $\Delta V = 0.00484$ sition; at 151 σg^{-1} for II \rightarrow II -0.0091 cm ³ g ⁻¹	d by moisture. $cm^{3}g^{-1}$ for the Mbar, $\Delta V =$ II and at 251 $^{-1}$ for III \rightarrow I.	Conditions for metastability of KNO ₃ III at atmospheric pressure are dis- cussed.	[43].
High pressure DTA up to 873 K and 40 kbar.	The melting maxima at a second r rises steep above 15 kb	curve passes th 6.4 kbar, pos maxima at 11 l ly with increa par.	arough a broad ssibly through kbar and then asing pressure	Three new polymorphs V, VI, and VII were found. The phase diagram of KNO ₃ seems very similar to that of RbNO ₃ or CsNO ₃ .	[51].
Kinetics of III → II transi- tion.	The III→II by two firs of these c rate constan	transition may st order proces an be expresse nt.	y be described sses, and each ed by a single	The existence of ferroelectric behaviour in the phase III polymorph permits direct recording of the rate of transition of the phase III \rightarrow phase II at temperatures far removed from the normal T_t at at- mospheric pressure.	[63].
Dielectric constant	The real part and the lo to 0.68 with transition i teresis.	t of ε varies from sses from seven h increasing ter s reversible an	m 4.45 to 12.10 ral thousandths nperature. The d exhibits hys-	In samples subjected to gamma rays, the P_s shows substantial decrease and E_c values show increase. No double hysteresis loop was observed. Results show phase III having two Curie points; the upper T_c increases while the lower T_c decreases with increasing pressure up to ~ 1.38 kbar (20,000 psi).	[35,46 64–68]
Electrical conductivity, dielectric constant and dielectric loss.	Anomaly is o and at ~ 39	bserved at ~ 40 17 and 381 K on 6	03 K on heating cooling.	The occurrence of a relaxation type of dielectric dispersion in the microwave region together with the contraction of the ferroelectric axis at the transition, suggests that ferroelectricity in KNO ₃ is an order-disorder phenomena.	[48, 69, 70]
Dielectric constant and spontaneous polarization.	The isotherm ition exhib pressures, pressure. Curie-Weis	al and isobaric ited sharp diele with ε _{max} ir KNO3-I obey ss law, with	$I \rightarrow III \text{ trans-}$ ec. peaks at all necreasing with rs a pressure		[71].
	$\left(\frac{1}{\epsilon(p)}\right)$	$\Big)_{T'} = \frac{p - p_0}{C^*} \text{ at } T'$	′ = 433 K,		
	$C^* = -2$	76 kbar and p_0	=4.68 kbar.		
	The KNO ₃ volves a s at $p = 1.7$ increase to Polarizatio KNO ₃ -III of 8 μ coul	II \rightarrow III isobaric mall jump in ϵ kbar) followed up to the III n loops were with $P_s(p)$ reach omb/cm ² . Meta	transition in- (from 5 to 7.5 d by a speedy \rightarrow I boundary. e obtained in ing a maximum astable KNO ₃ -		

KNO₃-Continued

Measurement technique	Observations	Remarks	References
	III was observed at room temperature and room pressure after specimens had first been exposed to high pressures (1.7-4.0 kbar) while in region III. In KNO ₃ -I, $K' = dT_0/dp$ is approximately 25 b/bbar		
Electrical conductivity	All the transitions are shown by conduc- tivity temperature curves. The II→I, III→I and I→III phase tran- sitions follow the kinetic equation	The phase transitions of KNO ₃ are volume reactions with a complete mutual dis- persion of both phases; the course of the reaction is controlled by nucleation.	[72–74].
	In $\alpha/(1-\alpha) = kT + c$, where α is the degree of conversion and t is the time		
Infrared spectroscopy	The transitions of KNO ₃ at 403,398, and and 388 K are associated with changes in the positions of bands at 720, 830, and 1055 cm ⁻¹ characteristic for the internal vibrations of NO ₃ . The temperature de- pendence is also given by the lattice vibrations along a , b , and c axes.	The analysis indicates that in the phase I the NO ₃ ⁻ ions are randomly oriented.	[75–79].
Far infrared reflectivity spectra over the range 20–400 cm ⁻¹ .	Fhe two infrared active lattice modes observed are described by parameters obtained from a classical oscillator analysis, which was confirmed by Kramers-Kronig analysis.	From the temperature dependence of the mode parameters and their contribution to their dielectric constant it was con cluded that the paraelectric phase is a disordered arrangement of electrica dipoles. Thus the paraelectric to ferro electric transition is an order-disorder transition.	e [80]. 1 1
Electron paramagnetic res- onance of Mn ⁺² in KNO ₃ . KNO ₃ .	The hyperfine coupling constant, half width, and line intensity show sudden changes at the T_t . The lines are much sharper in the high temperature phase of the crystal.	The observed changes are explained in terms of structural changes and NO ion rotation. Indications of the presence of a metastable γ-phase (ferroelectric phase) has also been found.	[81].
Polarising microscope with hot stage.	On heating, the transition boundary B_{II-I} starts from hot end of the crystal and moves on to the other end making the specimen somewhat polycrystalline. Further heating, brings about recrystallization. On cooling, the boundary B_{I-III} appears on the cooler end subsequently followed by B_{III-II} boundary.	The boundary B_{III-II} usually leaves many cracks after its passage. However, the speed of the boundary B_{I-III} is rather small as compared with that of the boundary B_{III-II} , and shortly after their appearance the boundary B_{III-II} often catches up with the boundary B_{I-III} pro- ceeds further to the hot end leaving no more cracks.	[82].
Ultraviolet spectroscopy	A gradual shift of absorption bands is found to accompany thermal expansion of the crystals and an abrupt change is seen at T_{t} , transformation showing hysteresis at 313 K has been detected.	The technique proves a sensitive means for the study of various thermodynamic effects in phase transformations.	[83].

KNO₃-Continued

Measurement technique	Observations	Remarks	References
Raman Scattering	In the ferroelectric phase a significant intensity increase was noted for all the covalent modes. A broad band at ~120 cm ⁻¹ is observed in the ferroelectric phase, the half-width of this band depends upon temperature. Two new lines at 65 and 133 cm ⁻¹ are found in the room temperature phase.	 Raman active modes in different crystal structures have been correlated. ¹ Strong asymmetric broadening of the line may be regarded as the result of superposition of bands due to scattering by bound and quasi-free anions. From theoretical considerations it is concluded that C⁵_{3v} is the most suitable space group to describe KNO₃-I, the high temperature phase. 	[15, 84-86].
Raman Spectra study of ferroelectric transition under pressure up to 800 bar (from room tempera- ture to 418 K).	The lattice dynamical behaviour of the direct high pressure II–III phase transi- tion is quite similar to that under atmos- pheric condition.	The structures of II and III phases are very close to one another. Raman spectra of the ferroelectric phase reveals that at high pressure, KNO ₃ -III is more stable than at atmospheric pressure.	[87].
Neutron diffraction at high pressures.	The pressure phase IV of KNO3 at ~15 kbar is noticed.		[88].
Viscosity measurements	Show evidence for II \rightarrow I transition.		[89].
Change in grain size	Number of grains per unit area increased from 4 to 70 during transformation at 393 K.		[90].

Rubidium Nitrate, RbNO₃, Trigonal, $C_{3v}^2 = P31m$, Z = 9, a = 10.479 Å, c = 7.452 Å, at 298 K.

It has been established by x-ray diffraction [91-95], DTA [25, 96], dilatometric [83, 91], calorimetric [97-99], electric conductivity [1, 100, 101] and optical [83] measurements that RbNO₃ undergoes the following phase transformations:

IV <u>437 K</u> III <u>492 K</u> II <u>564 K</u>

(Trigonal) (Cubic) (Rhombohedral) (Cubic) CsCl type NaCl type

Single crystal photographs at ~ 453 K suggest that RbNO₃-III is cubic with a = 4.36 Å containing only one molecule per unit cell. Korhonen [102] however, assigns a value of a twice as this from his studies of powder photographs, i.e., a=8.72 Å with Z=8. X-ray photographs of RbNO₃ single crystals heated through the IV \rightarrow III transformation indicate that the trigonal triad [00.1] of IV is transformed to the cubic triad [111] of III with the trigonal [10.1] direction becoming the cube edge direction [100]. Thus, during the III \rightarrow IV transition any one of the

four equivalent cube diagonals can give rise to the trigonal c-axis. Hence, in the transformation cycle, $IV \rightarrow III \rightarrow IV$, the crystals may come back to form IV in any of four orientations [101]. All these possibilities were observed. Accordingly, Finback and Hassel [103] suggest that the NO₃ ions are in free rotation in form III. Korhonen [102] suggests that the anion disorder is akin to the one in KNO₃ suggested by Fischmeister [39]. Form II is rhombohedral with a = 4.8 Å, $\alpha = 70^{\circ}28'$ (around 520 K) having one molecule per unit cell. Form I is cubic with one molecule per unit cell; a = 7.32 Å at ~ 573 K.

The thermal transformations in RbNO₃ were studied by DTA by Plyushchev et al. [96, 104] and Rao and Rao [25]. The electrical conductance of compressed powder pellets of RbNO₃ has been reported by Brown and McLaren [101]. The IV-III transition is marked by an increase in conductance by two orders of magnitude. After cycling, the conductance changes by a factor of 30 at the III-II transition in both the directions. Cycling also produces a change by three orders of magnitude in the

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IV-III transition in both the directions. These results were reproducible. The II-I transition is characterized by a change in the slope of the conductance curve.

Meinnel and Clinet [45] found an anomalous increase in dielectric constant (ϵ) at ~ 323 K. On cooling, the fall in ϵ was observed at ~ 313 K. Finback and Hassel [105] reported that RbNO₃-IV is pyroelectric. Dantsiger [34] concludes from dielectric and dilatometric studies that RbNO₃ has ferroelectric properties between the first and second phase transition points. Examination of single crystals of RbNO₃ by an optical microscope [1] shows that it crystallizes in the form of *c*-axis needles which are anisotropic and show parallel extinction. On heating, the IV \rightarrow III change was noticed at ~ 430 K with the crystals becoming isotropic. It is interesting to note that while cooling (i.e. III \rightarrow IV transition) the crystals retained their external shape as well as their single crystal character. Further heating results in the cracking of single crystals through the III \rightarrow II transition at ~ 500 K, and the crystals also become anisotropic. Around 563 K, the crystals become isotropic without further distortion.

High Pressure Transformations: Bridgman [52, 106] reported new polymorphs in RbNO₃ in the pressure and temperature ranges 0–50 kbar and 194–473 K, respectively, by his piston displacement method. Later he extended his measurements up to 100 kbar [16]. In his earlier work, Bridgman found similarity in the phase diagrams of RbNO₃ and CsNO₃ [48]. Rapoport and Kennedy [51, 107] also showed that the phase diagram of RbNO₃ above 2 kbar is quite similar to that of KNO₃ above 15 kbar and of CsNO₃. The corresponding phases have been found to be isostructural.

Measurement technique	Observat	tions		Remarks	References
X-ray diffraction	Transition IV→III III→II II→I	<u>Т</u> _t , К 437 492 564		 Structures IV, III, and II are related to one another while II and I are not related. Transitions between IV, III, and II appear to involve changes of positional randomization of Rb⁺. No evidence was available for such randomization in II→I transition. RbNO₃-II is rhombohedral and not tetragonal as suggested earlier [97]. This is confirmed by data from x-ray and dilatometric studies. The polymorphism in RbNO₃ seems to be sensitive to a temperature dependent effective ionic radius of the anion. X-ray and optical studies on single crystals of RbNO₃ indicate incomplete randomization of the NO₃⁻ ion orientations. 	[93, 95, 101– 103, 108– 110].
Differential thermal analysis and thermoanalytical meas- urements.	$\begin{array}{c cccc} \text{Transi-} & \Delta H_{tr} & E_{tr} \\ \text{tion} & \text{cal mol}^{-1} \text{ kc} \\ & & & \text{mol}^{-1} \text{ kc} \\ \hline & & & & \text{mol}^{-1} \text{ kc} \\ \hline & & & & & \text{mol}^{-1} \text{ kc} \\ \hline & & & & & & \text{mol}^{-1} \text{ kc} \\ \hline & & & & & & & \text{mol}^{-1} \text{ kc} \\ \hline & & & & & & & & \text{mol}^{-1} \text{ kc} \\ \hline & & & & & & & & & \text{mol}^{-1} \text{ kc} \\ \hline & & & & & & & & & & & & \\ \hline & & & &$	$ \begin{array}{cccc} a & \Delta S_{tr} \\ sal & cal \ mol^{-1} \\ ol^{-1} & deg^{-1} \\ \hline 55 & 2.11 \\ 50 & 1.53 \\ 55 & 0.42 \\ \end{array} $	ΔV % 2.1 10.0 1.0	The thermal hysteresis is related to the differences in volume of the transforming and transformed phases.	[2, 25, 96, 104, 108, 111].
Calorimetric measurements	The measurements un tions revealed fiv RbNO3. The transition energies	der improved c e endotherms have been repo	ondi- for rted	The first four endotherms at 440, 509, 563, and 575 K respectively are due to crystal transitions and the fifth one at 587 K is due to fusion. No phase transition was observed below room temperature as reported earlier by Former and Kielebuy [70]	[112]. [97, 99, 113].

RbNO₃

RbNO₃-Continued

Measurement technique	Observations	Remarks	References
Electric conductivity	Discontinuities in the plot of log σ versus $1/T$ are observed at all the transition points. IV-III transition at 431 K is marked by an increase in σ by a factor of 1000; the III \rightarrow II transition at 495 K is accompanied by a decrease in σ by a factor of 100; finally the II \rightarrow I transition at 559 K is indicated by a change in the slope. Cerisier and Guitard [114] find the results different from Brown and McLaren [101].	The conductivity behaviour is explained in terms of the crystal structure changes in RbNO ₃ .	[1, 74, 100- 102, 114, [115].
Dielectric and dilatometric measurements.	At 434 and 471 K RbNÔ ₃ undergoes con- siderable shrinkage and its dielectric constant increases considerably; at 471 K, Curie-Weiss law is followed with a Curie constant of 4.7×10^3 . Dependence of ϵ and tan δ on field intensity (50Hz) of an alternating electric field at 370 and 428 K are given. As the point of phase transition is approached, the non- linearity increases.	It is hypothesized that RbNO ₃ has ferro- electric properties below the point of the first phase transition and above the point of second phase transition. No trans- formation below room temperature was observed.	[37, 40]
	The hysteresis energy of the III \rightleftharpoons IV transition ($T_t \sim 437$ K) is a few thou- sandth of the ΔH_{tr} . It varies with the purity of the sample. ($\Delta V \sim 0.903$ cm ³ mol ⁻¹ at T_t .)	The transition in RbNO ₃ is a symmetry controlled transformation. The transi- tion is discontinuous and the expansion coefficient of the cubic form is normal and positive.	[94, 116].
Optical measurement	The temperature dependence of the ν_3 vibration frequency as well as that of lattice vibration along a , b , and c axes are studied.		[78, 101, 117].
Ultraviolet spectroscopy	The ultraviolet absorption bands shifts are observed at T_t . ΔV have been reported for various transformations.	The shifts in absorption bands are abrupt in cases where a crystal structure change accompanies the transition. In the cases of known crystal structure, these shifts have been correlated to changes in interatomic distances between cations and anions.	[83].
Nuclear magnetic resonance spectra of ¹⁴ N nuclei	Nuclear electric quadrupole coupling constants, assymmetry parameters of the N-nuclei and the orientation of groups with respect to the crystallo- graphic axis are determined.		[118].

Cesium Nitrate, CsNO₃, hexagonal, $C_{3v}^2 - P31m$, Z = 9, a = 10.87 Å, c = 7.76 Å below 434 K [118a].

Cesium nitrate undergoes a phase transformation around 434 K from phase II (hexagonal) to phase I (cubic) [103, 105, 119]. The reverse transformation (I \rightarrow II) takes place at a lower temperature (~422 K) showing considerable hysteresis. Phase I has been reported to be cubic with a = 4.499 Å at ~400 K and Z = 1 [103]. Ferroni et al. [119] have, however, suggested that the true unit cell should have eight such cubic units i.e. Z = 8 with a = 8.98 Å. This doubled cell parameter agrees well with the one given by Korhonen [120], who reports the space group for this phase to be Pa3. Finbak and Hassel [103] observed that the single crystals of CsNO₃ when heated above 473 K, were not destroyed. Single crystal photographs of CsNO₃ taken at 298, 473, and again at 298 K show that the Cs⁺ ion sub-lattice is very similar in both the structures. This indicates that the structure of CsNO₃ (I) is a slightly distorted version of the CsNO₃ (II) structure. According to Ferroni and others, the difference in structures of phases I and II is due to changes in the orientation of the NO₃⁻ ion, the Cs⁺ ion position being practically the same. Cini and Cocchi [121], from magnetic measurements, have shown that the high temperature phase is a centrosymmetric one. and is cubic.

DTA anomalies are reported by Plyuschev et al. [96, 104], Rao and Rao [25] and others. Sato [124] found a specific heat anomaly in 418–434 K range. Electrical conductivity measurements on polycrystalline pellets were made by McLaren [1] who found a rise in conductivity at T_t and a decrease in conductivity at 427 K on cooling. The conductivity changes by a factor of 3 on heating as well as on cooling. Meinnel and Clinet [45] measured

tivity (193-303 K).

the dielectric constant of $CsNO_3$ and found an anomaly at 393 K both on heating and cooling. Finbak and Hassel [105] report from single crystal studies that $CsNO_3$ -II is pyroelectric. Single crystals of $CsNO_3$ under a polarizing microscope showed no destruction of these crystals on cycling through the transition. There was, in general, no appreciable change in the orientation of form II after thermal cycling (i.e. $II \rightarrow I \rightarrow II$) [1, 104].

High Pressure Transformations: Bridgman [52, 106] reported new polymorphs in $CsNO_3$ in his high pressure investigations up to 50 kbar in 193–473 K range. He showed a similarity between the diagrams of RbNO₃ and CsNO₃ [48]. The phase diagrams of CsNO₃ were found to be quite similar to those of KNO₃, above 15 kbar, and RbNO₃, above 2 kbar by Rapoport and Kennedy [51, 107], who found the corresponding phases to be isostructural. Structural information on the high pressure polymorphs has not been reported in the literature.

Measurement technique	Observations	Remarks	Keterences
X-ray diffraction	Above 434 k (T_t) the structure due to Cs ⁺ ions is rhombohedral with $a=4.45$ Å and $\alpha=89^{\circ}40'$. However, the NO ₃ ⁻ ions within the various "Cs ⁺ only" rhombo- hedral cells are not equivalent. Conse- quently, the unit cell for CsNO ₃ is larger containing nine of the smaller units and with $a=10.87$ Å and $c=7.76$ Å.	The form below 434 K, is cubic with $a=4.49$ Å with one CsNO ₃ per unit cell [55]. However, Ferroni et al. [117] believe that the unit cell must include 8 of the smaller units with $a=8.98$ Å. Free rotation of NO ₃ ⁻ ions is a questionable hypothesis since the diameter of a freely rotating spherical NO ₃ ⁻ is larger than Cs-Cs distance along the ternary axis. The two structures differ only in NO ₃ ⁻ ion orientation.	[103, 105, 119, 120].
Differential Thermal Analy- sis.	$T_{\rm t}$. 434 K. $\Delta H_{\rm tr} \sim 350 \text{ cal mol}^{-1}$. $E_{\rm a} \sim 75 \text{ kcal mol}^{-1}$.	The thermal hysteresis is linearly related with the change in volume of the trans- forming and the transformed phases.	[25, 96, 104, 122].
Calorimetric measurements	$T_{\rm t}$ is reported to be 424.5-425 K. No phase transformation below room temperature was observed (also see ref. 66). $\Delta H_{\rm tr} = 893 \pm 80$ cal mol ⁻¹ . The molecular specific heats of CsNO ₃ up to the transition point were found to be represented by the following equation: $C_p = 9.84 + 46.4 \times 10^{-3}T$ for $T = 273 - 373$ K.	Free rotation of NO3 in CsNO3 is reduced from the variation of molar heat with temperature.	[113, 123, 124].
Dilatometry	Transition at 434 K is first order. The expan- sion coefficient of the cubic form is nor- mal and positive.	Hysteresis effects are sensitive to recrys- stallization and aging of the sample.	[94].
Electrical conductivity	The transformation is marked by a sharp change in conductivity.		[1, 125].
Dielectric constant and resis-	Anomaly is observed at point of phase		[70].

$CsNO_3$

transformation.

Measurement technique	Observations	Remarks	References
Optical examination in polar- ized light, polarized infra- red and laser induced Ra- man spectroscopy.	The spectra of single crystals of $CsNO_3-II$ in the region of the internal vibrations of NO_3^- indicate that these ions are posi- tioned at sites having C_1 symmetry and the unit cell symmetry of the trigonal space group is $C_3^1(C_3)$.	Raman spectra of the lattice vibrations are presented.	[105, 126, 127].
Ultraviolet spectra	Ultraviolet absorption band gradually shifts accompanying the transition at ~ 426 K.	The shifts in absorption maxima due to changes in temperature are interpreted in relation to changes in interionic distance.	[83].
Magnetic investigations	Single crystals of CsNO ₃ when held in a magnetic field behave anomalously while being heated carefully. This effect known as polyelectricity disappears at 437 K. By a technique in which powder CsNO ₃ is held in a sphere suspended in a uniform magnetic field, the anisotropic packing of the magnetically anisotropic cesium ni- trate causes a torque which is constant up to 437 K at which point it is completely nullified.	The observations confirm the centrosymme- try and cubic classification of the high tem- perature phase.	[121].

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2.3. Ammonium Nitrate, NH₄NO₃

(orthorhombic, D_{2h}^{13} -Pnmm, Z=2, a=4.942 Å,

$$b = 5.438$$
 Å, $c = 5.745$ Å at 298 K)

Ammonium nitrate has five modifications below the melting point (442 K). The transformations between the various phases designated as I, II, III, IV, and V can be described as follows [1-6]:

crystals of NH₄NO₃ phase IV were grown from aqueous solution. The water present in the specimen greatly affects T_t and the velocity of this metastable transition which also depends upon the maximum temperature reached and the time of heat treatment [5]. The occurrence of this transition between modifications IV-II was found to be associated with special drying of the sample or its immersion in a nonsolvent [9, 10]. The metastable transition has been observed when the melt is cooled at a rate greater than 2 K per minute and does not show up on heating [11]. Brown and McLaren [12] from their study using various techniques showed that all the transformations were observed in the dry solid except the $IV \rightleftharpoons III$, which was only found to take place in the presence of moisture. The structures I, II, IV, and V were found to be mutually related, forms II, IV, and V being distorted versions of form I. Form III does not bear any structural similarity to other stable forms.

Transitions in ammonium nitrate have been found to be largely time independent [13] and therefore, a well defined T_t can be specified. The presence of the metastable phases, however, gives rise to some complication in the mechanism of transformation. From x-ray analysis, the phase transitions have been interpreted as rotation-disorder transitions. Kamayashi and Yamakani [14] have reported all the transitions of NH₄NO₃ showing anomalies in the dielectric measurements and DTA. Some of these transitions . were found to follow large thermal hysteresis.

Existence of a low temperature modification, VII, of ammonium nitrate below 103 K has been substantiated by microscopy, x-ray diffraction and thermal analysis [11]. NH₄NO₃ quenched at 77 K was found to consist of modifications IV and VII [11]. Specific heat measurements showed an anomaly at ~ 212 K [15] which, however, was not verified by DTA [16] and x-ray diffraction [16a]. In the low temperature rotation photographs, superstructure lines were found. Jaffray [17] repeated this work using a copper block with one hole and a copper block with two holes (NaCl as reference)



A metastable transition, orthorhombic (IV) \rightleftharpoons tetragonal (II) at 318-323 K has also been reported by many workers [4-8] particularly when single

and showed an anomaly between 208 and 216 K. The sample was cooled below 173 K and the measurements were made from this temperature upward keeping a suitable warming rate. These studies indicated a new transformation at a lower temperature. It is concluded from Jaffray's results that it is to this new polymorphic transformation at 113– 123 K that the modification in Raman Spectrum observed by Volkringer et al. [18] between 81 and 198 K can be attributed.

No major effect was observed on the transitions of NH₄NO₃ if small amounts of Na, Li, Ag, or Tl nitrates were present, but the transition characteristics were found to change in the presence of K, Rb or Cs-nitrates [19-21]. Addition of KNO₃ has a remarkable effect on the condition of NH₄NO₃. It decreases the density of NH₄NO₃ slightly, lowers the transition temperatures, lowers the expansion on transition, reduces the hygroscopicity and reduces the number of contact points as well as caking. It, however, does not affect the degree of hydration [22]. Effect of other impurities like $Cu(NO_3)_2$, $Mg(NO_3)_2$, $Zn(NO_3)_2$, $MnSO_4$, and $Na_2B_4O_7$ on the transitions was also studied [23]. Stabilization of the cubic phase was observed when CsCl and other halides were added. With NaNO₂ and CsNO₂, the tetragonal phase was stabilized [24]. Stabilization of the polymorphs of NH₄NO₃ as crystallized on a mica cleavage surface seemed to be a consequence of the close correspondence between the parameters of the stabilizer and those of the ammonium nitrate polymorph concerned [24]. All the mixtures from pure NH_4NO_3 to as far as 8 percent NH₄Cl were found to crystallize as homogenous mixed crystal phases of isometric (cubic) symmetry [25]. The cubic phase (I)- tetragonal (II) inversion changes from 398.5 K for pure NH₄NO₃ to 382 K for the solid solution containing 2.5 percent NH₄Cl. At 382 K, the curve of unmixing of solid solutions was encountered and along this curve, the phenomena of mixing and unmixing of solid solutions was found to take place and could be observed directly [25]. Addition of (NH₄)₂SO₄ affects the IV \rightleftharpoons III phase transition of ammonium nitrate. With increase in sulfate content from 2 to 30 wt percent, the T_t of NH₄NO₃ increases from 310 to 311.5 K. At higher concentrations of (NH₄)₂SO₄, double salts are formed and there is no phase transition in the 298-323 K range [26, 27]. Nagatani [10] added octadecylamine, its nitrate or acetate to NH₄NO₃ in aqueous or cyclohexane solution in such a way that the additives precipitated on the surface of ammonium nitrate particles. DTA and x-ray diffraction showed that the effects of these additives between 0.03 and 0.3 wt percent was to extend the tempera-

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ture region of stable existence of phase IV and to eliminate the transition III \rightarrow IV at 305 K.

Deuterated Ammonium Nitrate, ND₄NO₃.

Hovi et al. [28] measured the deutron magnetic resonance line-widths in ND₄NO₃ between 100 and 403 K. They obtained values of 255, 308.5, 366, and 400.5 K with a maximum uncertainty of ± 2 K for the transformation temperatures of $V \rightarrow IV$, $IV \rightarrow$ III, III \rightarrow II and II \rightarrow I phase transformations respectively. Niemela and Lohikainen [29] studied the spin-lattice relaxation times of deutrons in ND_4NO_3 . The modification III of this substance could not be observed by them, similar to the results of Brown and McLaren [12] and Nagatani et al. [30] for dry samples of NH₄NO₃. Pöhyönen et al. [31] employed a modified DTA technique for a study of the various transformations in deuterated ammonium nitrate. The equilibrium temperature in the transformations $IV \rightleftharpoons III$, $III \rightarrow II$ and $II \rightleftharpoons I$ were observed as, 302.8, 361.52 ± 0.06 and $400.58 \pm$ 0.04 K, respectively. The melting point of ND₄NO₃ was found to be 1.2 K greater than that of NH₄NO₃ due to the isotope effect. In the $I \rightleftharpoons II$ transformation, thermal hysteresis was not observed as indicated earlier by a number of workers in the case of NH₄NO₃ [12, 32]. Superheating of modification II was not found to take place at the transformation $II \rightarrow I$, while supercooling of the modification I was observed at the transformation $I \rightarrow II$. Considerable superheating and supercooling proved characteristic of the III and II phases at the II \rightleftharpoons III transformation. Small thermal hysteresis was observed during this transformation. The III \rightleftharpoons IV transformation was also found to be associated with small thermal hysteresis. Modifications III and IV of ND₄NO₃ supercooled by 0.7 and 0.5 K, respectively. Consideration of the effect of deuteration on the Gibbs function of various modifications of ammonium nitrate indicated that the interaction of the NH_4^+ group with the lattice seemed to be strongest in modification III.

High Pressure Transformations: Janecke [33] found all the known transformations of NH_4NO_3 at higher pressures with his electrically heated pressure apparatus. The transitions were found only partially manifested by an uneven change in the pressure. In many cases, the change was found to be gradual over a temperature interval, and the pressure curves were rectilinear before and after the transition. The intersection of these curves corresponded to the transition point. Phase diagrams between 273 and 473 K were determined by Bridgman [34] at pressures between 0.98 bar (1 kg cm⁻²) and 11.77 kbar (12000 kg cm⁻²). These show a new modification of ammonium nitrate. Recently, Rapoport and Pistorius [35] have also found a new modification VI during their study of the phase transformation of ammonium nitrate by DTA at high pressures; the pressure and temperature ranges of their study were 0–35 kbar and 223–623 K, respectively. The univarient lines of the I–VI, IV–VI, and I–IV transitions were found to meet at a triple point near 9.5 kbar and 529 K.

Leskovich [36] studied the effect of pressure on the polymorphic transformations of ammonium nitrate between stable modifications V(T < 255 K), IV(255-305.1 K) and III(305.1-357.2 K). The average value for the increase in the volume expansion for the $IV \rightarrow III$ transition at normal pressures was found to be 6.5 percent. The temperature for the start of the IV-III transition was 316 K at a pressure of 392.24 bar. Leskovich [37] further found that modification IV does not show relaxation of pressure because of a minimum molar volume. The modification III possesses the largest molar volume of all known crystal modifications of this salt and easily transforms to modification IV at 323 K. Cerisier [38] studied the electrical conductivity of dehydrated NH₄NO₃ (polycrystalline pellet) at 1-600 bar and 355-442 K. In this temperature range, ammonium nitrate exists in two different forms. Measurements under increasing and decreasing temperatures showed a hysteresis loop related to a structural transformation.

NH₄NO₃

Measurement technique	Observations	Remarks	References
X-ray diffraction	Transition T_t , K (approx.) $V \rightleftharpoons IV$ 255 $IV \rightleftharpoons III$ 305 $III \rightleftharpoons II$ 357 $II \rightleftharpoons I$ 398The structural information for various phases are: 398 I. cubic, $Z=1$, $a=4.36$ Å at 403 KII, tetragonal, $Z=2,a=5.712$ Å $c=4.924$ Å at 363 KIII, orthorhombic, $Z=4$, $a=7.197$ Å $b=7.716$ Å $c=5.845$ Å at 323 KIV,* orthorhombic, $Z=2$, $a=5.756$ Å $b=5.452$ Å $c=4.931$ Å at 296 K	A metastable transition at 323 K has also been reported. In pulverized samples con- taining octadecylamine, its nitrate etc., complicated thermal hysteresis effects in the V-II phase change are observed. The transition involves a new reversible phase V* between V and II. T_t , $V \rightleftharpoons V^*$ is 315 K and T_t , $V^* \rightleftharpoons II$ is 318 K, both being λ -type transitions.	[1-8, 12, 39-46].
Dilatometric measurements	 *The room temperature structural informations given in the heading is from the NBS monograph. V, tetragonal.† a = 7.925 Å c = 9.820 Å at 255 K †Also reported pseudo-hexagonal. Z = 6, a = 5.75 Å, c = 15.9 Å below 255 K [2]. The transitions have been found to be associated with considerable thermal hysteresis. T_i's by several authors do not differ by more than ±1.5 K. 	Water present in the specimen greatly af- fects the transition temperature and ve- locity. In dry samples the transition often proceeds as a single crystal transforma- tion without any appreciable change in orientation. The kinetics of the transition	[6, 7, 43, 47–50].

 NH_4NO_3 - Continued

Measurement technique	Observations	Remarks	References
	Grinding of NH ₄ NO ₃ increased the rate $d\alpha/dt$. Recrystallization in smaller crystals had similar effect. Lattice defects present in the surface of phase III probably belong to a higher melting modification rather than to lower melting phase IV. The volume change (ΔV) is as follows:	The equations similar to those describing topochemical reaction were used to cal- culate the curves of (IV-III) transforma- tion isotherms. $\ln (1-\alpha) = -kt^n$ and $\frac{d\alpha}{dt} = B\alpha^{2/3} = (1-\alpha)^{2/3},$	[51-58].
	$III \rightleftharpoons II - 0.0148 \text{ cm}^3$ $II \rightleftharpoons I 0.0220 \text{ cm}^3$	where $\alpha =$ degree of transformation t = time in minutes k & n are constants and $k^{1/n}$ is the reaction rate constant. For III-II transformation, α is given by $\ln (1-\alpha) = -(kt)^3$, the rate constant k rapidly increased when the temperature was further removed from T_t .	
Differential Thermal Analy- sis.	The transition II \rightleftharpoons III, III \rightleftharpoons IV and IV \rightleftharpoons V were found to show consid- erable hysteresis. Dry NH ₄ NO ₃ was not found to show IV \rightarrow III transition but a direct transition IV \rightarrow II. The T_t shows a linear change with the logarithm of water content.	The conditions for the appearance and disappearance of the metastable transi- tion around 318 K (II \rightarrow IV) and the shift of T_t by the heat-treatment were studied in detail. The adsorbed water in the samples gave rise to a sharp large peak.	[6, 12,14, 59–62].
	heat of transitions IV-V 0.13 kcal mol ⁻¹ III-IV 0.42 kcal mol ⁻¹ II-III 0.32 kcal mol ⁻¹ I-II 1.03 kcal mol ⁻¹		
	Rotation disorder transition of NH4NO3 have been investigated.	NH ₄ NO ₃ can be used as a temperature standard because the transition reac- tions are not time dependent. Meta- stable phases, however, make the mecha- nism of transition slightly complicated.	[13].
Calorimetric measurements, specific heat etc.	For a carefully dried sample, the V ≓ IV transition was found to occur at 265 K. An anomalous increase in heat capacity above 190 K was observed.	An analysis of the heat capacity below 100 K yielded estimates for the fre- quencies of torsional oscillation of NO ₃ ⁻ ion and NH ⁴ ₄ ion in phase V.	[63–66].
	The direct transition between V and II is observed in NH ₄ NO ₃ treated with some surface active agents. For this transition $\Delta H_{tr} \sim 777.7$ cal mol ⁻¹ $\Delta S_{tr} \sim 2.61$ cal mol ⁻¹ K ⁻¹ The ΔH_{tr} and ΔS_{tr} for other transitions are as follows:	 NH⁺₄ ion is found to rotate freely in phase III in contrast to fully excited torsional oscillation in phase IV. The transition V-II is considered to occur as a combined phenomena of orientational order-disorder of the two ione NH⁺ and NO⁻ 	
	$\begin{array}{c c} \Delta H_{\rm tr} & \Delta S_{\rm tr} \\ \hline \\ $	The small anomaly at 156 K seems to be due to the existence of a new phase VII as reported earlier [11].	

	I		
Measurement technique	Observations	Remarks	References
Dielectric constant and dispersion etc.	 All the transitions have been found to show considerable hysteresis. The measurements did not show any transition near 213 K. The phase transition IV ≓ III ≓ II gave no significant effect on the nature of the two abnormal dielectric dispersions obtained between 25Hz and 50kHz. 	Polymorphic transitions appear distinctly in capacitance-temperature curves. The dielectric constant of the phase II was found to be much higher than that of phase III, which is associated with the motion of the NO ₃ groups in the unit cell.	[14, 67–70].
Ionic conductivity measure- ments.	Abrupt changes in conductivity were found at T_t 's.		[12, 67, 71, 72].
Microscopic observations on single crystals at high temperatures.	Three different facet planes (010), (011), and (001) were studied. In the II \rightarrow IV transition, the single crystal splits into two kinds of crystallites with a common c-axis but exchanged a- and b-axes. The interface between the split crystallites is parallel to the (110) plane which could be a twin plane. In the IV \rightarrow II transition the split crystal- lites rejoin into a single phase. The result- ant phase in both transitions is needle shaped. The transformations IV \rightleftharpoons III and III \rightleftharpoons II were found to reconstruct and proceed according to a mechanism of distortion and recrystallization in the presence of water vapour or drops of a saturated solution of NH-NO.	The splitting during the II \rightarrow IV transition occurs so as to reduce the stress due to change in the lattice constants. The II phase grows in the (230) plane of the IV phase in the IV-II transition whereas the IV phase grows in the two equivalent planes (230) and (320) of the tetragonal II phase in the reverse transition. The metastable transition IV \rightleftharpoons II proceeds according to a rearrangement mechanism. No crystals of phase III were produced from a saturated solution of NH ₄ NO ₃ even at its optimum temperature of formation. Crystals of II and IV produced from the same solution transformed into III when given a needle shock, which indicates the necessity of crystal nuclei due to lattice distortion	[73, 74].
Birefringence	The transitions were recorded by change in birefringence at T_t 's.		[48].
Optical studies	 T_t's 318.3 K (II'-IV) 320.8 K (IV-II) A phase II' of tetragonal or lower symmetry was observed as the samples were annealed in the stability range of NH₄NO₃ (III). Some optical properties of NH₄NO₃(III) were revised resulting in a positive optical sign and the optical axis angle 	The orientation relations in the different phase transitions were also studied. Addi- tion of KNO ₃ lowers the II'-IV transition tion temperature and decreases the 2V values.	[75].
Ultraviolet spectroscopy	$2V_{\gamma} = 86 \pm 1^{\circ}$. A gradual shift of absorption bands has been found to accompany the thermal expansion of the crystals. At T_t 's more abrupt changes in absorption spectra have been observed.	The shifts in absorption maxima due to temperature change have been inter- preted in relation to changes in the dis- tance between cations and anions.	[32].
	$\begin{array}{c} \underline{\text{Iransition}} \\ \overline{\text{II}} \rightarrow \overline{\text{III}} \\ \overline{\text{III}} \rightarrow \overline{\text{III}} \\ \overline{\text{III}} \rightarrow \overline{\text{III}} \\ \overline{\text{III}} \rightarrow \overline{\text{III}} \\ \overline{\text{III}} \rightarrow \overline{\text{III}} \\ +1.04 \end{array}$		
Density measurements	The III \rightleftharpoons IV transition is found to accompany gradual change of the density and occurs over a temperature interval of approx. 3 K.		[76].

NH4NO3-Continued

Measurement technique	Observations	Remarks	References
Grain size measurements	Change in grain size is reported during the 360 K (III ≓ II) transformation in NH₄NO₃. The number of grains per unit area increased from 2 to 36.		[77].

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2.4. Thallous Nitrate, TINO₃

(orthorhombic, Z = 8, a = 6.287 Å, b = 12.31 Åű c = 8.001 Å at 298 K)

Ferrari et al. (1) and Hinde and Kellet [2] have reported that the room temperature structure of thallous nitrate (form III) is orthorhombic and belongs to one of the two possible space groups, D_{2h}^{16} -Pbnm or C_{2v}^{9} -Pbn2₁. The unit cell constants of the room temperature structure given by these authors agree well with those of Brown and McLaren [3] and Swanson et al. [4]. Hinde and Kellet [2] suggested that the true unit cell may be regarded as being equivalent to the stacking in the direction of the *c*-axis, of two smaller cells possessing the *c*-parameters equal to half the true value.

Thallous nitrate shows two phase transitions:



Phase II is hexagonal with a = 10.543 Å, c = 7.431 Å, sp.gr. P31m and Z = 9 [5]. Phase I is cubic with a = 4.326 Å at 443 K in agreement with the value reported by Finbak and Hassel [7]. Brown and McLaren [3] have also pointed out that the unit cells of phases II and I are related in the same manner as forms IV and III of RbNO₃. Finbak and Hassel [7] suggested that the NO₃ ion in form I is spherically symmetrical, being in a state of free rotation. Phase transitions of thallous nitrate have been reviewed by Newns and Staveley [6] and McLaren [8], who have discussed the results from thermodynamic, electrical, magnetic, optical and crystallographic measurements.

High Pressure Transformations: Bridgman [9, 10] studied the phase diagram of thallous nitrate up to 50 kbar and 473 K and later extended the study up to 100 kbar [11]. He pointed out that the phase boundary between phases I and II has very nearly the same slope in the pressure-temperature plane as that between phases II and III of RbNO₃ and phases I and II of CsNO₃. The one atmosphere transition temperatures for the above phases are very close suggesting a similarity between the corresponding phases [12].

Measurement technique	Observations	Remarks	References
X-ray diffraction	$T_{\rm t}$'s, 348 and 416 K for the phase transitions III \rightleftharpoons II and II \rightleftharpoons I, respectively.		[1–5, 8].
Dilatometric studies	Both the transitions are followed by increase in volume, ΔV being 0.0034 and 0.0156 of unit volume at 273 K, respectively.		[13].
Direct differential calorimetry	$\Delta H_{\rm tr}$ for II \rightarrow I transition has been observed to be 907 ± 1.5 percent cal mol ⁻¹ .	This value is somewhat higher than that de- termined by indirect methods.	[14].
Heat capacity and thermal co- efficient measurements.	$T_{\rm t}$'s. 352 and 416 K (on heating) and 416 K on cooling. No sharp transformation was observed on further cooling, although there was some indication of a very slug- gish transformation in 353-293 K range.	After cooling from the first heating immedi- ate reheating again showed the transition at 352 K thereby giving a positive evidence of III → II transformation.	[8].
Heat capacity measurements.	Mean heat capacities of TlNO ₃ has been measured as a function of temperature. The molar heats between 273-373 K. can be expressed by $C_p = 10.95 + 42.66 \times 10^{-3} T$. Extrapolation to 273 K gave the specific heat C_0 at that temperature. The specific heat C_t at any temperature (t in °C) was then calculated by the equation, $C_m = (C_0 + C_t)/2$; a sudden increase in C_t was found at T_t .	 The results confirm that thallous nitrate is capable of existing in 3 allotropic modifications. Free rotation of NO₃ in TlNO₃ has also been confirmed by the measurements of variation of molar heat with temperature. 	[15, 16].
Measurements of entropies of transition.	$ \frac{\Delta S_{tr}}{T_{t} \cdot K} = \frac{\Delta V}{\begin{array}{c} cal \mod^{-1} K^{-1} \\ 348 \end{array}} = \frac{0.7}{0.4} \\ 416 \qquad 2.18 \qquad 1.4 $	It seems unlikely that the III \rightarrow II transi- tion in TINO ₃ involves orientational dis- order. This is contrary to previous find- ings of McLaren [8].	[6, 14,17].
High pressure DTA meas- urements (up to 45 kbar).	Phase diagram of TINO ₃ has been studied up to 923 K and 40 kbar. T_{1} , 352 and 417 K. No DTA signals cor- responding to the III \rightarrow II transition could be observed possibly due to the extreme sluggishness and small latent heat. Experimental points on the II/I phase boundary can be fitted by the relation. $t(^{\circ}C) = 144.6 + 7.91P - 0.062P^{2}$.	It is possible that orthorhombic phase (III) of TlNO ₃ may be isostructural with RbNO ₃ -V and CsNO ₃ -II. The II \rightleftharpoons III transition in TlNO ₃ is quite sluggish just like RbNO ₃ IV \rightleftharpoons V and CsNO ₃ II \rightleftharpoons III phase transitions.	[18].
Electric conductance meas- urements (dc & ac con- ductivity.	Transition II → I was accompanied by a large increase in conductivity.	Conductivity measurements of Brown and McLaren showed a drop in the σ values at 353 K (III-II transition point). Re- cycling showed that the fall in conduct- ance at this transition is probably asso- ciated with the removal of moisture and that in perfectly dry samples little or no change at this temperature may be observed.	[3, 19].
Dielectric constant and re- sistivity.	Small maxima occur at the high tempera- ture transitions. A low temperature transition has also been demonstrated at 238 ± 5 K by the anomalous dependence of dielectric constant and resistivity on temperature		[20, 21].

TINO₃ - Continued

Measurement technique	Observations	Remarks	References
Ultraviolet spectroscopy	A gradual shift of absorption bands is found to accompany the thermal expan- sion of the crystals.	In cases where crystal-structures are known, shifts in absorption maxima due to changes in temperature have been interpreted in relation to changes in dis- tances between cations and anions. UV absorption spectroscopy provides a sensi- tive means for studying various thermo- dynamic effects in phase transformation.	[22].
Grain size measurements	The number of grains per unit area de- creased from 2 to 1 in TINO₃ at III → II, transformation 345.8 K.		[23].
NMR studies	No abrupt changes in line-width at the transition temperatures were found. Immediately above and below the melt- ing point, the magnetic resonance line was of the order of one tenth of a gauss wide. The line-width increased very rapidly as the temperature was lowered and was too large to be observed at room tem- perature.	It is suggested that the low temperature line-width is determined predominantly by nuclear spin exchange taking place among the nuclear moments present.	[24].
Optical measurements	Single crystals grown from aqueous solu- tion, when examined under the polarizing microscope, were found to be aniso- tropic. On heating the III \rightarrow II trans- formation at ~ 353 K was observed. Form II was also found to be anisotropic. II \rightarrow I transformation was observed at ~ 423 K, the crystal changing to be isotropic. On cooling, I \rightarrow II transforma- tion was observed at slightly lower temperature.	The crystals retain their external shape and also their crystallographic orienta- tions even after being taken through four $II \rightarrow I \rightarrow II$ cycles. The extinction angle was usually less definite, suggest- ing some randomization of orientation around a mean value.	[3].

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2.5. 3d-Transition metal nitrates

The limited information available in the literature

3 d-Transition metal nitrates

Substances and measurement technique	Observations	Remarks	Refer- ences
Chromium (III) nitrate (hydrat	ed), $Cr(NO_3)_3 \cdot 9H_2O$, monoclinic, $P2_1/c$, $a = 1$	3.915 Å, $b = 9.681$ Å, $c = 10.983$ Å and $\beta = 84^{\circ}$	°16′ [1]
Specific heat	Cr(NO ₃) ₃ · 9H ₂ O undergoes a second order transition at 158 K.	The transition has been attributed to the onset of partial rotation of the water molecules within the crystal.	[2].
Dielectric measurements	Transition at 158 K has not been found to have any observable effect on polariza- bility.	· ·····	[3].
	Cobalt(II) nitrate (hydrated), Co(NO	$O_3)_2 \cdot 6H_2O$	L
Specific heat	Co(NO ₃) ₂ · 6H ₂ O undergoes a second order transition at 158 K.	The transition has been attributed to the onset of partial rotation of the water molecules within the crystal.	[2].
Thermal analysis and dilatom- etry in liquid media. X-ray diffraction at low temper- atures.	 Curves were obtained showing the variation in volume as a function of temperature (in the range 93 K-room temperature). After several thermal cycles, a new thermal anomaly was found accompanied by a contraction of the crystal in the 253-275 K region. These measurements confirm the existence of three forms I, II and III hexahydrates of cobalt nitrate. I, monoclinic, a = 15.09 Å, b = 6.12 Å, 	 Addition of water causes thermal anomalies (heat evolution) at some definite temperatures, the extent of which depends upon the quantity of water added. The thermal anomalies when the water is absorbed was also detected even when the water of hydration was lost by dessication. When the samples were kept in diethylether, the anomaly shifted from 239 to 252 K. On complete evaporation after the first thermal cycle, the transition temperature was found to shift and return to 239 K in a third thermal cycle. Immersion of the crystals in petroleum ether or toluene caused no modification in thermal curves. Crystal was found to disintegrate at 198 K transformations. 	[4-8].
	$c = 12.67 \text{ Å}, \beta = 119^{\circ}$ II. $a = 12.58 \text{ Å}, b = 6.29 \text{ Å}, c = 12.24 \text{ Å}$ III. Structure could not be accertained		
	Nickel (ID nitrate (hydrotod) Ni/N).)	
triclinic	intener (ii) intrate (liyulateu), Milite	53/2 51120	
$a = 7.694 \text{ Å}, b = 11.916 \text{ Å}, c = 5.817 \text{ Å}, \alpha = 102.3^{\circ} \beta = 102.4 \text{ Å}, \gamma = 105.9^{\circ} and Z = 2, \text{ sp.gr.P1}$			[10].
Thermal measurements, Heat capacity etc.	Ni(NO ₃) ₂ ·6H ₂ O shows a second order at 150 K.	The transition is attributed to the onset of partial rotation of the water molecules within the crystal. The transition tem- perature is dependent on the no. of water molecules in the crystal.	[2, 11].
	33		

3 d-Transition metal nitrates - Continued

Substances and measurement technique Observations		Remarks	Refer- ences
Dielectric measurements	The transition at 150 K was found to be unassociated with any dielectric anomaly.		[3].
	Nickel (II) nitrate (hydrated), Ni(NO ₃)	2 · 2H ₂ O	
Heat capacity	It showed a sharp λ-anomaly at 4.105± 0.005 K.	The anomaly is characteristic of a transition to a magnetically ordered state at $T_{\rm N}$.	[12].
	Copper (II) nitrate, Cu(NO ₃) ₂		
Spectroscopic studies	Transition from phase II to phase I was observed. Infrared spectra of anhydrous unsublimed cupric nitrate samples showed that metal-nitrate vibration is lower in energy for the low temp. phase II than for the high temp. phase I.	The unsublimed sample was found to be a mixture of both forms.	[13].
	Copper (II) nitrate (hydrated), Cu(NO ₃)	₂·2.5H₂O	
Proton magnetic resonance (up to magnetic field 50kOe at tem- perature below 1 K).	The copper ions form pairs with an ex- change interaction $-J/k$ of about 5 K. In magnetic fields around 36 kOe, the much weaker inter-pair exchange J' lead to short- and long-range order below 0.55 and 0.16 K, respectively.	The phase transformation at 0.16 K is characterized by a spontaneous com- ponent of the time averaged magnetic moment of the copper ions perpendicular to the external field and disappears below 29 and 42 kOe.	[14].
Heat capacity (Temp. range: 0.5 K-4.2 K) Magnetic susceptibility (powdered sample).	 In zero applied field, C_p, exhibited a Schottky anomaly having the maximum value of 0.51R at 1.82 K. A broad maximum was found at 3.2 K; measurements down to 0.4 K suggest that χ_p vanishes as T goes to zero. The susceptibilities of needle like monoclinic crystals of this salt exhibit small nearly uniaxial anisotropy about the b or needle axis. The temperature variation of X 	The data are quantitatively described by assuming that Cu^{+2} ions exist in this salt as isolated pairs (binary clusters) coupled by isotropic antiferromagnetic exchange with $-J/k=5.18$ K. The behaviour is quite unlike that of a typical three dimensional antiferromag- net. There is a possibility that Cu^{+2} moments in this salt might be coupled by isotropic antiferromagnetic exchange interaction either in isolated pairs (binary clusters) or in extended linear chains	[15].
	axis. The temperature variation of $\chi_{ }$ and χ_{\perp} is similar to χ_p .	clusters) or in extended linear chains.	
	Zinc(II) nitrate (hydrated), ZN(NO ₃) ₂ :	6H ₂ O	
Dilatometric studies	When up to 0.8 extra mole of water is present in this compound, an expansion is observed after the expected contrac- tion during the cooling cycle. If as little as 0.08 mole of water is absent from the stoichiometric 6, little or no volume change is observed during cooling and a contraction followed by an expansion, is observed during the heating cycle.		[17].

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2.6. Silver Nitrate, AgNO₃

(orthorhombic, space group: one of the four D_2^1 , D_2^2 , D_2^3 and D_2^4 , Z = 8, a = 6.995 Å, b = 7.328 Å, c = 10.118 Å, at 299 K)

Lindley and Woodward [1] reported the unit cell dimensions to be a = 6.997 Å, b = 7.325 Å, c = 10.118A with space group Pbca and Z=8. This orthorhombic phase of silver nitrate (II) transforms at 432.5 K to a rhombohedral phase I which has a hexagonal unit cell with $a = 5.203 \pm 0.005$ Å. $c = 8.522 \pm 0.005$ Å (space group R3m) at 437 [2]. McLaren [3] has reviewed the phase transition of silver nitrate and has discussed the changes observed in crystallographic, thermodynamic, electrical and optical properties. Newns and Staveley [4] have described the II \rightarrow I transition in AgNO₃ as a first order phase change which is followed by a volume contraction of about 1 percent [5] and an entropy change of 1.37 eu [6]. A metastable phase, III, with rhombohedral structure has also been reported to be formed on cooling AgNO₃I from well above 433 K [7]. Davis et al. [9] have reported the volume change at the transition around 432 K to be too sluggish to become apparent, but a marked change in slope was observed above 438 K. This result does not agree with the previous results of volume change at the transition [5,9a] of silver nitrate

as a function of temperature. On cooling a sample chilled from melt, the conductance decreased sharply at about 438 K, although such a discontinuity was not observed while reheating. Optical studies of Ubbelohde and coworkers [10, 11] show a sharp change in the absorption spectrum at T_t . Fermor and Kjekshus [12] have found that AgNO₃ exhibits another transition at 238±5 K, which was demonstrated by an anomalous dependence of dielectric constant and resistivity on temperature.

Fischmeister [8] found that on heating polycrystalline samples of AgNO₃, the II \rightarrow I transition takes place around 432 K. The transition was reported to involve excessive fragmentation of the crystal so that satisfactory x-ray lines could only be obtained after prolonged recrystallization near the melting point.

Mauras [13] found that the transformations II \rightarrow I and I \rightarrow II in silver nitrate do not occur at the same temperature. There is a difference in the transformation temperatures which is caused by the volume change accompanying the transformation. Kennedy and Schultz [14] reported that the transformations at ~ 432.4 K becomes quite sluggish on undercooling the sample to room temperature. Maziers' and Van't Hoff [7] reported that silver nitrate forms a metastable phase at 353 K on cooling. This modification can persist for hours before it changes to the stable orthorhombic form. They also found that single crystals of silver nitrate nucleated spontaneously at the transition point. A maximum superheating of 14 K was noted.

High Pressure Transformation: Janecke [15] studied the $II \rightarrow I$ transition at high pressures. Bridgman [16] studied the change in volume, latent heat of transition, difference in compressibility, thermal expansion and specific heat up to 12 kbar, which was later extended to 50 kbar [17, 17a]. Four high pressure polymorphic forms were reported. Extending the measurements up to 100 kbar did not yield new polymorphic forms [18, 18a]. Rapoport and Pistorius [19] determined the phase diagram of silver nitrate by means of DTA and volumetric methods up to 45 kbar. In addition to the four phases, metastable AgNO₃-V could also be obtained by suitable manipulation above 21 kbar at temperatures below 323 K. The metastable AgNO₃ I \rightarrow V transition is reversible. AgNO₃-V reverts to stable AgNO₃-II, if left under pressure overnight. Genshaft et al. [20] measured the volume change with increasing pressure in the temperature range 73-673 K for pressures up to 40 kbar.

Measurement technique	Observations	Remarks	References	
X-ray diffraction	T ₁ . 433 K. Transition from orthorhombic to rhombo- hedral.	 Microscopic and x-ray methods establish that II → I and I → II transitions take place by formation of a seed in the crystal matrix and subsequent growth of this seed. Depending on the number of nascent crystallization centres, transitions of two types occur: (i) single crystal → single crystal type (ii) single crystal → polycrystal type. 	[2,3,21].	
		There is no mutual crystallographic link between new and matrix crystalssssses between new and matrix crystals during the II \rightleftharpoons I transition.		
Calorimetry	T_t , 432.4 K ΔH_{tv} , (approx.) 0.58 kcal mol ⁻¹	Heat capacity data differ from those re- ported by Janz et al. [23, 24] from drop calorimeter measurements	[6, 22–25].	
Differential thermal Analysis	Examination of the cooling curves showed that either a direct reconversion to the orthorhombic variety took place or a new metastable phase appeared below 353 K; the latter was more easily formed when the sample had been heated well above 433 K and consisted of microcrystalline powder instead of one single crystal.	Grinding the sample gives a T_t 5.5 K higher than that of the unground sample. Effect of the grinding seems to be kinetic, namely the formation of a barrier to the transition.	[7, 26, 27].	
Ultraviolet spectroscopy	A gradual shift of absorption bands is found to accompany thermal expansion and more abrupt changes in absorption spectra are observed at transformation points from one crystal structure to another.	By means of the techniques described, ultraviolet absorption spectroscopy proves a sensitive means for studying various thermodynamic effects in phase transformations.	[11].	
Change in grain size and number.	The number of grains per unit area decreased from 7 to 4 for $AgNO_3$ at 433 K.		[28].	
Kinetic study of AgNO ₃ (between 243 K and 444 K).	It was found that the transformation is faster in larger crystals. The trans- forming crystals suffer plastic deforma- tion and the growth rates depend on crystallographic direction.	The rate of $I \rightarrow II$ transformation reaches a maximum at 375 K. The peak of this rate curve is shifted to higher temperatures by addition of 0.225 atom percent of Cd. ⁺² Empirical relations governing the growth have been discussed.	[14, 29].	
ł	Activation energy in the temperature range 303-373 K has been found to be 21.14 kcal mol ⁻¹ . At higher tempera- tures below the equilibrium point (433 K), the apparent activation energy approaches zero. It is suggested that a different process limits the rate in this region.	Theory of rate process was applied by Eyring et al. [29].		
Low temperature dielectric and resistivity measure- ments (193-303 K).	An anomalous dependence of ϵ and ρ on temperature at T_t is observed.	The hysteresis suggests the existence of disorder within the room temperature phase on heating.	[12].	

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3. Carbonates

The carbonates of alkali metals, alkaline earth metals, thallium, some of the 3*d*-transition metals and silver have been reported to undergo phase transformations. Of these, the alkaline earth metal carbonates have been investigated extensively.

3.1. Alkali Metal Carbonates

Alkali metal carbonates are highly reactive even at low temperatures and undergo varying degrees of dissociation at higher temperatures. This results in contamination of specimens complicating studies of these compounds. There is not much work reported on phase transformations of these solids in the literature. Following is an account of the available information on individual carbonates.

Lithium Carbonate, Li₂CO₃, monoclinic, I2/c, Z = 4, $a = 8.11 \text{ Å}, b = 5.00 \text{ Å}, c = 6.21 \text{ Å} and <math>\beta = 109^{\circ}41'$ [1].

Reisman [2] reported a phase transformation in this compound at 683 ± 3 K from his DTA studies. In the absence of CO₂, an additional heat effect appeared at 623 K. The 683 K transformation is not affected by the 623 K heat effect which indicates that the latter is due to either a phase transformation in Li₂O or more probably to the eutectic solidification in the high carbonate region of the system Li₂O-Li₂CO₃, obtained on dissociation [3]. Semenov and Zabolotskii [3] from their DTA, electrical conductivity and gas volumetric studies show a new phase transformation in Li₂CO₃ at 439 K.

Sodium Carbonate, Na₂CO₃, monoclinic, Z = 4, a = 8.90 Å, b = 5.24 Å, c = 6.04 Å and $\beta = 101.2^{\circ}$ at 296 K [4].

There are two solid state phase transformations in Na_2CO_3 below melting point [4]:

621 k		169 V
III 054 F	→ II - 4	$\xrightarrow{02 \text{ K}}$ I
c-centered	c-centered	primitive
monoclinic	monoclinic	hexagonal
e crystal data fo	r phases II a	nd I are as follows:
Z = 4, a = 9.000	Å, $b = 5.24$	Å, $c = 6.31$ Å, and
=96.9° (713 K);]	I, Z = 2, a = 9	9.01 Å, $b = 5.20$ Å,
=6.50 Å, and β=	$=90^{\circ}$ (773 K)	. $\gamma - \beta$ transition is

 $(2a+b)_{\alpha}=a_{\beta}, \quad a_{\alpha}=b_{\alpha}=b_{\beta},$

and

 $c_a = c_{\beta}$. Dubbeldam and DeWolff [5] show that phase III is a deformed version of hexagonal phase I. Thermal measurements of Popov and Galchenko [6] show that the transition III \rightarrow II is of second order with $\Delta H_{tr} \sim 200$ cal mol⁻¹, while II \rightarrow I is of first order with $\Delta H_{tr} \sim 450$ cal mol⁻¹. Jaffray and Martin [7] however, reported that III \rightarrow II transition is not accompanied by any change in latent heat or modification. Thermodynamic investigations [8] in the temperature range 15-300 K did not show any anomaly.

Potassium Carbonate, K_2CO_3 , monoclinic, a = 5.658 Å, b = 9.858 Å, c = 6.916 Å and $\beta = 98.30^{\circ}$ at 386 K [9].

Th

II.

β=

c =

gradual

and

Makrov and Shul'gina [10] on the basis of their DTA studies reported that K₂CO₃ undergoes transformations at 523, 703, and 898 K. Jaffray and Martin [7] found second order transitions in K_2CO_3 at 683 and 738 K accompanied with thermal hysteresis. Reisman [2] from DTA studies differentiated between the results obtained in air and carbon dioxide. He concluded that potassium carbonate undergoes only one phase transformation (at 695 K \pm 2 K) and that other thermal effects occurring in atmospheric conditions are due to the impurities such as KOH and KCl. Schneider and Levin [9] studied the phase transformation in this solid by x-ray, DTA and differential scanning calorimetry. They substantiated Reisman's result that K₂CO₃ undergoes one reversible transformation and that other heat effects in air must be associated with impurities. High temperature x-ray diffraction and differential scanning calorimetry [9] show T_t to be 693 ± 5 K. Schneider and Levin [9] concluded that the monoclinic to hexagonal transformation is of second order. The crystal data for the hexagonal phase is as follows: at 698 K a = 5.705 Å and c = 7.169 Å.

Rubidium, *Carbonate* (No crystallographic data seem to be available).

Reisman's DTA studies [2] show a second order phase transformation (II \rightarrow I) in Rb₂CO₃ at 576±2 K. No new heat effects were observed in the presence of air. High pressure DTA studies of Pistorius and Clark [11] showed no transition up to 40 kbar at 298 K. The I/II transition line rises with pressure to the triple point at 9 kbar, 675 K, where the I/II transition line splits up into two separate transition lines with the appearance of a new phase III. The DTA signals associated with the new transitions become somewhat smaller with increasing pressure and are not observed beyond 27 kbar. Decompression retraces the behaviour in the reverse direction.

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3.2. Alkaline Earth Metal Carbonates

Thermal as well as pressure transformations are known in CaCO₃, SrCO₃ and BaCO₃. Pauling [1] has shown that the different structures of these carbonates are determined by the cation-anion radius ratio; thus, for values of 0.67 or below, the favourable structure is calcite type with a primary cation coordination of 6. MgCO₃ crystallizes in the calcite structure and the radius ratio in this case is 0.47. When the radius ratio is above 0.67 but below 0.85, the aragonite phase with a pseudohexagonal-orthorhombic structure (where the ligancy of cations is 9) is favoured. It is interesting that the critical value of radius ratio of 0.67 is the exact value for $CaCO_3$ which is dimorphous. Above a radius ratio of 0.85, other structures are possible just as in $RbNO_3$ or $CsNO_3$, where the primary cation coordination is likely to be 12.

Calcium carbonate, CaCO₃, hexagonal (calcite), $D_{3d}^6 - R\overline{3}c$, Z=6, a=4.989 Å and c=17.062 Å at 299 K.

Other than calcite, CaCO₃ exists as aragonite (orthorhombic, D_{2h}^{16} -Pbnm (Pnma), Z = 4, a = 4.959Å, b = 7.968 Å and c = 5.741 Å at 299 K) [2] and vaterite (hexagonal, Z = 12, a = 7.16 Å and c = 16.98Å at 298 K) forms [3, 4, 5]. Meyer [6] reported vaterite to have a pseudohexagonal form with space group D_{2h}^{16} -Pbnm and Z=4, the plane of the CO₃ group being parallel to the c-axis. Both aragonite and vaterite forms transform to the stable calcite phase on heating [7]. Preparation of aragonite and its transformation to calcite have been the subject of investigation by many workers [8]. Presence of small amounts of strontium stabilizes the aragonite phase. Attempts to prepare very pure aragonite (without traces of Sr^{+2}) have not been very successful [7, 9].

Transformation of aragonite to calcite $(A \rightarrow C)$ takes place in the range 753-773 K, the actual T_t varying with the nature and amount of impurities present [7]. The $A \rightarrow C$ transformation is irreversible at normal pressures and proceeds by a reconstruc-

tive mechanism involving a change from 6 to 9 in the primary coordination [8]. Thus, the $A \rightarrow C$ transformation is sluggish and is associated with a large energy of activation. The effect of various impurities on the enthalpy and temperature of transformation as well as on the dissociation of calcite have been reported in detail by Rao and coworkers [7]. Meyer [6] and Kamhi [5] proposed the C_s and C_{2v} symmetry, respectively, for the carbonate ion. Infrared spectroscopic investigations by Sato and Matsuda [10] as well as Sterzel [11] have confirmed the C_{2v} symmetry of the CO_3^{-2} ion as proposed by Kamhi [5].

Vaterite transforms to calcite either directly or through the aragonite phase as an intermediate [12, 13]. Transformation of vaterite takes place in the region 623-673 K with an enthalpy of ~ 200 cal mol⁻¹ [6, 7]. The kinetics of the vaterite \rightarrow calcite transformation have been reported by Northwood and Lewis [14]. Northwood and Lewis observed x-ray line broadening of vaterite samples which were ground; the line broadening was attributed to the existence of microstrains in the vaterite lattice.

High pressure Transformations: Calcite transforms to the aragonite phase under pressure, the aragonite phase being stable at high pressures. In addition to calcite and aragonite phases, two other phases, II and III, were discovered by Bridgman [15] under isothermal compression of ordinary calcite at room temperature. Discontinuities in the isothermal compressibility values were detected at 14 and 18 kbar corresponding to calcite \rightarrow CaCO₃-II and CaCO₃- $II \rightarrow CaCO_3$ -III transitions, respectively. The existence of these phases was confirmed by independent powder x-ray diffraction studies of Jamieson [16] and Davis [16a], although with divergent structural inferences. According to Jamieson [16], the phases I, II, and III of CaCO₃ are characterised by varying degrees of orientational disorder of the carbonate ion and are related to the normal calcite structure. Davis [16a], however, doubted the anion rotation mechanism of calcite \rightarrow CaCO₃-II transition. The results of Jamieson [16], Davis [16a] and Rapoport [17] indicate that CaCO₃-II is isostructural with the ferroelectric KNO₃ phase III or with the high temperature anion disordered phase of NaNO₃ and that CaCO₃-III is isostructural with the high pressure orthorhombic phase IV of KNO₃. Fong and Nicol [17a], from their Raman spectral studies, however, disagree with the above results that show isostructural relations between CaCO₃ and alkali metal nitrates.

Calcite, on grinding, is known to produce aragonite [18]. Leiserowitz and coworkers [18a] have reported a shock-induced calcite-aragonite transformation. Northwood and Lewis [14] have examined the effect of microstrains on the calcite \rightarrow aragonite equilibrium. The transformation is initiated by the nucleation of the aragonite phase at these microstrain sites and is followed by growth of the aragonite phase. The kinetics of the calcite-aragonite pressure transformation have been studied by Davis and Adams [19] employing x-ray diffraction.

Measurement technique	Observations	Remarks	References
x-ray diffraction	T _t (aragonite-calcite), 723 K	During the transformation the [001] direc- tion in aragonite changes to [111] direc- tion in calcite structure. Single crystal aragonite breaks into calcite as polycrys- talline aggregate in the course of the phase transition.	[20-29].
	Vaterite changes progressively to calcite and aragonite structures during ball milling. The vaterite to calcite and/or aragonite transition is affected by air or water vapour.	The samples of vaterite during ball milling develop microstrains and this is indicated by line broadening in diffraction patterns. The structure of vaterite can be described by a disordered stacking sequence of single layers of trigonal symmetry. mostly related by glide reflections. sometimes by screws parallel to the c axis	[12-14, 30].
X-ray diffraction under high pressures (up to 773 K and 15 kbar).	The rates of transformation are both tempera- ture and pressure dependent. Around 673 K. the rate of calcite-aragonite change at	Extrapolation of experimental data indi- cates that the transformation rate would be negligible at 298 K. Phase diagram of	[19.31].

 $CaCO_3$

 $CaCO_3 - Continued$

Measurement technique		Observa	tions		Remarks	References
~ 15 kbar is similar to the reverse transfor- mation at 1 bar. E_a , 106 kcal mol ⁻¹ at 1 bar. Metastable forms of calcite, I, II and III are possible intermediate phases during calcite- aragonite transformation.		calcite-aragonite in the range 10 to 12.7 kbar and 683 to 848 K is presented. Aragonite is the stable form at 20 kbar and 298 K, with respect to calcite II and III. Aragonite and vaterite showed no transi- tion up to 24.4 kbar. Calcite undergoes changes in agreement with the thermo- dynamic evidence that calcite II is an anion-disordered form of normal calcite.	[16, 32].			
	Transition	$\Delta H_{\rm tr}$ cal mol ⁻¹	$\Delta S_{\rm tr}$ cal mol ⁻¹ K^{-1}	ΔG (1, T) cal mol ⁻¹		
	$I \rightarrow II$ $II \rightarrow III$ $I \rightarrow arago$	+10 - 381	0.032 -1.28	46 438		
	nite	-370	-1.24	273		
					Crystals with calcite structure in quenched assemblages are uniaxial indicating that the biaxial nature of inverted calcite is not due to pressure. Hence the constraint imposed by aragonite morphology during the quenching and inversion to calcite has been sufficient to strain the calcite structure.	[33].
Shock induced calcite	Implosion of j the product is present in yield of arag	oure calcit . If, howe n calcite, in conite as de	e leaves only ver, 10 perce mplosion give etected by x-r	v CaO as ent water es a good rays.	Since it is known that a combination of shear with hydrostatic pressure accel- erates the rate of phase change in the di- rection allowed by the pressure-tempera- ture relationship of the compressed phases, the transformation of calcite to aragonite should take place, in shock loaded calcite. The transformation may be considered to be an ionic displace- ment from a distorted FCC to a distorted HCP arrangement which must involve shear since it cannot be expected to re- sult from mere compression	
Effect of grinding calcite samples.	 Aragonite is obtained in small yields for small duration of grinding. With greater periods of grinding substantial proportions of calcite are converted to aragonite. Mechanical grinding of calcite in ball mills for up to 90 hrs. yields 70 percent aragonite and 30 percent calcite in an equilibrium mixture. 			ields for a greater oportions e. ball mills aragonite uilibrium	 The calcite-aragonite transformation may be compared to the process of 'slip' fre- quently observed in metal crystals. Transformation is reported to be charac- teristic of nucleation-growth process. The nucleus is probably formed by atomic movements produced by microstrains during grinding. 	[16, 35, 35a]
Differential thermal analysis.	$T_{\rm t}, 660-761 { m K}$ $\Delta H_{\rm tr}, 50 { m cal m}$ $E_{\rm a}, 100 { m kcal m}$ $\Delta H_{\rm tr}, 230 { m cal}$ countered purity.	(aragonite ol ⁻¹ (for p nol ⁻¹ mol ⁻¹ is th with 1 at	e-calcite) ure aragonite ne maximum om percent) value en- Sr ⁺² im-	Effect of varying amounts of Sr^{+2} and other cations on T_t and ΔH_{tr} as well as E_a has been investigated. Smaller cations like like Li ⁺ , Na ⁺ , Mg ⁺² , Cd ⁺² show rela- tively low T_t , but E_a is unaffected except by Cd ⁺² . It is likely that cations like Na ⁺ or Cy ⁺³ may produce some anion or cat- ion vacancies which affect such trans- formations.	[7, 28, .36–39].

$CaCO_3 - Continued$

Measurement technique	Observations	Remarks	References
	$T_{\rm t}$, 623–673 K (vaterite-calcite transforma- tion) $\Delta H_{\rm tr}$, 200 cal mol ⁻¹		[7].
Kinetic study of A-C transformation.	The transformation of aragonite to calcite was accompanied by a change in crystal- lite size around T_t . A marked contraction in the unit cell volume of aragonite, before it got transformed to calcite, was reported.	A model based on surface nucleation and progress of the reaction by interfacial growth is found to explain satisfactorily the complete course of the transforma- tion of aragonite to calcite.	[39a].
Dilatomatry	 Isothermal expansion at T_t, is ~ 2.5 percent at the aragonite-calcite transformation. The transformation is always preceded by an induction period, which is affected by i) mixing of fine calcite crystals with aragonite phase ii) rapid cooling of the sample iii) atmosphere, e.g., when atmosphere is rich in CO₂, the induction period is considerably short 	Hysteresis of about 5–8 K was noticed. For samples purified by zone-refining, the hysteresis was maximum. The T_t differs slightly with the process of preparation of the sample. Speed of the transforma- tion is proportional to time up to about 50 percent transformation for natural ara- gonite.	[40-44].
	$ \begin{array}{c c} Temp. & E_a (transfor-range mation) & E_a (nuclea-tion) \\ \hline (K) & (kcal mol^{-1}) & (kcal mol^{-1}) \\ \hline 639-679 & 60 & 90 \\ \hline \end{array} $		
	683–723 84 72 The molar volume of vaterite decreases during its transformation to calcite or aragonite.	The kinetics of vaterite-calcite transforma- tion is similar to that of aragonite-calcite transformation.	[41].
High pressure experiments on C-A transformation by volume change method.	The transition takes place around 4.35 kbar and at 373 K.	The effect of various impurities on the cal- cite-aragonite equilibrium is discussed. Aragonite is a metastable phase of CaCO ₂ at 1 bar and 298 K	[45-49].
Electrical conductivity at various pressures.	Equilibrium points for calcite-aragonite from conductivity experiments: $\frac{T, K}{302.1} = \frac{P, kbar}{3.980}$ $311.2 = 4.130$ $325.6 = 4.500$ $350.1 = 4.800$	All normal natural occurrences of aragonite must be due to metastable formation rather than equilibrium, since the geo- thermal gradient lies completely in the calcite field.	[50].
Refractive index measure- ments.	Complexly twinned calcite results from a quenched assemblage of $CaCO_3$, liquid and vapour. These inverted calcite crystals are biaxial with optic axial angles ranging from nearly 0 to 20° (for aragonite, the optic axial angle is 18°). The isogyres appear to remain just as sharp as those in a uniaxial calcite crystal, but the crystals exhibit undulose extinction. This phenomena was noted in the range 673-1073 K and 8-20 khar.	The uniaxial crystals with calcite mor- phology in quenched assemblages in- dicate that the biaxial nature of inverted calcite is not due to pressure.	[33].
Infrared spectroscopy	IR absorption spectra show changes at ~ 4 kbar and is strongly suggestive of the cal- cite-aragonite transformation.	However, x-ray diffraction studies on un- loading do not confirm this transition. The change in IR-absorption spectra may be associated with minor structural distortions in calcite.	

CaCO₃-Continued

Measurement technique	Observations	Remarks	References
Electron diffraction	The diffraction patterns showed the follow- ing orientation relation: $[\overline{1}10]_{aragonite} \parallel [\overline{1}2\overline{1}0]_{calcite}$ $[001]_{aragonite} \parallel [0001]_{calcite}$	The orientation relation suggests that the transformation is martensitic type shear being on the (001) aragonite plane.	[52].
Electron microscopy	Aragonite undergoes a sudden and violent transformation to calcite when heated by the electron beam.	Twins and dislocations disappear leaving a strained crystal of aragonite or occasion- ally calcite structure.	[28, 53].
Kinetics of aragonite to calcite transformation in solution.	The transformation proceeds by subsequent nucleation and growth of calcite on aragonite surface. E_a , 57.4 kcal mol ⁻¹ .	The fraction of aragonite transformed to calcite at 323-440 K is proportional to the reaction time. The E_a value is discussed in terms of a loosely hydrated calcium bicarbonate ion pair. Effect of ions like Ba ⁺⁺ , Sr ⁺⁺ , Pb ⁺⁺ , or SO ⁼ ₄ on the calcite-aragonite equilibrium is discussed.	[54–57].
	The transition from vaterite involves nuclea- tion and growth of aragonite in vaterite.	Geologically common ions have specific effects on the transformation.	[58].
Kinetics study (by Hahn emanation).	The rate of transformation (aragonite-calcite) is quite large above 723 K at the heating rate of 6 K min ⁻¹ . Around 783 K the trans- formation is maximum. Calcite dissociates at ~ ¹ 183 K at atmospheric pressures.	Results by this technique are confirmed by x-ray diffraction measurements.	[59, 60].
Ultrasonic studies (up to 38 kbar).	Longitudinal velocities decrease sharply from 5.3 km sec ⁻¹ at a mean pressure of 4 kbar to minimum of 4.8 km sec ⁻¹ at 8 kbar. Transverse velocities decrease from 3.1 to 2.9 km sec ⁻¹ . Bulk and rigidity moduli also show a 10 percent decrease as the minimum density increases by about 1.7 percent.	These observed changes are attributed to calcite aragonite transformation. The low and high pressure phases possibly coexist over a considerable pressure range. The maximum and minimum in the in- vestigations have also been attributed to the formation of metastable forms of calcite viz. calcite I, II etc.	[61, 62].

Strontium carbonate, SrCO₃, orthorhombic, D_{2h}^{16} . Pmcn, Z=4, a=5.107 Å, b=8.414 Å and c= 6.029 Å at 299 K.

Strontium carbonate undergoes a phase transition around 1200 K from the orthorhombic (aragonitetype) structure to a hexagonal (calcite-type) structure [63]. The transformation was first pointed out by Boeke [64]. In the hexagonal structure, the lattice constants are a=5.092 Å and c=9.53 Å [63]. The transformation is similar to the aragonite-calcite transition of CaCO₃. The ΔH_{tr} of the transition is 4.0 kcal mol⁻¹ [65] typical of a first order transition. Lander [63] could not detect any other transition in SrCO₃ up to 1575 K in his x-ray diffraction studies. However, Baker [66] reports that under careful conditions a second endothermic transition occurs at 1690 K. This change takes place from the hexagonal to a cubic modification. The transitions in SrCO₃ are believed to be the result of anionrotational disorder.

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Measurement technique	Observations	Remarks	References
x-ray diffraction	T_{t} , 1185 K (orthorhombic-hexagonal)	The transition is related to the rotational activity of the CO_3^{-2} ions	[63].
Calorimetry	$T_{\rm t}, 1197 {\rm K}$ (orthorhombic-hexagonal); $\Delta H_{\rm tr}, 4.0 {\rm kcal \ mol^{-1}}$ $T_{\rm t}, 1690 {\rm K}$ (hexagonal-cubic); $\Delta H_{\rm tr}, 0.800 {\rm kcal \ mol^{-1}}$ (calculated).	The hexagonal-cubic transition (T_t , 1690 K) was observed in an atmosphere of CO ₂ (at ~ 20 bar pressure), to prevent the SrCO ₃ decomposition. T_t is slightly reduced (by ~ 6 K) by the presence of impurity.	[65, 66].
DTA (at high pressures)	$T_{\rm t}$, 1203 K (orthorhombic-hexagonal) $\Delta H_{\rm tr}$, 4.7 kcal mol ⁻¹ ΔV , 1.49 ± 0.1 cm ³ mol ⁻¹	Hexagonal-cubic transition was not detecta- ble. ΔV calculated from the slope of $P-T$ curves agrees well with the experimental data.	[67].
Hahn emanation method (coprecipitation with ThX).	<i>T</i> _t , 1198 K (orthorhombic-hexagonal)	Changes in crystal structure show an in- crease or a decrease in emanation power due to loosening of crystal structure and consequent increase in surface area and/ or diffusion rate.	[59, 60, 68].

Barium carbonate, BaCO₃, orthorhombic, D_{2h}^{16} -Pmcn, Z=4, a=5.314 Å, b=8.904 Å and c= 6.430 Å at 299 K.

Two transformations have been reported in BaCO₃ [63]. At 1076 K, BaCO₃ transforms to a calcite type hexagonal phase (a = 5.206 Å, c = 10.55

Å). Around 1249 K, a transition to a cubic phase takes place. These transformations are believed to be due to the onset of rotational disorder of anions. The pressure dependence of the transitions have been reported by Rapoport and Pistorius [68] employing high pressure DTA.

Measurement technique	Observations	Remarks	References
X-ray diffraction	T_t (orthorhombic \rightarrow hexagonal), 1076 K. T_t (hexagonal \rightarrow cubic), 1249 K. For cubic phase, $a = 6.96$ Å at 1233 K.	The transformations are discussed in terms of rotational disorder of CO_3^{-2} ions and by analogy to alkali nitrate transformations. No new phases are known above the cubic phase up to 1573 K.	[63].
Calorimetry	$\begin{array}{c c} \underline{Transition} \\ \text{Orthorhombic to} \\ \text{hexagonal } (T_t, \\ 1079 \text{ K}) \end{array} \xrightarrow{\Delta T, \text{ K}} \Delta H_{tr} \\ \underline{\Delta T, \text{ K}} \\ 50 \\ \underline{\text{kcal mol}^{-1}} \\ 3.880 \\ \hline 3.880 \end{array}$		[65].
	Hexagonal to 20 0.700 cubic (<i>T</i> _t , 1241 K)		
DTA (at high pressures)	$T_{\rm t}, 1072$ K; $\Delta H_{\rm tr}, 4.49$ kcal mol ⁻¹ ; ΔV , 1.25 ± 0.09 cm ³ mol ⁻¹ . $T_{\rm t}, 1233$ K.	No new phases are known. The ΔV calculated from the slope with Clausius- Clapeyron equation agrees well with experimental values. Studies on the higher transition were subjected to limitation because of incipient decompo- sition of BaCO ₃ . Doubtful indications of a higher order transition in the range 673-773 were noticed.	[15, 67].
Hahn emanation (coprecipi- tation with ThX).	$T_{ m t},$ 1083 K (orthorhombic-hexagonal)	Changes in crystal structure show an increase or a decrease in emanation power due to loosening of crystal struc- ture and consequent increase in surface area and/or diffusion rate.	[59, 60, 68].

BaCO₃

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3.3. Thallous Carbonate, Tl₂CO₃

(monoclinic, I2/m- $C_{2\mu_2}^{3,5}$, Z=4, $a=7.55\pm0.02$ Å, $b=5.38\pm0.02$ Å, $c=10.58\pm0.02$ Å and $\beta=94^{\circ}47'[1]$)

Vorländer et al. [2] reported a single transition at 501 K. Tranquard et al. [3], however, showed that this transition occurs only when commercial material is used. Tl_2CO_3 purified by fractional crystallization is reported to show two new transitions at 473 and 536 K instead of the above phase transition [3]. These transitions between the phases III \rightarrow II and II \rightarrow I, were also confirmed by Pistorius and Clark [4] at transition temperatures 485.5 ± 2 and 533.5 ± 1 K, respectively.

High Pressure Transitions: Pistorius and Clark [4] failed to detect any high pressure transformation at 293 K up to 44 kbar. In their phase diagram studies, Pistorius and Clark [4] found that the II/I transition line falls with pressure to the I/III/II triple point at 3.4 kbar, 525 K. The resulting III/I transition slowly rises with pressure, passes through a broad maximum at 18.7 kbar, 536.8 K and then falls with increase of pressure. The III/I transition terminates at a triple point I/IV/III at 29 kbar, 532 K. A weak DTA signal observed at 34.9 kbar, 478 K is attributed to the III/IV phase transition, IV being a high pressure phase. The IV/I transition line rises with pressure and terminates at a triple point I/V/IV at 35.1 kbar, 501 K. The IV/V transition point was ascertained only be a considerable increase in slope at this point. Phase V is also a high pressure phase. The DTA signals associated with the IV/I and V/I transitions seem to be very similar to those associated with the III/I transition.

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3.4. 3d Transition Metal Carbonates

Heat capacity measurements in the temperature range 1.6-80 K [1, 2] revealed that carbonates of manganese, iron, cobalt, and nickel show antiferromagnetic to paramagnetic transitions at 29.5, 30.6, 17 and 22.2 K, respectively. Measurements

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in the temperature range 70-300 K did not show any anomaly in these carbonates except in $CoCO_3$ which shows an anomaly due to the sorbed water [3]. Crystal structure for all these rhombohedral carbonates are tabulated by Graf [4].

3d Transition metal carbonates			
Substances and measurement technique	Observations	Remarks	Refer- ences

Manganese carbonate, MnCO₃, calcite type, $D_{3d}^6 - R\overline{3c}$, Z = 2 (rhomboheral cell, and Z = 6 (hexagonal cell), a = 4.777 Å and c = 15.67 Å at 298 K

Heat capacity (Temperature range: 1.6–80 K).	An antiferromagnetic-paramagnetic transi- tion at 29.5 K is shown by a heat capacity anomaly. At liquid helium temperature the heat capacity obeys the law $C_{\rm M} = aT^3$, where $a = 18.0 \pm 0.7 \times 10^{-4} \mathrm{J \ mol^{-1} \ K^{-4}}$	Excitation of the second branch of the spin wave spectrum is observed at temperature close to $T_N/10$ (T_N , 32.4 K). The results provide an experimental confirmation of the spin wave theory.	[1, 2]′
(Temperature range: 70–300 K).	No anomaly was observed. A continuous increase of heat capacity with tempera- ture was found. The total entropy, consisting of the lattice and magnetic parts was also determined.	The entropy of magnetic ordering con- stitutes 14.7 percent of the total entropy. The earlier results of Anderson [5] differ from those of Kostryukov and Kalinkina [3] possibly due to the nature and quantity of impurities.	[6].
Magnetic measurements	Magnetic susceptibility was found to increase abruptly below $T_{\rm c}$, 31.5 K and to vary considerably with the field.	The observed anomalies are interpreted by postulating that below $T_{\rm C}$, MnCO ₃ goes over to an antiferromagnetic state in which the moments of the sub- lattices do not fully compensate each other.	[3].

Iron carbonate, FeCO₃, rhombohedral (calcite type), a = 4.6887 Å, c = 15.373 Å [4]

Heat capacity (Temperature range: 1.6–70 K).	Transformation at 30.6 K is associated with change from antiferromagnetic to para- magnetic state. Nuclear heat capacity has not been observed for FeCO ₃ showing that Fe has zero magnetic moment.	In FeCO ₃ the spins are parallel to the princi- pal axis so that the magnetic heat capacity should be practically nonexistent at low temperatures.	[1].
(Temperature range: 70–300 K)	No maximum is observed in this range. The total entropy of FeCO ₃ comprises of i lattice and magnetic contributions. The latter is 10.6 percent of the lattice en- tropy. The entropy of magnetic ordering constitutes 13.9 percent of the total entropy.		[3].

3d Transition metal carbonates-Continued

Substances and measurement technique	Observations	Remarks	Refer- ences
Cobalt carbonate, ($CoCO_3$, rhombohedral (calcite type), $R\overline{3}c$, $Z =$	6, $a = 4.659$ Å and $c = 14.957$ Å at 299 K.	
Heat capacity (Temperature range: 1.6–70 K).	Transformation at 17 K is associated with a change from antiferromagnetic to para- magnetic state. At liquid helium temperature, the magnetic heat capacity obeys the law $C_M = aT^3$, where $a = 13.5 \times 10^{-4} \text{ J} \cdot \text{mol}^{-1} \text{ K}^{-4}$.	The results agree with those given by magnetic measurements. Excitation of the second branch of the spin-wave spectrum is observed at temperature close to $T_N/3$.	[1].
(Temperature range: 70–300 K)	Maxima found at 270 K, is attributed to the sorbed water.		[3].
	The total entropy is comprised of the lattice and magnetic contributions. The mag- netic contribution for CoCO ₃ is 8.3 percent of the lattice entropy.	At 298.15 K, the entropy of magnetic ordering contributes 13.0 percent of the total entropy.	
Magnetic measurements	Magnetic susceptibility increases abruptly below T _c , 17.5 K and varies consider- ably with field.	It is postulated that below T_c , the substance goes over to an antiferromagnetic state in which the moment of the sublattices do not fully compensate each other.	[6].
Nickel carbonat	e, NiCO ₃ , rhombohedral (calcite type), $D_{3d}^6 - a = 4.609$ Å and $c = 14.737$ Å at	R3c, Z=6, for hexagonal unit cell, 298 K.	
Heat capacity (Temperature range: 1.6–70 K).	The transition at 22.2 K is associated with a change from antiferromagnetic to paramagnetic state. At liquid helium temperature, the magnetic heat capacity obeys the law $C_{\rm M} = aT^3$, where $a =$ $15.3 \times 10^{-4} \mathrm{J mol^{-1} K^{-4}}$.	The results agree well with those obtained from magnetic measurements.	[1].
(Temperature range: 70–300 K)	No anomaly is obtained in this tempera- ture range. The entropy of magnetic ordering was found to constitute 10.6 percent of the total entropy.		[3].
Magnetic measurements	 Between 60 and 290 K the Curie-Weiss relation represents the temperature dependence of the susceptibility of nickel carbonate (both green as well as yellow modifications). The proportionality of the magnetization with the field disappears at 40 K and the material becomes ferromagnetic at 4 K. 		[7].

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3.5. Silver Carbonate, Ag₂CO₃

(monoclinic, $C_2^2 - P2_1$, Z = 2, a = 4.836 Å, b = 9.555Å, c = 3.235 Å and $\beta = 92.64^\circ$ at 298 K)

Ag_2CO_3

Measurement technique	Observations	Remarks	References
X-ray diffraction with impure samples.	With the ratio of dopant Y(III) and Gd(III) to Ag, $n \ge 0.005$ a new orthorhombic crystal structure is reported with a = 13.94 Å, $b = 5.97$ Å, $c = 5.30$ Å.		[1].
Heat capacity (room tempera- ture – 453 K).	A rapid increase in the heat capacity was observed above 423 K.	The anomaly is possibly due to the dis- sociation of the sample.	[2].
Differential thermal analysis	Two endotherms, first at 458 K and the second above 500 K were found. A small exotherm was also detected.	 The first is attributed to a reversible transition and the second to the dissociation. The exotherm is attributed to the annealing out of defects in Ag₂O. 	[3–5].
Differential scanning calo- rimetry (with the sample sealed in CO ₂ atmosphere to prevent decomposition).	Two reversible endotherms in the temper- ature range 440-475 K were found. The first also observed previously [3] has $\Delta H_{\rm tr}$, 730±80 cal mol ⁻¹ and the second found only in this work has $\Delta H_{\rm tr}$, 473±30 cal mol ⁻¹ .		[6].
EPR studies of impure samples.	EPR studies on γ -irradiated Y(III)-Doped Ag ₂ CO ₃ also indicate the presence of a new crystal structure. The same crystal structure is thermally attained in undoped Ag ₂ CO ₃ at approximatly 423 K under an atmosphere of CO ₂ .	The results agree well with x-ray diffrac- tion studies.	[1].

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