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ALKALI OXIDE-TANTALUM OXIDE AND ALKALI OXIDE-NIOBIUM OXIDE IONIC CONDUCTORS

by

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16. Abstract

A search was made for new cationic conducting phases in alkali-tantalate and niobate systems. The phase equilibrium diagrams were constructed for the six binary systems Nb_2O_5-$LiNbO_3$, Nb_2O_5-$NaNbO_3$, Nb_2O_5-$KNbO_3$, Ta_2O_5-$NaTaO_3$, Ta_2O_5-$LiTaO_3$ and Ta_2O_5-$KTaO_3$. Various other binary and ternary systems were also examined. Pellets of nineteen phases were evaulated (by the sponsoring agency) by dielectric loss measurements. Attempts were made to grow large crystals of eight different phases. The system Ta_2O_5-$KTaO_3$ contains at least three phases which showed peaks in dielectric loss vs. temperature. All three contain structures related to the tungsten bronzes with alkali ions in non-stoichiometric crystallographic positions.

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SUMMARY

This report summarizes work carried out between October 1972 and October 1973 under an agreement with the National Aeronautics and Space Administration, Lewis Research Center (Interagency Order C-29933-C) to study the phase equilibria of alkali oxide-tantalum and niobium oxide systems and synthesis of phases which might have interesting ionic conductivity.

The phase equilibrium relations of six systems were investigated in detail. These consisted of lithium, sodium and potassium tantalate, and niobate with the corresponding tantalum and niobium oxide. In addition, various other binary and ternary systems involving alkali oxides were examined in lesser detail. In all, thirteen phases were found to contain structures of sufficient interest to warrant further investigation. Nineteen phases were prepared as solid pellets and transmitted to LeRC for evaluation by dielectric loss measurement. Attempts were made to grow eight different phases as large single crystals, and two were submitted to LeRC for evaluation.

In terms of ionic conductivity, the most interesting phases from a structural point of view are those containing large tunnels only partially occupied by alkali ions. The potassium tantalate system contained four such phases, designated GTB, TTBs, HTB, and TTB (see table 6 for meaning of these initials). In all cases, the TB refers to a tungsten bronze type structure. Those phases which exhibit a maximum in the dielectric loss vs. temperature curves proved to be high temperature phases which are generally metastable at room temperature and do not have favorable melting characteristics for crystal growth directly from the melt.

In the coming year efforts will be expanded to include rubidium systems as well as antimonates and mixed tantalum-tungstates, in an effort to isolate an ionic conducting phase with favorable crystal growth possiblities.

INTRODUCTION

In the search for new ionic conductors, compounds in oxide systems need to be examined for structure types where packing of the complex ions of the skeletal structure has the potential to produce loosely bound alkali ions.

The compounds of alkali oxides with tantalum oxide and with niobium oxide represent a class of such materials. The program summarized in this report involved the investigation of the phase diagrams to determine the phases which are actually contained in these systems and to define selected phases of potential interest as solid ionic conductors. Subsequent to this determination specimens were prepared of single phase polycrystalline ceramic pellets for screening measurements and, finally, attempts were made to grow single crystals of those materials which appeared most interesting and feasible. All the phases encountered were identified by single crystal x-ray diffraction patterns and/or identity with previously reported structures. For fast ion transport, it is probably advantageous to have an alkali ion in a "non-stoichiometric" crystallographic position. For commerical utilization of ionic conductivity, it is necessary to limit systems to those which will contain little or no electronic conductivity and, therefore, do not contain an element which is easily reduced during the synthesis. The Ta^{+5} ion is apparently very difficult to reduce [1], and thus is ideally suitable as a host lattice for alkali "super-ionic-conductivity". Some preliminary work on alkali tantalate and niobate systems has been previously summarized by the present authors [2]. A complete detailed analysis of these systems is presently being prepared for publication and will be submitted to the Journal of Solid State Chemistry in the near future [3, 4, 5, 6].

DISCUSSION OF RESULTS

The System Nb_2O_5-$LiNbO_3$

A phase equilibrium diagram for the system Li_2O-Nb_2O_5 was published by Reisman and Holtzberg [7]. However, this diagram does not show the compound $LiNb_3O_8$ which is known to occur in this system [8, 9, 10], nor does it show the solid solution of Nb_2O_5 in $LiNbO_3$ [11] which has been found to be important in the production of large optical quality crystals. A phase equilibrium diagram indicating these corrections was previously published [2]; and this diagram is reproduced here, essentially unchanged, in figure 1. The experiments performed in this laboratory to check this diagram are listed in table 1. The unit cell dimensions of the phases will be given in the summary table of x-ray data near the end of this report (Table 12).

The Nb_2O_5-$LiNbO_3$ system contains only two intermediate phases, the compound $LiNb_3O_8$ and another phase which occurs at a very narrow compositional range near Li_2O:14Nb_2O_5. This phase was reported independently by the present authors [2] and by Norin and Nolander [12] to have the N-Nb_2O_5 structure. Only this phase and $LiNbO_3$ itself may be considered to have any interesting non-stoichiometric properties.

A detailed analysis of the work performed in this system, including x-ray diffraction patterns, will be published in the near future [3].

The System Ta_2O_5-$LiTaO_3$

No phase equilibrium diagram for this system had been published prior to our preliminary work reported in reference [2]. The final phase diagram is shown in figure 2 and the experimental data from which it was constructed are listed in table 2. The present diagram differs from that given in [2] only in the first 5 mole percent Li_2O content and near the melting point of $LiTa_3O_8$.

Lithium oxide has been found to stabilize the low temperature polymorph of Ta_2O_5 (L-Ta_2O_5); and, therefore, non-stoichiometric solid solutions appear on both sides of this system. There is only one intermediate compound, $LiTa_3O_8$, but it is trimorphic and apparently has no appreciable non-stoichiometric region within the binary phase diagram. The low temperature form of $LiTa_3O_8$ is isostructural with $LiNb_3O_8$, the intermediate form is isostructural with the mineral wodginite, and the high temperature form is similar in structure to $LiTa_6O_{15}F$ and $LiNb_6O_{15}F$ [13].

The unit cell dimensions will be listed in the summary table of x-ray data near the end of the report (Table 12) and a detailed analysis of the work performed in this system, including x-ray diffraction patterns, will be published in the near future [3].

The System Nb_2O_5-$NaNbO_3$

This system has been studied by several different groups and phase equilibrium diagrams were published by Reisman, Holtzberg and Banks [14], and by Shafer and Roy [15]. The former group reported a 1:4 and a 1:14 compound whereas the second reference shows 1:4, 1:7, and 1:10 compounds. These type of ratios represent mole ratio of alkali oxide to niobium (or tantalum) oxide. Sten Andersson [16] has shown that the high Nb_2O_5 content phase occurs at the 1:13 ratio ($NaNb_{13}O_{33}$) from crystal structure analyses [17] and found the other phase to occur at the 1:3 ratio ($NaNb_3O_8$). He found the compounds $Na_2Nb_4O_{11}$ and $NaNb_6O_{15}(OH)$ only in hydrothermal experiments at 500-700°C and 2000 atm. In a crystal structure analysis of Andersson's $NaNb_3O_8$ crystals, D. C. Craig and N. C. Stephenson decided that the composition of the crystal they examined was most likely $Na_{13}Nb_{35}O_{94}$ [18].

The phase equilibrium diagram which we have determined for this system is given in figure 3 and the experimental data from which it was determined are listed in table 3. We confirm the 1:13 compound but do not find any other between this and the "$NaNb_3O_8$" phase. The latter is apparently a non-stoichiometric solid solution with a tetragonal tungsten bronze-type substructure and an orthorhombic superstructure (TTBs). In addition $Na_2Nb_4O_{11}$ was found in equilibrium at low temperatures (below about 1000°C) and specimens near the 1:6 ratio was found to react with atmospheric moisture at temperatures between about 700-900°C to form $NaNb_6O_{15}(OH)$ without the necessity for hydrothermal techniques.

The unit cell dimensions of these phases will be listed in the summary table of x-ray data near the end of the report and a detailed analysis of the work performed in this system, including x-ray diffraction patterns, will be published in the near future [4].

The System Ta_2O_5-$NaTaO_3$

The phase equilibrium diagram for this system had not been reported prior to our preliminary paper [2] although Reisman [19] had made a sub-solidus study up to 1300°C. The diagram given in figure 4 is similar to that of [2] but has been reevaluated for the melting relations of the distorted tetragonal tungsten bronze-like phase (TTBs) between about 20 and 25 mole % Na_2O. This is the only non-stoichiometric phase in the system although apparently a very small amount of Na_2O may be incorporated in L-Ta_2O_5, increasing the phase transition temperature. The only other phase in the system is $Na_2Ta_4O_{11}$ which has a hexagonal structure similar to the monoclinic $Na_2Nb_4O_{11}$.

The experimental data from which figure 4 has been constructed are listed in table 4. The unit cell dimensions of these phases will be listed in the summary table of x-ray data near the end of this report. A detailed analysis of the work performed in this system, including x-ray diffraction patterns, will be published in the near future [4].

The System Nb_2O_5-$KNbO_3$

A phase equilibrium diagram for this system was previously reported by Reisman and Holtzberg [20]. Additional information on compound formation, crystal growth, and unit cell dimensions has been published by Guerchais [21], Whiston and Smith [22], and Nassau et al [23]. The phase equilibrium diagram determined in the present study is shown in figure 5 and the experimental data from which it was constructed are listed in table 5.

The system was found to contain six intermediate phases. The unit cell dimensions of each phase are listed in the summary table near the end of this report. From these dimensions it is apparent that at least three of these phases have non-stoichiometric-type structures. These are designated in the phase diagram as GTB, TTBs, and TTB and occur at about 11.5, 16-20, and 35 mole % K_2O respectively. The former has a structure similar to that reported by Gatehouse for a rubidium niobate phase [24] and herein referred to as a Gatehouse tungsten bronze (GTB). The other two have a distorted tetragonal tungsten bronze structure (TTBs) and an undistorted 'bronze' structure (TTB) respectively.

The unit cell dimensions of the 2:3 phase indicate a layer of niobia octahedra with all the potash possibly located in planes. The hydrated form of this phase reveals different x-ray diffraction intensity distributions depending on the hydration direction and rate. This phenomena may possibly indicate different distributions of K^+ ions which depend on the hydration. Ionic conductivity of this phase in a direction parallel to the cleavage, that is, parallel to the K^+ and/or H_2O motion should be investigated more carefully.

A detailed analysis of the work performed in this system, including x-ray diffraction patterns, will be published in the near future [5].

The System Ta_2O_5-$KTaO_3$

The phase equilibrium diagram published for the system K_2O-Ta_2O_5 by Reisman et al contained only two compounds between Ta_2O_5 and $KTaO_3$ [25]. The preliminary diagram published by the present authors [2] indicates nine equilibrium phases in this region and two other metastable phases. The present diagram, figure 6, differs from the previous only in the estimated width of the non-stoichiometric phases. The experimental data from which this diagram was constructed are listed in table 6.

The system was found to contain four stable non-stoichiometric regions in addition to five stable, apparently stoichiometric, phases. The phases with non-stoichiometric type structures include a Gatehouse tungsten bronze (GTB) at about 11.5 mole % K_2O, an orthorhombic distorted tetragonal tungsten bronze with superstructure (TTBs) between about 15-20 mole % K_2O, a hexagonal tungsten bronze (HTB) at about 21.75 mole % K_2O, existing over a very narrow temperature region below the solidus, and an undistorted tetragonal tungsten bronze with no superstructure at ~34 mole % K_2O. Figures 7, 8, 9, and 10 show the results of measuring the dielectric loss (epsilon) versus temperature at a number of frequencies for these four non-stoichiometric phases. The GTB and HTB phases show excellent ionic mobility. Unfortunately, single crystals of these phases have not yet been grown. The difficulty is due mainly to the very narrow primary phase field. An attempt must be made to find a system with wider primary phase regions for these structures, possibly in systems with Rb_2O, which can then be ion exchanged.

Other Systems

In the course of this study, a considerable number of specimens were investigated with compositions not included in the six systems described previously. The ternary systems involving these six systems with MoO_3 were all examined briefly for the purposes of growth of small crystals [2]. The compositions of the crystal growth preparations will be detailed at a later date [3, 4, 5, 6].

Several of these six binary systems were also examined in conjunction with WO_3, especially the psuedo-binary joins $NaTaO_3$-WO_3 and $KTaO_3$-WO_3. The $NaTaO_3$-WO_3 system proved to be completely non-binary and contained mostly solid solutions of sodium tungstates in the sodium tantalate type phases. However, the $KTaO_3$-WO_3 system is apparently a psuedo-binary system below the solidus and contains at least five phases. The compositions of the phases are about 25, 50, 50, 70, and 90 mole % WO_3. The ternary system $KTaO_3$-WO_3-K_2WO_4 has been found to be a promising flux system for crystal growth of both the pyrochlore and hexagonal tungsten bronze (HTB) type phases. Further work on this ternary will be conducted in the next year.

Some compositions in the Li_2O-Ta_2O_5-WO_3 system were prepared and examined for the purpose of introducing non-stoichiometry into the H-$LiTa_3O_8$ structure. Other compositions in the system Li_2O-Ta_2O_5-TiO_2 were also prepared for the same purpose. The WO_3 gave single phase non-stoichiometric solid solutions but showed no ionic mobility (table 7). The TiO_2 specimens did not exhibit solid solution.

A study of the Li_2O-TiO_2 system or rather of the Li_2TiO_3-TiO_2 system revealed only one high temperature intermediate phase. This phase has the ramsdellite structure; but, unfortunately, melts incongruently with the peritectic very close in composition and temperature to the eutectic.

Thus, single phase crystals could not be pulled from the melt. Experiments in the Li_2O-TiO_2-MoO_3 ternary also did not reveal any ideal flux compositions for crystal growth of this phase. The ramsdellite lithium titanate did not exhibit appreciable ionic mobility (table 7). Other experiments with K_2O-Li_2O-TiO_2 and K_2O-MgO-TiO_2 revealed a new structure type [26] which also failed the ionic mobility screening tests.

The only experiments performed under this contract which did not involve mixed oxides were conducted in the system NaF-AlF_3-Na_2GeF_6 in an attempt to produce Ge doped $NaAlF_4$. These experiments were not successful and no $NaAlF_4$ was obtained.

A few compositions involving the systems $NaSbO_3$-Sb_2O_4 and $KSbO_3$-Sb_2O_4 have been prepared in order to survey possible compound formation in these systems, because Aurivillius [27] has reported K^+ ions to occur in large tunnels in some potassium antimonates. In addition, several specimens were examined in the ternary systems $KSbO_3$-Sb_2O_4-SiO_2 and $KSbO_3$-Sb_2O_4-Al_2O_3 in an attempt to explain the published data of Spiegelberg [28] who reported a primitive cubic "polymorph" of $KSbO_3$ prepared in a porcelain crucible. These experiments were successful in demonstrating that a small amount of both Si^{+4} and Al^{+3} promote the formation of this cubic polymorph. These and similar antimonate systems will be examined in greater detail in the coming year.

Polycrystalline Specimen Preparation

The sections of this report dealing with the phase equilibrium relationships in alkali niobate and tantalate systems have described several phases which, from structual considerations alone, would appear to be worthy of screening for their potential as fast ion conductors. Accordingly, polycrystalline specimens were prepared and submitted to Lewis Research Center for dielectric and conductivity measurements.

The choice of composition and thermal treatment for use in pellet fabrication of a desired phase was made on the basis of the compositional and temperature stability limits of the phase as determined in the phase equilibrium studies. These limits are not always compatible with the sintering characteristics of the powders and, as a consequence, it was not possible to prepare high density pellets of some of the phases of interest. Several alkali titanate pellets of interest were also prepared as an outgrowth of work under a previous contract. All compositions for use in pellet fabrication were given blending and calcining treatments similar to those utilized in the preparation of compositions for phase equilibrium studies. In the case of phases wherein alkali loss was anticipated during sintering or where a minimum temperature of stability necessitated rapid cooling of the pellets, the exact composition of the pellet was chosen to give as much latitude as possible in the sintering treatment. The appropriate 1:1 alkali niobate or tantalate was used as one constituent of the batch in these systems to avoid the use of carbonates.

Conventional ceramic dry pressing and sintering techniques were utilized for pellet preparation. Dry pressing was performed in steel dies at nominal pressures of the order of 10,000 to 18,000 psi. No organic binders or other additives were utilized except as noted. In general, several test heatings were necessary to determine a suitable time-temperature relationship for sintering. In some cases, excessive recrystallization during sintering, regardless of the schedule followed, prevented the formation of physically sound pellets. As discussed below, hot pressing was found useful in some cases.

The starting compositions after calcining, as well as the as-fired surface and interior of the sintered pellets, were characterized by x-ray diffraction techniques to insure that the final pellets were homogeneous and single phase.

Tables 8, 9, and 10 summarize the compositions, heat treatments and x-ray characterizations of the pellets submitted for evaluation. The results of screening tests conducted by LeRC are given in Table 7.

Crystal Growth

The growth of large single crystals of the various non-stoichiometric phases found in the alkali niobate and tantalate systems is complicated by many factors: (1) some of the desired phases do not exist in equilibrium with the liquid, (2) incongruency, and (3) volatility of the alkali. For these reasons only a few of the compounds found in the phase equilibrium studies were grown successfully. These were the congruently melting compounds and those incongruent compounds which existed in equilibrium with a liquid over a wide temperature range. In all crystal growth attempts the molten material was contained in either platinum or iridium crucibles which were heated inductively and the desired phase pulled either by the conventional Czochralski technique, or by an approximation to top seeded solution growth.

A number of the more interesting phases do not lend themselves to growth by the more conventional techniques and it will be necessary to explore various flux growth techniques in an effort to obtain crystals of a size suitable for physical property measurements.

The crystal growth experiments (table 11) are summarized as follows:

Nb_2O_5-$KNbO_3$

7:13 Phase (TTB)

Growth of the 7:13 phase was attempted from a melt composition of $36.5K_2O:63.5Nb_2O_5$. The first material to crystallize was the 4:9 phase, on continued pulling a small amount of 7:13 phase crystallized out on the side of the 4:9 phase as a polycrystalline mass. As the pull continued the remainder consisted of single phase 2:3. Several different melt compositions were tried and the results were essentially the same, in all cases the 4:9 phase crystallizes out and as more material is removed the composition of the crystallizing phase shifts to the 2:3 phase. Apparently the temperature-composition region over which the 7:13 exists in equilibrium is too small to successfully obtain crystals by the pulling technique.

$12K_2O:88Nb_2O_5$ (GTB)

Attempts to pull the (GTB) bronze-like phase $12K_2O:88Nb_2O_5$ at a melt composition of $15K_2O:85Nb_2O_5$ resulted in a polycrystalline multiphase mass. This result was not unexpected as an inspection of the phase diagram indicates a very narrow compositonal range where this phase is in equilibrium with the melt. This situation makes it extremely difficult to grow large crystals of the 12:88 phase any place in the K_2O-Nb_2O_5

binary. Only by going to a flux system can one possibly expect to grow this phase.

$17.5K_2O:82.5Nb_2O_5$ (TTBs)

Attempts to grow the TTB phase from a melt composition of $20K_2O:80Nb_2O_5$ resulted in essentially single phase polycrystalline TTB with very fine grain size. This phase would be a likely candidate for top seeded solution growth (TSSG) or possibly the accelerated crucible rotation technique (ACR).

$Ta_2O_5:KTaO_3$

TTB Phase

As determined from phase equilibria studies, the TTB phase melts incongruently. For the crystal growth attempts, a melt composition of $45K_2O:55Ta_2O_5$ was chosen. With this composition and using a pull rate of 0.2 in/hr crystals of the desired phase were grown. The maximum diameter attained was the order of 1/8 in. diameter at the stated pull rate. The growth of larger crystals would necessitate much slower growth rates, as with top seeded solution growth.

$Ta_2O_5:LiTaO_3$ System

1:3

Single crystals of the 1:3 phase were grown both "on composition" and from compositions slightly rich in Li_2O. The "as-grown" crystals were light brown to colorless depending upon cooling rate. Subsequent annealing in air removed all traces of brown color. The reason for this change in color is not known.

5:95 Phase

The 5:95 phase or L-Ta_2O_5 has been grown in sizes up to as large as 2 cm long and 1.5 cm diameter. This is an incongruent melting compound and growth was by top seeded solution growth starting at a composition of $15Li_2O:85Ta_2O_5$. These are the first large crystals of L-Ta_2O_5 ever grown and are being used for a structure determination using neutron diffraction, in order to obtain a better knowledge of the mechanism of nonstoichiometry. The crystals are almost colorless when first grown but gradually turn yellow on exposure to light.

Nb_2O_5-$NaNbO_3$ System

1:3 Phase

Single crystals of the 1:3 phase could be readily pulled from a melt of the stoichiometric composition, however, there was a problem with cracking which limited the size of usable crystals obtained. The cause of cracking was not investigated.

Ta_2O_5-$NaTaO_3$ System

21:79 Phase (TTBs)

All attempts to grow crystals of the bronze-type phase by induction heating at ambient pressures were unsuccessful due to the rapid loss of Na_2O from the melt.

Structural Mechanisms of Non-stoichiometry in Alkali-Niobates and Tantalates

An abnormally large number of phases have been found in the six systems examined and discussed in this report. In addition to the end members, the Li_2O systems contain two and three phases with Nb_2O_5 and Ta_2O_5 respectively whereas the Na_2O systems contain two and four phases each and the K_2O systems, six and nine phases each. The unit cell dimensions of each of these phases is listed in table 12 together with the pertinent crystallographic data where known.

The occurrence of the tungsten-bronze-type structures in these alkali niobate and tantalate binary systems is somewhat disconcerting, as the A_xBO_3 compositional range does not fall in these systems for any value other than x=1. It is quite evident, therefore, that it is impossible to have niobium and tantalum oxygen octahedra and pentagonal bipyramids form in a network structure in which only a non-stoichiometric amount of alkali ions compensate the framework for electrical neutrality. One possible hypothetical alternate of oxygen vacancies is both esthetically displeasing and structurally unsound. Furthermore, such structures have not been previously found to exist.

HTB

The most likely explanation, and one based on preliminary structural evidence of a similar phase, is that of interstitial niobium (or tantalum) ions. B. M. Gatehouse [24] has shown that niobium can occur interstitially in a rubidium hexagonal tungsten bronze structure in the 9-fold tricapped-prism interstitial vacancy common to all of the tungsten bronze-type structures. Gatehouse has suggested that the composition of this hexagonal bronze phase would be $RbNb_{3.4}O_9$ or 22.72 mole % Rb_2O. Some hypotheses can be made, on the basis of Gatehouse's work, concerning the mechanism of non-stoichiometry in the phases observed in this study.

In the system Ta_2O_5-$KTaO_3$, a phase having the hexagonal tungsten bronze structure has been observed to occur at about 21.75 mole % K_2O. By analogy to the $RbNb_{3.4}O_9$ phase, this can be considered to be $KTa_{3.4}O_9$. However, this formula would indicate 22.72 mole % K_2O which is definitely not the case. The composition 21.75 mole % K_2O would correspond to the formula $K_{0.95}Ta_{3.41}O_9$ and this non-stoichiometric phase must contain alkali vacancies as well as tantalum interstitials.

TTB

This same analogy may be used to explain the non-stoichiometry in the tetragonal tungsten bronze phases which occur with no sign of superstructure in both the Ta_2O_5-$KTaO_3$ and Nb_2O_5-$KNbO_3$ systems. The formula for one unit cell of the tetragonal tungsten bronze structure is $A_6B_{10}O_{30}$. If all the B ions have a valence of +5, then the formula for the ideal end member would be $K_6^{+1}B_{10.8}^{+5}O_{30}$ or 35.71 mole % K_2O. In the Nb_2O_5-$KNbO_3$ system this phase has been observed at ∿35 mole % K_2O corresponding to the formula $K_{5.83}Nb_{10.83}O_{30}$. In the Ta_2O_5-$KTaO_3$ system, this phase has been observed at ∿33 1/3 mole % K_2O corresponding to the formula $K_{5.45}Ta_{10.91}O_{30}$.

GTB

In his paper on rubidium niobates, Gatehouse discussed a new structure type containing 4-, 5-, 6-, and 7-sided tunnels which may be partially occupied by alkali ions. This phase has been called the Gatehouse tungsten bronze in the present paper and was observed to occur at about 11.5 mole % K_2O in both the Ta_2O_5-$KTaO_3$ and Nb_2O_5-$KNbO_3$ systems. Gatehouse was unable to arrive at a correct composition for this phase, but in a personal communication confirmed the proposed structure:

> ". . . having recently obtained some magnificent lattice image photographs which completely confirm the basic structure--7-sided holes and all."

The basic formula for this structure is $A_8B_{54}O_{146}$. If all the B ions have a valence of +5 and the excess is supplied via interstitual B^{+5} ions then the ideal end member composition would be $A_8^{+1}B_{54}^{+5} + 2.8O_{146}$. This ideal formula would correspond to 12.35 mole % alkali oxide. The formula for the observed 11.5 mole % composition would be $K_{7.4}B_{54} + 2.92O_{146}$ when B is either Nb^{+5} or Ta^{+5}. The solid solution region probably goes down to at least a composition of $K_7B_{57}O_{146}$ (10.94 mole % K_2O) and possibly even slightly lower in K^+ content. It should be pointed out that this hypothesis involves K^+ ions in both the six and seven (or possible four) sided tunnels whereas Gatehouse explicitly stated that the seven- and four-sided tunnels appeared to be empty. It is obvious that the details of this structure need to be examined with more accurate data. Dr. Gatehouse has informed us that he is now refining three dimensional crystallographic data on his rubidium niobate, and NBS will attempt to do an accurate single crystal crystallographic study of the chemically well-characterized potassium niobate phase.

TTBs

The case of the TTBs phase, that is, the orthorhombic tetragonal tungsten bronze with superstructure indicating that one of the <u>a</u> tetragonal axes is tripled, is more complex then the other three. This phase occurs in all four systems of sodium and potassium with niobium and tantalum. In the Nb_2O_5-$NaNbO_3$ system, it occurs between about 22.5 to 27.5 mole % Na_2O and between about 19.5 and 25.5 mole % Na_2O in the Ta_2O_5-$NaTaO_3$ system.

However, in the Nb_2O_5-$KNbO_3$ and Ta_2O_5-$KTaO_3$ systems, this same structure type occurs between about 15 and 20 mole % K_2O. Although the absolute limits of these have not been accurately located, these rough limits of about 15 to 27.5 mole % alkali oxide must be explained.

D. C. Craig and N. C. Stephenson [18] have examined the crystal structure of a specimen of $NaNb_3O_8$ supplied by S. Andersson [16]. They concluded that the particular crystal examined had the composition $Na_{13}Nb_{35}O_{94}$ or 27.08 mole % Na_2O rather than the 25 mole % Na_2O suggested by Andersson. Stephenson reports that the tripled "tetragonal-tungsten-bronze" cell has a basic structure of $Na_6Nb_{34}O_{94}$ and that twelve excess positive charges must be accommodated by Na and/or Nb distributed in the eight 5-sided tunnels. He considers only the cases of $Nb^{+5} + 7Na^+$ and $2Nb^{+5} + 2Na^+$ and says that the former more nearly coincides with the experimental intensities. In this paper [18], Craig and Stephenson dismiss the possibility of Nb^{+5} in the three sided tunnels as being ". . . incompatible with the directional properties of the bonding orbitals of niobium (V)." This statement is subject to considerable doubt and leaves open the actual position of the "interstitial" niobium. Apparently Craig and Stephenson did not consider the possibility that this phase might have a non-integral number of Na^{+1} and Nb^{+5} ions, that is, be a composition in the middle of a non-stoichiometric solid solution.

The basic-structure of the tripled tetragonal tungsten bronze (TTBs) unit cell is, therefore, $[A_6^{+1}B_{34}^{+5}O_{94}]^{-12}$ and contains a maximum of eight excess positions for alkali ions. The composition can, therefore, vary from a maximum alkali content of $A_{14}^{+1}B_{34.8}^{+5}O_{94}$ with 28.7 mole % alkali oxide to a minimum alkali content of $A_6^{+1}B_{36.4}^{+5}O_{94}$ with 14.15 mole % alkali oxide. It is noteworthy that the limits of the observed phases, 15 to 27.5 mole % alkali oxide, occur just within the theoretical minimum and maximum values of 14.15 to 28.7 mole % alkali oxide.

In the above four cases, therefore, the most likely structural mechanism for non-stoichiometry is that of transition metal interstitials plus alkali ion vacancies. However, other mechanisms can also be found in the six systems discussed in this report.

Other Phases

The N-Nb_2O_5 phase stabilized by Li_2O can be considered to be $Li_2O:14Nb_2O_5$ or $Li_{18}(Li_{0.45}Nb_{31.55})O_{80}$ with Li^+ ions substituting for Nb^{+5} and also present in interstitial four-sided channels. This non-stoichiometric phase is thus accounted for by a mechanism of alkali substitution plus alkali interstitials.

The high temperature form of $LiTa_3O_8$ or $Li_2Ta_6O_{16}$ is apparently isostructural with $LiTa_6O_{15}F$ and $Ta_4W_2O_{16}$. Either fluorine or tungsten ions can be utilized to generate a non-stoichiometric phase and the structural mechanism is thus alkali ion vacancies plus cation (or anion) substitution.

The low temperature form of Ta_2O_5 (L-Ta_2O_5) is stabilized by the addition of Li_2O. This structure is apparently intrinsically non-stoichiometric with the formula $Ta_{22}O_{55}$ and five oxygen "vacancies" [25]. The Li^+ ions either substitute for Ta^{+5} creating more anion vacancies or more likely occur interstitially filling some of the anion "vacancies" already present or a mechanism of cation substitution plus anion interstitials.

It should be remembered that all of the mechanisms discussed in this section are hypothetical and must be checked by careful single crystal x-ray diffraction or even neutron diffraction studies. Until such studies can be made, our understanding of the structural mechanisms by which nature compensates a non-stoichiometric phase for electrical neutrality will remain poorly understood.

SUMMARY OF RESULTS

1. The phase equilibria of various alkali tantalates have been studied up to and including liquidus temperatures and phase equilibrium diagrams have been constructed most consistent with the experimental data in the systems:

   Ta_2O_5-$LiTaO_3$
   Ta_2O_5-$NaTaO_3$
   Ta_2O_5-$KTaO_3$

2. The phase equilibria of various alkali niobates have been studied up to and including liquidus temperatures and phase equilibrium diagrams have been constructed most consistent with the experimental data in the systems:

   Nb_2O_5-$LiNbO_3$
   Nb_2O_5-$NaNbO_3$
   Nb_2O_5-$KNbO_3$

3. Pellets of nineteen phases were transmitted to the sponsoring agency for evaluation and the following three compositions were found to show peaks in the dielectric loss vs. temperature, indicating some ionic mobility.

   $11K_2O:89Ta_2O_5$ - Gatehouse tungsten bronze structure (GTB)
   $21.75K_2O:78.25Ta_2O_5$ - Hexagonal tungsten bronze structure (HTB)
   $34K_2O:66Ta_2O_5$ - Tetragonal tungsten bronze structure (TTB)

4. Attempts were made to grow large crystals of eight different phases and two crystals were transmitted to the sponsor for evaluation.

FUTURE WORK

1. The most interesting phases in the K_2O-Ta_2O_5 system (GTB and HTB) did not have phase equilibria relations favorable for crystal growth from the melt. Preliminary examination of the Rb_2O-Nb_2O_5 and Rb_2O-Ta_2O_5 systems suggests that these systems may be more favorable for melt growth of the GTB and HTB type phases. The phase equilibria in these systems will be examined in more detail and attempts made to grow crystals which might then be ion exchanged.

2. Small crystals of the hexagonal tungsten bronze phase in the system $KTaO_3$-WO_3 have been successfully grown from a potassium tungsten oxide flux. Attempts will be made to grow larger single crystals of this phase for dielectric loss and/or ionic conductivity measurements.

3. A cubic phase of $KSbO_3$, similar to the high pressure polymorph previously demonstrated to exhibit ionic mobility, has been successfully synthesized by the addition of a small amount of either SiO_2 or Al_2O_3. The phase equilibria of the Sb_2O_4-$NaSbO_3$ and Sb_2O_4-$KSbO_3$ systems will be studied and the effects will be studied of various impurities on the stabilization of the cubic modifications of $KSbO_3$ and $NaSbO_3$. Attempts will be made to prepare single crystals of these cubic phases and/or other interesting alkali antimonates.

References

[1] D. R. Kudrak and M. J. Sienko, J. Inorg. Chem. 6 (1967) 880.

[2] R. S. Roth, H. S. Parker, W. S. Brower and J. L. Waring, Fast Ion Transport in Solids, Solid State Batteries and Devices, Ed. W. Von Gool. Proceeding of the NATO sponsored Advanced Study Institute, Belgirate, Italy, September 1972, North Holland Publ. Co., Amsterdam (1973) pp. 217-232.

[3] R. S. Roth, H. S. Parker, W. S. Brower (to be submitted to J. Solid State Chem.)

[4] R. S. Roth, H. S. Parker, W. S. Brower, J. L. Waring and D. B. Minor to be submitted to J. Solid State Chem.)

[5] R. S. Roth, H. S. Parker, W. S. Brower and J. L. Waring (to be submitted to J. Solid State Chem.)

[6] R. S. Roth, H. S. Parker, W. S. Brower and D. B. Minor (to be submitted to J. Solid State Chem.)

[7] A. Reisman and F. Holtzberg, J. Am. Chem. Soc. 80 (1958) 6503.

[8] M. Lundberg and S. Andersson, Acta Chem. Scand. 19 (1965) 1376.

[9] M. Lundberg, Acta Chem. Scand. 25 (1971) 3337.

[10] B. M. Gatehouse and P. Leverett, Cryst. Struct. Comm. 1 (1972) 83.

[11] P. Lerner, C. Legras and J. P. Dumas, J. Cryst. Growth 3, 4 (1968) 231.

[12] R. Norin and B. Nolander, Acta Chem. Scand. 25 (1971) 741.

[13] M. Lundberg, Acta Chem. Scand. 19 (1965) 2274.

[14] A. Reisman, F. Holtzberg and E. Banks, J. Am. Chem. Soc. 80 (1958) 37.

[15] M. W. Shafer and R. Roy, J. Am. Ceram. Soc. 42 (1959) 482.

[16] S. Andersson, Acta Chem. Scand 21 (1967) 1777.

[17] S. Andersson, Acta Chem. Scand. 19 (1965) 557.

[18] D. C. Craig and N. C. Stephenson, J. Solid State Chem. 3 (1971) 89.

[19] A. Reisman, J. Am. Chem. Soc. 66 (1962) 15.

[20] A. Reisman and F. Holtzberg, J. Am. Chem. Soc. 77 (1955) 2115.

[21] J. E. Guerchais, Bull. Soc. Chim. Fr. (1962) 103.

[22] C. D. Whiston and A. J. Smith, Acta Cryst. 19 (1965) 169.

[23] K. Nassau, J. W. Shiever and J. L. Bernstein, J. Electrochem. Soc. 116 (1969) 348.

[24] B. M. Gatehouse, D. J. Lloyd and B. K. Miskin, in "Solid State Chemistry" Proc. 5th Materials Research Symposium, NBS Special Publication 364 (1972) 15.

[25] A. Reisman, F. Holtzberg, M. Berkenblit and M. Berry, J. Am. Chem. Soc. 78 (1956) 4514.

[26] R. S. Roth, H. S. Parker and W. S. Brower, Mat. Res. Bull. 8 (1973) 327.

[27] B. Aurvillius, Arkiv. f. Kemi. 25 (1964) 505.

[28] P. Spiegelberg, Ark, f. Kemi. Min. och. Geol. 14 [5] (1940) 1.

FIGURE CAPTIONS

Figure 1 Phase equilibrium diagram for the system Nb_2O_5-$LiNbO_3$ redrawn to conform with accepted published data.

o - liquidus [7]

◒ - transition [7]

● - solidus and solid solution boundary [7,11]

X - present work

Figure 2 Phase equilibrium diagram of the system Ta_2O_5-$LiTaO_3$, mostly from reference [2].

o - completely melted

- - partially melted

● - no melting

Figure 3 Phase equilibrium diagram of the system Nb_2O_5-$NaNbO_3$

X - liquidus values from reference [4]

o - completely melted

◒ - partially melted

● - no melting

dotted line - a phase resulting from reaction with atmospheric moisture

Figure 4 Phase equilibrium diagram for the system Ta_2O_5-$NaTaO_3$

o - completely melted

◒ - partially melted

● - no melting

X - quenched specimen

Figure 5 Phase equilibrium diagram for the system Nb_2O_5-$KNbO_3$

X - liquidus values from reference [20]

o - completely melted

◒ - partially melted

● - no melting

Figure 6 Phase equilibrium diagram for the system Ta_2O_5-$KTaO_3$

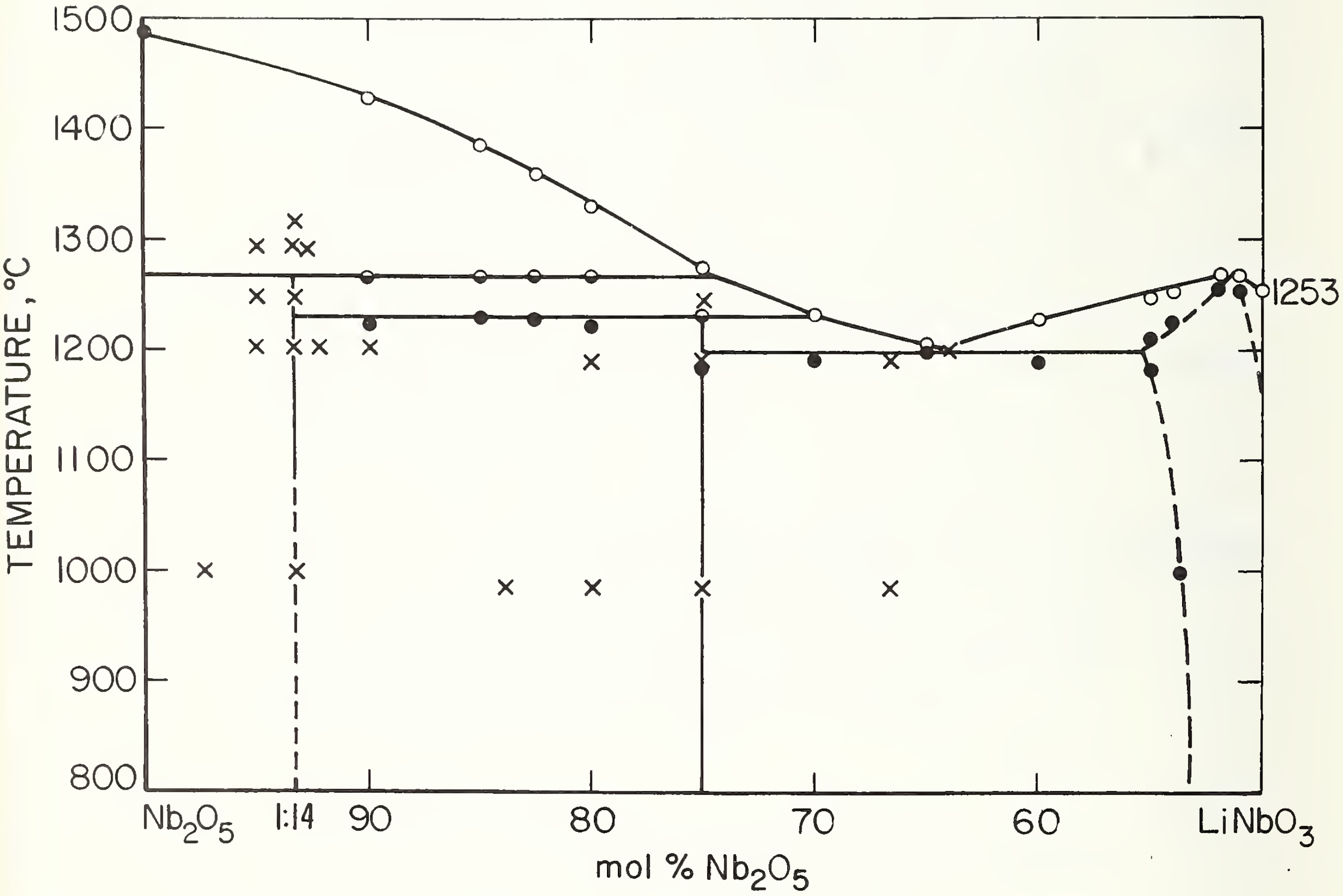
● - solidus and liquidus values from reference [25]
o - completely melted
◒ - partially melted
X - no melting

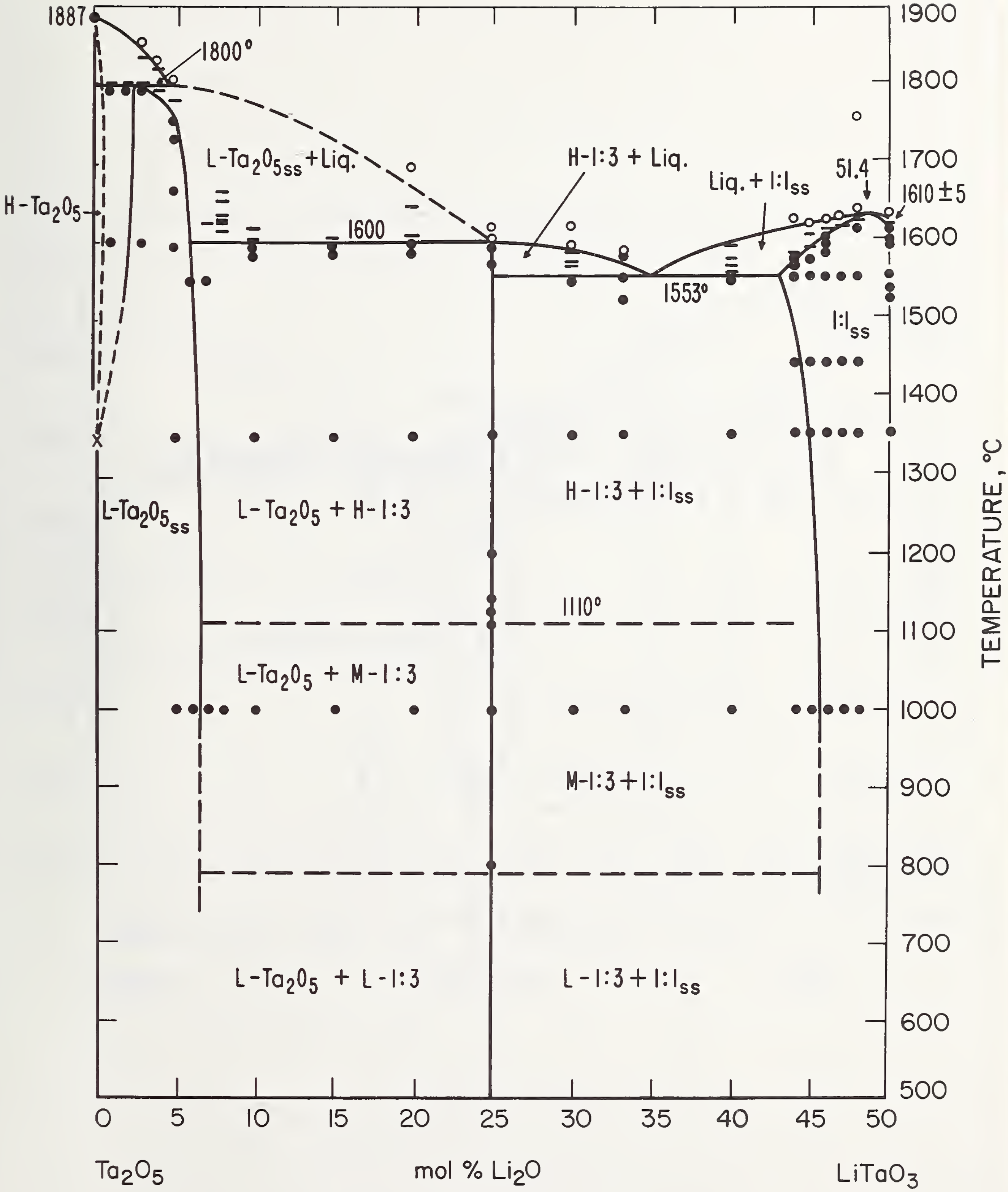
Figure 7 Dielectric loss (epsilon-2) versus reciprocal temperature (theta = 10^3 x degrees Kelvin^{-1}) for a specimen of $11K_2O:89Ta_2O_5$ (sample No. 27) having the structure of the Gatehouse Tungsten Bronze (GTB).

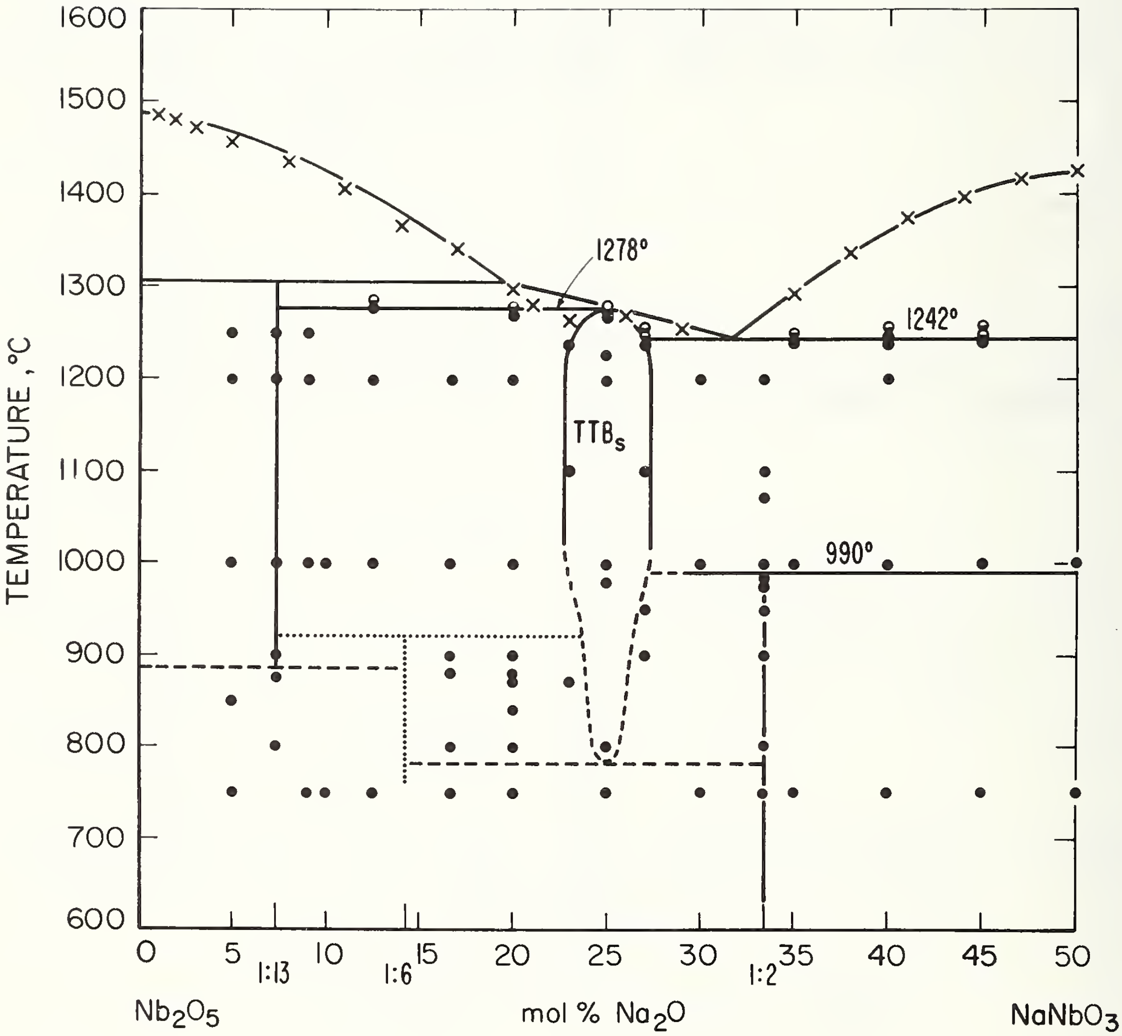
Figure 8 Dielectric loss (epsilon-2) versus reciprocal temperature (theta = 10^3 x degrees Kelvin^{-1}) for a specimen of $16.67K_2O:83.33Ta_2O_5$ (sample No. 23) having the structure of a Tetragonal Tungsten Bronze modified by superstructure to a tripled cell with orthorhombic (TTBs).

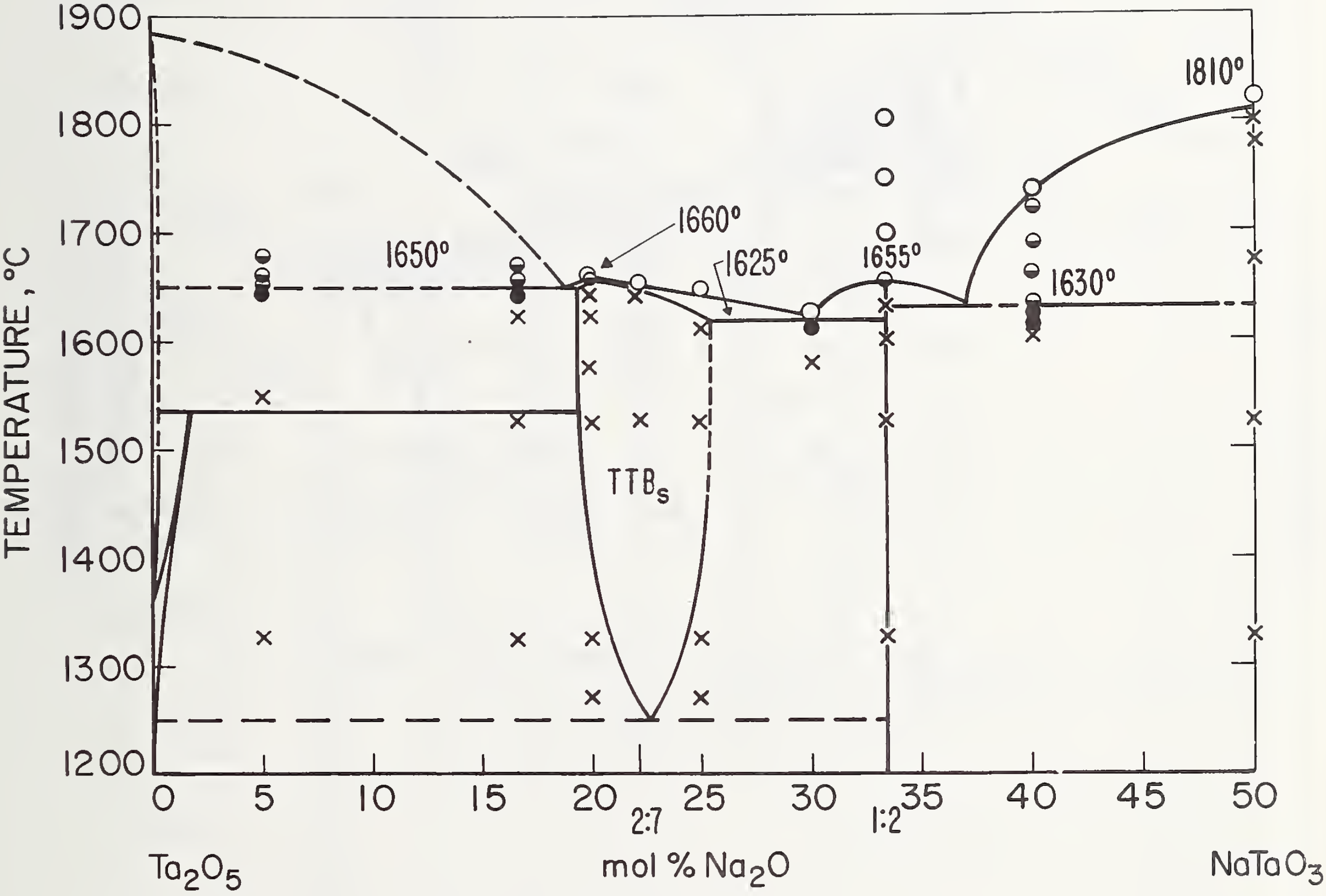
Figure 9 Dielectric loss (epsilon-2) versus reciprocal temperature (theta = 10^3 x degrees Kelvin^{-1}) for a specimen of $21.75K_2O:78.25Ta_2O_5$ (sample No. 39) having the structure of a Hexagonal Tungsten Bronze (HTB).

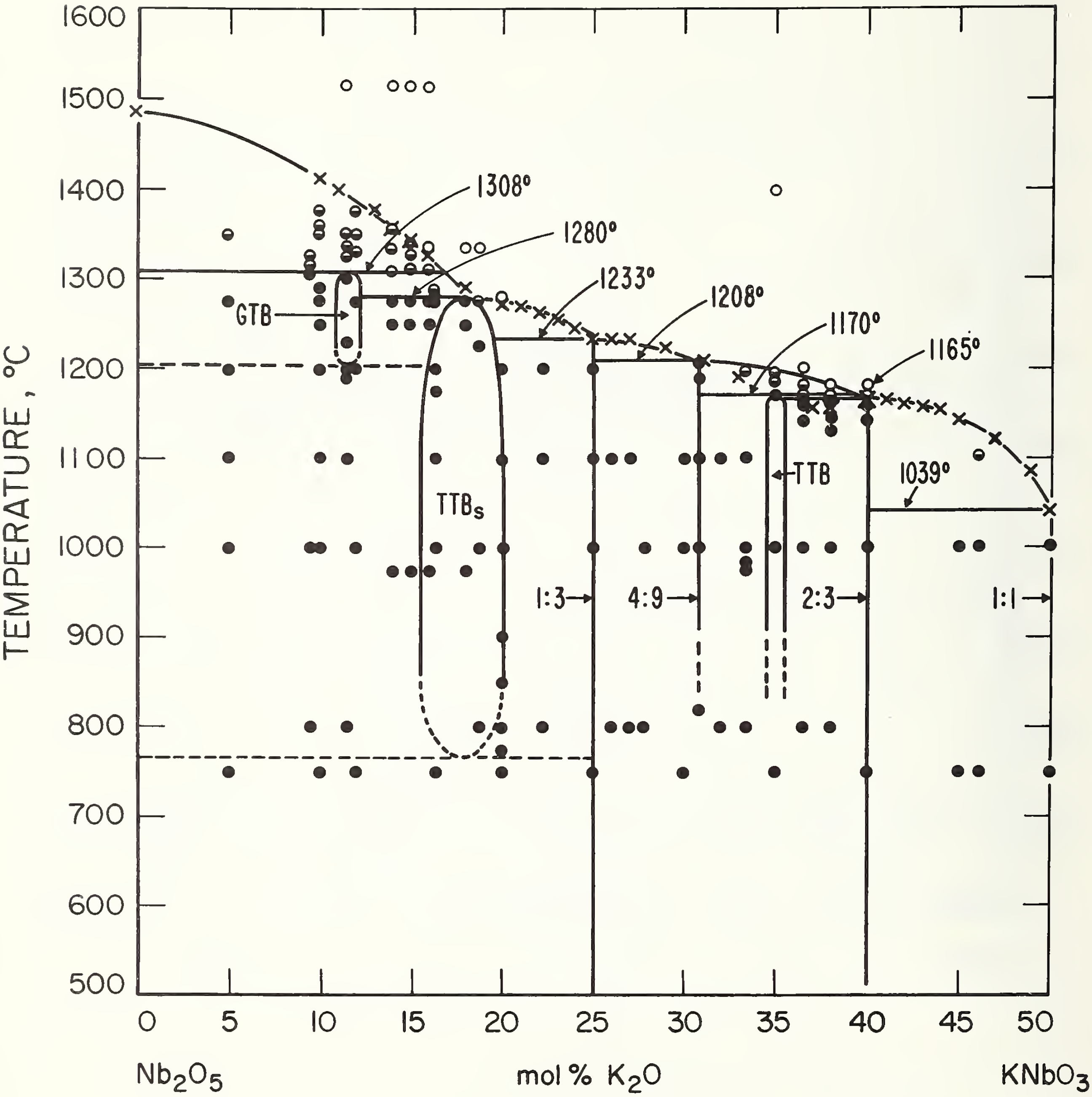
Figure 10 Dielectric loss (epsilon-2) versus reciprocal temperature (theta = 10^3 x degrees Kelvin^{-1}) for a specimen of $34K_2O:66Ta_2O_5$ (sample No. 28) having the structure of a Tetragonal Tungsten Bronze with no superstructure (TTB).

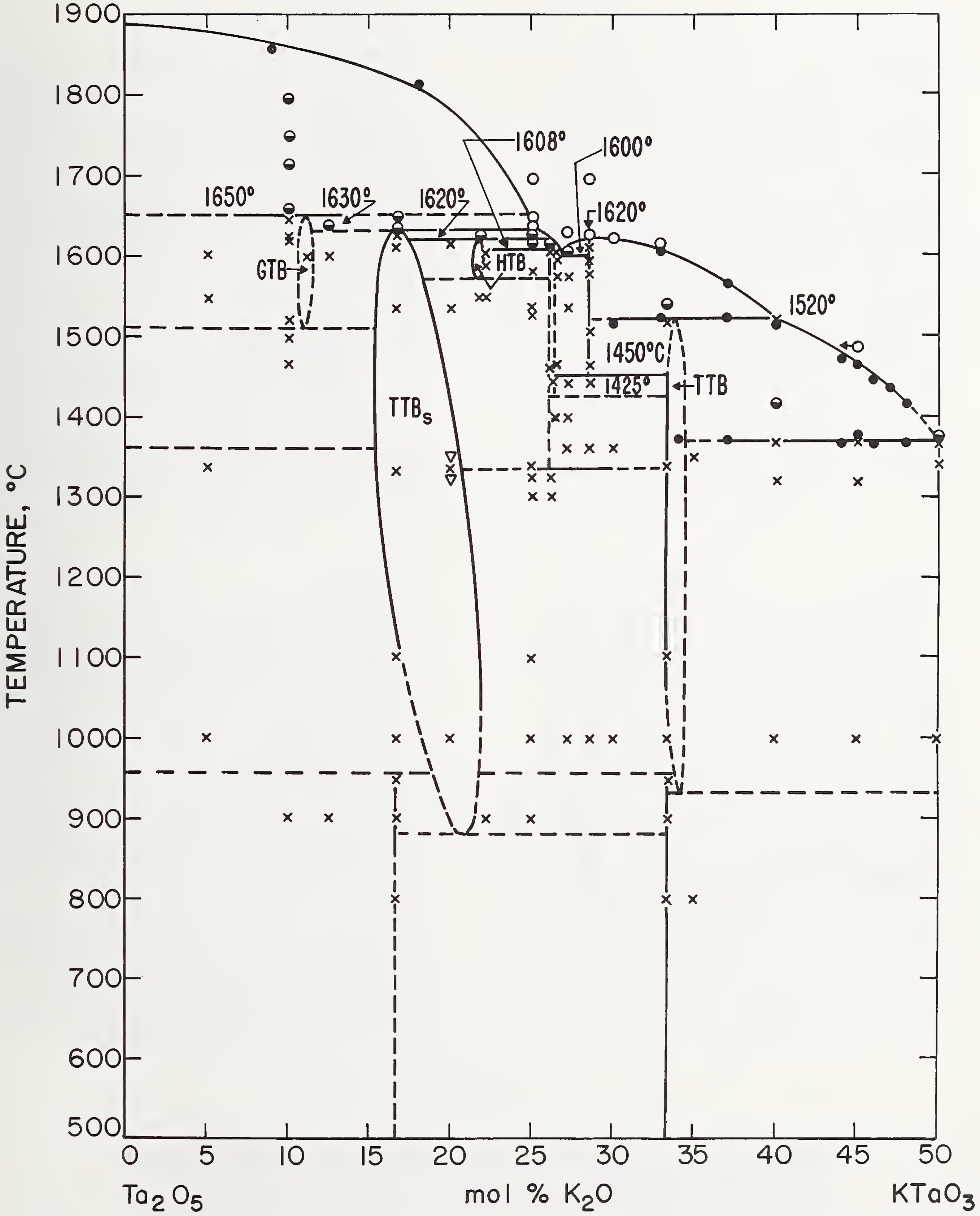

1500
1400
1300
1200
1100
1000
900
800
TEMPERATURE, °C
1253
Nb_2O_5
1:14
90
80
70
60
$LiNbO_3$
mol % Nb_2O_5


1887
1800°
L-Ta$_2$O$_5$ss + Liq.
H-1:3 + Liq.
Liq. + 1:1ss
51.4
1610 ± 5
H-Ta$_2$O$_5$
1600
1553°
1:1ss
L-Ta$_2$O$_5$ss
L-Ta$_2$O$_5$ + H-1:3
H-1:3 + 1:1ss
1110°
L-Ta$_2$O$_5$ + M-1:3
M-1:3 + 1:1ss
L-Ta$_2$O$_5$ + L-1:3
L-1:3 + 1:1ss
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
TEMPERATURE, °C
0
5
10
15
20
25
30
35
40
45
50
Ta$_2$O$_5$
mol % Li$_2$O
LiTaO$_3$


1600
1500
1400
1300
1200
1100
1000
900
800
700
600
TEMPERATURE, °C
1278°
1242°
990°
TTB_s
0
5
10
15
20
25
30
35
40
45
50
1:13
1:6
1:2
Nb_2O_5
mol % Na_2O
$NaNbO_3$


1900
1800
1700
1600
1500
1400
1300
1200
TEMPERATURE, °C
1810°
1660°
1650°
1625°
1655°
1630°
TTB_s
0
5
10
15
20
2:7
25
30
1:2
35
40
45
50
Ta_2O_5
mol % Na_2O
$NaTaO_3$


1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
TEMPERATURE, °C
1308°
1280°
1233°
1208°
1170°
1165°
1039°
GTB
TTBs
TTB
1:3
4:9
2:3
1:1
0
5
10
15
20
25
30
35
40
45
50
Nb2O5
mol % K2O
KNbO3


1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
TEMPERATURE, °C
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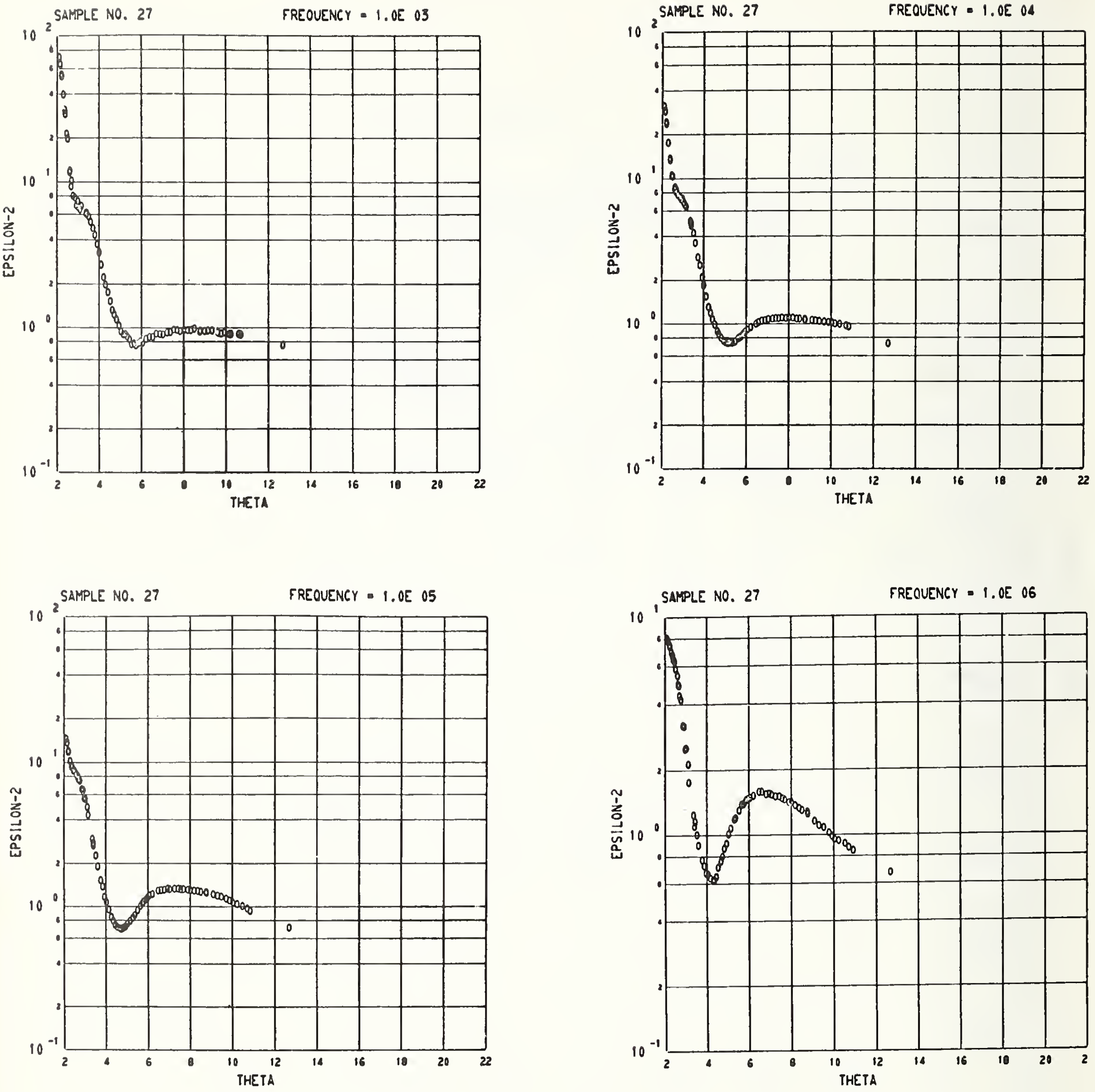
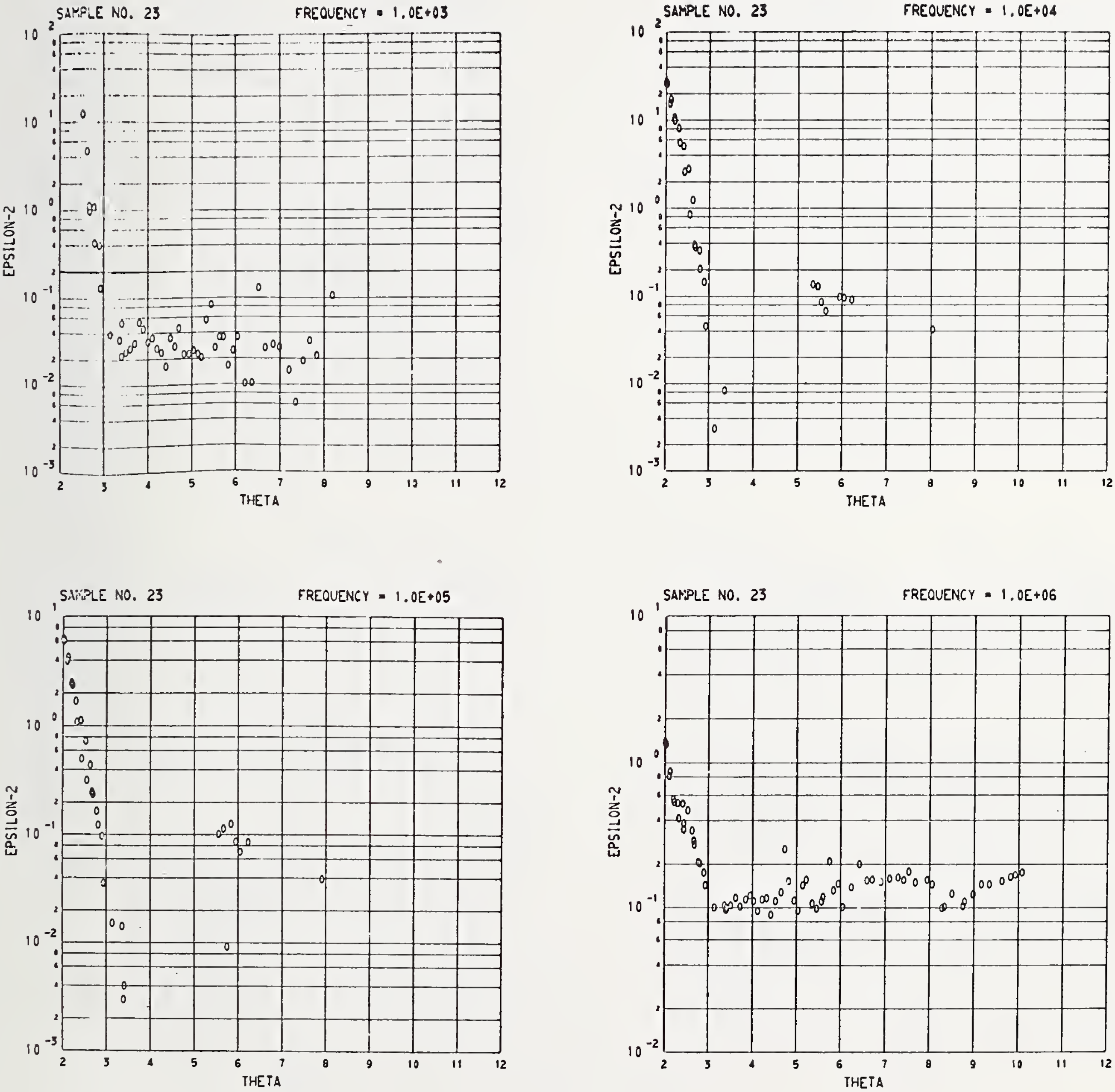
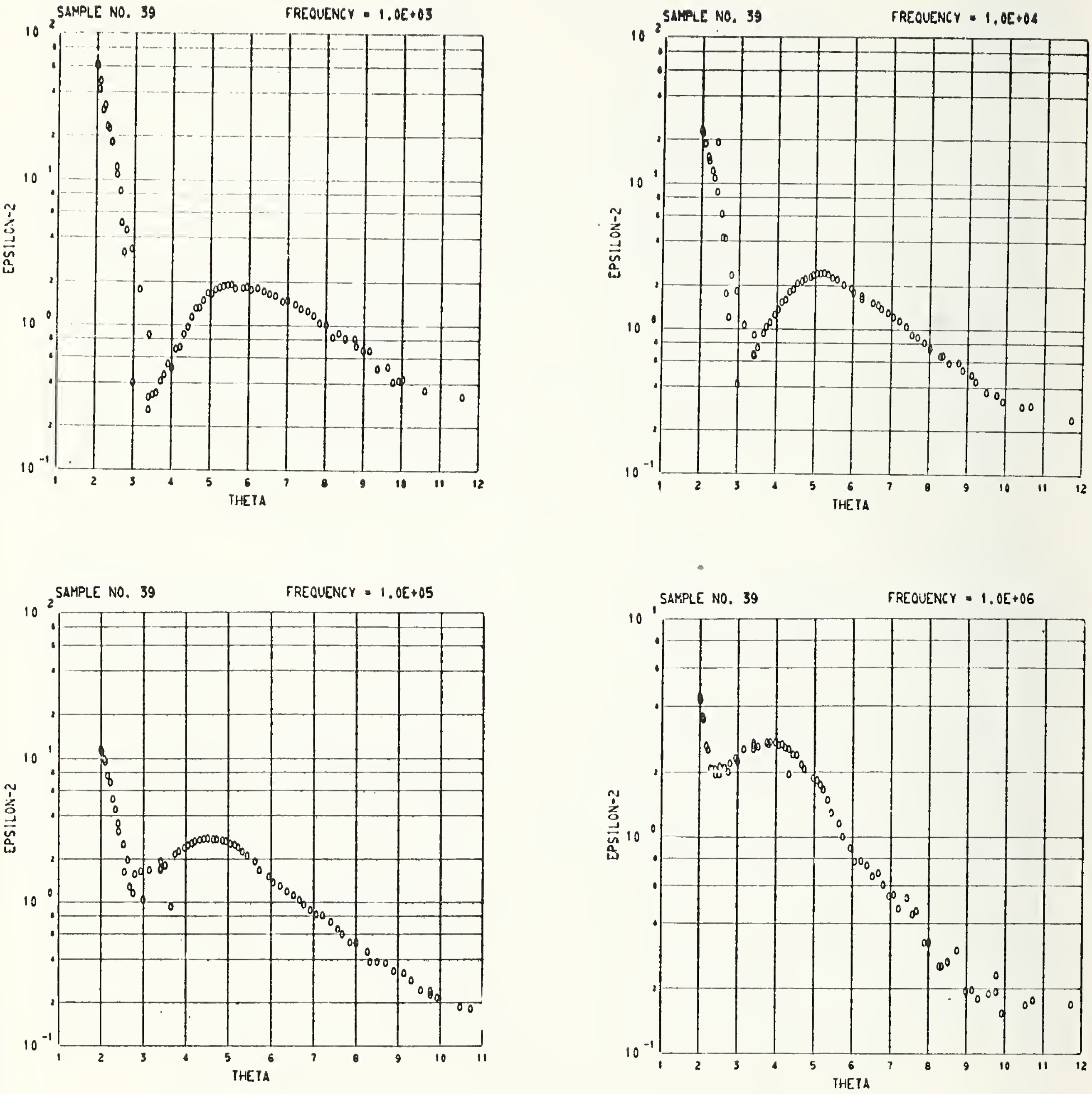
1630°
1620°
1608°
1600°
1620°
GTB
HTB
TTB$_s$
1520°
1450°C
1425°
TTB
0
5
10
15
20
25
30
35
40
45
50
Ta$_2$O$_5$
mol % K$_2$O
KTaO$_3$



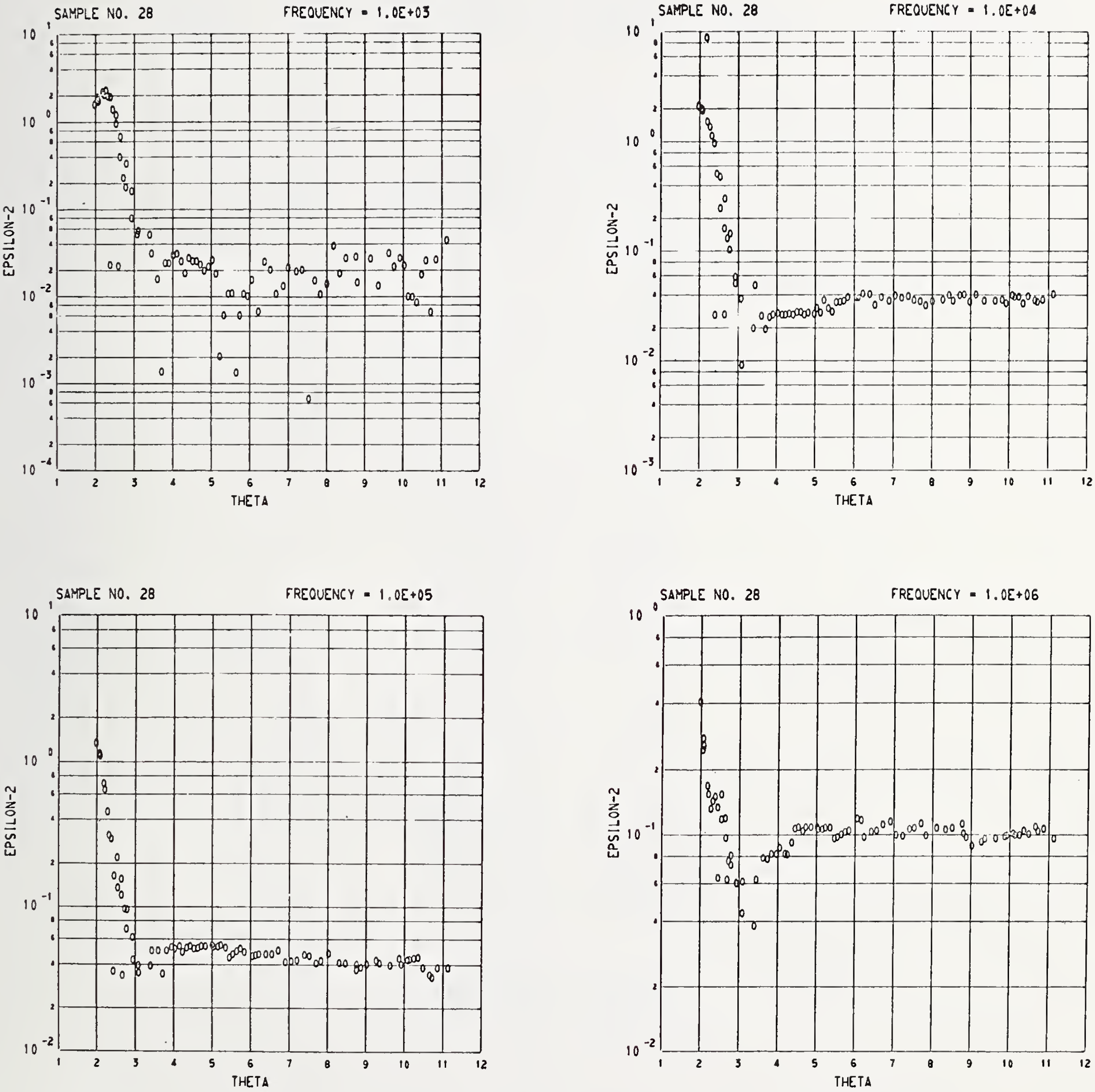
Dielectric loss (epsilon-2) versus reciprocal temperature (theta = 10^3 x degrees Kelvin^{-1}) for a specimen of $11K_2O:89Ta_2O_5$ (sample No. 27) having the structure of the Gatehouse Tungsten Bronze (GTB).



Dielectric loss (epsilon-2) versus reciprocal temperature (theta = 10^3 x degrees Kelvin^{-1}) for a specimen of 16.67K_2O:83.33Ta_2O_5 (sample No. 23) having the structure of a Tetragonal Tungsten Bronze Modified by superstructure to a tripled cell with orthorhombic symmetry (TTBs)



Dielectric loss (epsilon-2) versus reciprocal temperature (theta = 10^3 x degrees Kelvin^{-1}) for a specimen of $21.75K_2O:78.25Ta_2O_5$ (sample No. 39) having the structure of a Hexagonal Tungsten Bronze (HTB).



Dielectric loss (epsilon-2) versus reciprocal temperature (theta = 10^3 x degrees Kelvin^{-1}) for a specimen of $34K_2O:66Ta_2O_5$ (sample No. 28) having the structure of a Tetragonal Tungsten Bronze with no superstructure (TTB)

TABLE 1: EXPERIMENTAL DATA FOR THE SYSTEM Nb_2O_5-$LiNbO_3$

Composition Mole % [a]		Initial Heat Treatment [b]		Final Heat Treatment [c]		Results of Physical Observation	Results of X-Ray Diffraction Analyses [d]
Nb_2O_5	Li_2O	Temp. °C	Time Hrs.	Temp. °C	Time Hrs.		
97.50	2.50	1000	96	--	--	---	H-Nb_2O_5 + 1:3 + N-Nb_2O_5 (tr)
95.00	5.00	1000	63	--	--	---	-----
				1202	20	---	N-Nb_2O_5+ H-Nb_2O_5
				1249	19	Not melted	" "
				1274	24	Not visibly melted	-----
				1294	22	Not visibly melted	N-Nb_2O_5 + H-Nb_2O_5
				1318	24	Not visibly melted	-----
				1336	23	Some liquid present	-----
93.33	6.67	1000	63	--	--	---	H-Nb_2O_5 + 1:3
				1202	20	---	N-Nb_2O_5
				1249	19	Not melted	N-Nb_2O_5
				1274	24	Not melted	-----
				1294	22	Not visibly melted	N-Nb_2O_5 [a]
				1318	24	Partially melted	H-Nb_2O_5 + 1:3 + N-Nb_2O_5
				1336	23	Partially melted	-----
92.86	7.14	1000	60	--	--	---	-----
				1294	22	Not melted	N-Nb_2O_5 + H-Nb_2O_5 + 1:3
92.31	7.69	1000	63	--	--	---	-----
				1202	20	Not melted	N-Nb_2O_5 + 1:3
				1248	18.75	Partially melted	-----
90.00	10.00	1000	63	--	--	---	-----
				1202	20	Not melted	N-Nb_2O_5 + 1:3
83.33	16.67	985	64	--	--	Not melted	-----
				1244	20	Partially melted	-----
80.00	20.00	985	65	--	--	Not melted	1:3 + H-Nb_2O_5
				1190	96	Not melted	1:3 + N-Nb_2O_5
				1224	25	Not melted	-----
75.00	25.00	985	65	--	--	Not melted	1:3
				1190	96	Not melted	1:3
				1224	25	Not melted	---
				1244	20	Partially melted	N-Nb_2O_5 + 1:3 + 1:1
70.00	30.00	1000	70.5	--	--	Not melted	-----
				1183	23	Not melted	-----
				1195	24	No visible melting	-----
				1203	25	Some melting	-----
				1207	23	Some melting	-----
				1215	24	Some melting	-----
66.67	33.33	985	65	--	--	---	1:1 + 1:3
				1190	96	Not melted	1:1 + 1:3
				1224	25	Melted	-----
63.99	36.01	1000	70.5	--	--	---	-----
				1183	23	Not melted	-----
				1195	24	Partially melted	-----
				1203	25	Melted	1:1 + 1:3
				1207	23	Melted	-----

[a] For ease and accuracy of weighing Li_2O was added to Nb_2O_5 as $LiNbO_3$ not as the oxide end member.

[b] All specimens were initially calcined in Pt crucibles at the indicated temperature and time.

[c] All subsequent heat treatments were quenched in sealed Pt tubes from the indicated temperature.

[d] All phases identified are given in order of amount present at room temperature (greatest amount first). The phases are not necessarily those present at the temperature to which the specimen was heated.
H-Nb_2O_5 - the high temperature form of Nb_2O_5
N-Nb_2O_5 - a metastable form of Nb_2O_5 apparently stabilized by Li_2O.
1:3 - $LiNb_3O_8$
1:1 - $LiNbO_3$ solid solution

[e] These experiments suggest that the N-Nb_2O_5 phase melts incongruently between 1294° and 1318° rather than at the 1268° value given by Reisman.

TABLE 2: EXPERIMENTAL DATA FOR THE SYSTEM Ta_2O_5-$LiTaO_3$

Composition Mole % a/		Initial Heat Treatment b/		Final Heat Treatment c/		Results of Physical Observation	Results of X-Ray Diffraction Analyses d/
Ta_2O_5	Li_2O	Temp. °C	Time Hrs.	Temp. °C	Time Hrs.		
99	1	1000	60	--	--	-----	-----
				1600	19.00	No melting	H-Ta_2O_5 + L-Ta_2O_5 ss
				1795	0.17	No melting	" "
				1805	0.17	Partially melted	-----
98	2	1000	60	--	--	-----	-----
				1600	24.00	No melting	L-Ta_2O_5 ss + H-Ta_2O_5
				1795	0.17	No melting	" "
				1806	0.25	Partially melted	" "
97	3	1000	60	--	--	-----	-----
				1600	24.00	No melting	L-Ta_2O_5 ss
				1795	0.17	No melting	"
				1803	0.17	Partially melted	-----
				1842	0.03	Partially melted	-----
				1855	0.03	Completely melted	-----
96	4	1000	60	--	--	-----	-----
				1794	0.17	Partially melted	-----
				1820	0.33	Partially melted	-----
				1834	0.33	Completely melted	-----
95	5	1000	10	--	--	-----	-----
				1350	24.00	No melting	L-Ta_2O_5 ss
				1594	16.00	No melting	"
				1597	0.50	No melting	-----
				1667	0.17	No melting	-----
				1732	0.17	No melting	-----
				1757	0.17	No melting	-----
				1782	0.17	Partially melted	L-Ta_2O_5 ss
				1809	0.17	Completely melted	"
94	6	1000	10	--	--	-----	L-Ta_2O_5 ss
				1550	16.00	No melting	-----
93	7	1000	10	--	--	-----	L-Ta_2O_5 ss + M-1:3
				1550	24.00	No melting	" "
				1625	16.00	Partially melted	L-Ta_2O_5 ss
92	8	1000	10	--	--	-----	-----
				1615	1.00	Partially melted	-----
				1625	0.75	Partially melted	-----
				1627	0.75	Partially melted	-----
				1635	0.50	Partially melted	-----
				1653	0.50	Partially melted	-----
				1663	1.00	Partially melted	L-Ta_2O_5 ss + H-1:3
90	10	1000	10	--	--	-----	-----
				1350	24.00	No melting	L-Ta_2O_5 ss + H-1:3
				1583	0.50	No melting	-----
				1590	16.00	No melting	L-Ta_2O_5 ss + H-1:3
				1593	0.50	No melting	-----
				1607	0.75	Partially melted	L-Ta_2O_5 ss + H-1:3 + 1:1
				1618	0.50	Partially melted	-----
85	15	1000	10	--	--	-----	-----
				1350	24.00	No melting	-----
				1583	0.50	No melting	-----
				1593	0.75	No melting	-----
				1605	0.50	Partially melted	-----
80	20	1000	10	--	--	-----	M-1:3 + L-Ta_2O_5 ss
				1350	24.00	No melting	H-1:3 + L-Ta_2O_5 ss
				1580	1.00	No melting	" "
				1595	1.00	No melting	-----
				1609	0.50	Partially melted	-----
				1642	0.50	Partially melted	-----
				1646	0.50	Partially melted	-----
				1695	0.75	Probably completely melted	-----

75	25	800	307	--	--	-----	L-1:3 + M-1:3
		1000	10	--	--	-----	M-1:3
				1077	312.00	No melting	"
				1110	42.00	No melting	"
				1111	307.00	No melting	H-1:3
				1126	96.00	No melting	"
				1130	16.00	No melting	"
				1143	16.00	No melting	"
				1144	115.00	No melting	"
				1205	18.00	No melting	"
				1265	18.00	No melting	-----
				1350	24.00	No melting	H-1:3
				1573	16.00	No melting	"
				1592	1.00	No melting	-----
				1601	1.00	Completely melted	-----
				1616	1.50	Completely melted	H-1:3 + L-Ta_2O_5 ss + 1:1
		1000	10	--	--	-----	-----
		1205	18	--	--	-----	-----
				1130	16.00	No melting	-----
				1143	16.00	No melting	-----
				1144	115.00	No melting	-----
		1000	10	--	--	-----	-----
		1250	30	--	--	-----	H-1:3
				1077	312.00	-----	H-1:3
				1111	307.00	-----	-----
				1126	96.00	-----	-----
70	30	1000	10	--	--	-----	-----
				1350	24.00	No melting	-----
				1545	0.50	No melting	-----
				1555	0.50	Partially melted	-----
				1566	1.00	Partially melted	-----
				1572	0.75	Partially melted	-----
				1587	0.50	Partially melted	-----
				1594	0.25	Probably completely melted	-----
				1616	0.75	"	-----
				1616	0.50	"	H-1:3 + 1:1 ss
66.67	33.33	1000	10	--	--	-----	M-1:3 + 1:1 ss
				1350	24.00	No melting	H-1:3 + 1:1 ss
				1525	2.50	No melting	-----
				1551	2.50	No melting	-----
				1555	0.50	Probably some melting	-----
				1567	1.00	Considerably melted	-----
				1578	2.00	Completely melted	-----
				1581	0.25	Completely melted	-----
				1583	3.00	Completely melted	H-1:3 + 1:1 ss
60	40	1000	10	--	--	-----	-----
				1350	24.00	No melting	-----
				1547	0.50	No melting	-----
				1555	0.50	Partly melted	-----
				1566	0.50	Partly melted	-----
				1572	0.50	Partly melted	-----
				1590	1.00	Considerably melted	-----
56	44	1000	10	--	--	-----	-----
				1348	66.00	No melting	1:1 ss + H-1:3
				1440	70.00	No melting	"
				1550	0.75	No melting	-----
				1565	0.50	No melting	-----
				1576	0.50	No melting	-----
				1581	0.50	Partially melted	-----
				1622	0.50	Completely melted	-----
55	45	1000	10	--	--	-----	-----
				1348	66.0	No melting	1:1 ss
				1350	24.00	No melting	1:1 ss + H-1:3 (tr)
				1440	70.00	No melting	1:1 ss
				1550	1.00	No melting	-----
				1572	0.75	No melting	1:1 ss
				1587	0.50	Partially melted	-----
				1606	0.50	Partially melted	-----
				1617	0.75	Completely melted	-----
54	46	1000	10	--	--	-----	-----
				1348	66.00	No melting	1:1 ss
				1440	70.00	No melting	"
				1550	1.00	No melting	-----
				1581	0.50	No melting	-----
				1592	0.50	No melting	-----
				1605	0.50	No melting	-----
				1612	0.50	Partially melted	-----
				1624	0.50	Completely melted	-----

53	47	1000	10	--	--	-----	-----
				1348	66.00	No melting	1:1 ss
				1440	70.00	No melting	"
				1550	1.00	No melting	-----
				1612	0.50	Just begun to melt	-----
				1623	0.50	Completely melted	-----
52	48	1000	10	--	--	-----	1:1 ss
				1348	66.00	No melting	"
				1440	70.00	No melting	"
				1550	1.00	No melting	-----
				1612	0.75	No melting	-----
				1623	0.50	Just begun to melt	-----
				1637	0.33	Completely melted	-----
				1754	0.17	Completely melted	-----
50	50	Starting material		--	--	Powder	1:1
				1348	19.00	No melting	"
				1522	16.00	No melting	"
				1538	2.50	No melting	"
				1553	20.00	No melting	-----
				1592	1.00	No melting	-----
				1598	1.75	No melting	-----
				1607	1.00	No melting	-----
				1612	1.00	No melting	-----
				1616	1.00	Partially melted	-----
				1630	0.50	Completely melted	-----
				1633	1.00	Completely melted	-----

[a/] For ease and accuracy of weighing, Li_2O was added to Ta_2O_5 as $LiTaO_3$ not as the oxide end member.

[b/] All specimens were initially calcined in Pt crucibles at the indicated temperatures and time.

[c/] Specimens were heated in both open and sealed Pt tubes and seemed to show no difference or discrepancy in results, as very little, if any, volatilization takes place even from the melt.

[d/] All phases identified are given in order of amount present at room temperature (greatest amount first). The phases are not necessarily those present at the temperature to which the specimen was heated.

H-Ta_2O_5 - The high temperature polymorph of Ta_2O_5.
L-Ta_2O_5 ss - A solid solution of the low temperature polymorph of Ta_2O_5 stabilized by Li_2O.
L-1:3 - The low temperature polymorph of $LiTa_3O_8$ isostructural with $LiNb_3O_8$.
M-1:3 - The medium temperature polymorph of $LiTa_3O_8$ isostructural with the mineral woodgenite.
H-1:3 - The high temperature polymorph of $LiTa_3O_8$ isostructural with $LiTa_6O_{15}F$ and $Ta_4W_2O_{16}$.
1:1 ss - A solid solution of $LiTaO_3$.

TABLE 3: EXPERIMENTAL DATA FOR THE SYSTEM Nb_2O_5-$NaNbO_3$

Composition Mole % a/		Initial Heat Treatment b/		Final Heat Treatment c/		Results of Physical Observation	Results of X-Ray Diffraction Analyses d/
Nb_2O_5	Na_2O	Temp. °C	Time Hrs.	Temp. °C	Time Hrs.		
95	5	750	69	--	--	-----	H-Nb_2O_5 + 1:2
		1000	69	--	--	Not melted	1:13 + H-Nb_2O_5
				1200	21	Not melted	"
				1250	21	Not melted	-----
92.86	7.14	800	69	--	--	-----	H-Nb_2O_5 + 1:6
				875	19.5	Not melted	"
				900	140	Not melted	1:13 + H-Nb_2O_5 + 1:6
				1200	21	Not melted	1:13
		1000	164	--	--	Not melted	"
				1250	67	Not melted	"
		1225	64	--	--	Not melted	-----
				1000	234	Not melted	1:13
90.01	9.09	750	69	--	--	-----	H-Nb_2O_5 + 1:2
		1000	69	--	--	Not melted	1:13 + TTBs + H-Nb_2O_5
				1200	22	Not melted	1:13 + TTBs
				1250	21	Not melted	"
90	10	750	64	--	--	-----	H-Nb_2O_5 + 1:2
		1000	69	--	--	Not melted	1:13 + TTBs
87.5	12.5	750	69	--	--	-----	H-Nb_2O_5 + 1:2
		1000	69	--	--	Not melted	1:13 + TTBs
				1200	22	Not melted	"
				1278	72	Partially melted	"
				1285	1	Partially melted	"
		800	114	--	--	-----	-----
		1225	8	--	--	Not melted	1:13 + TTBs
83.33	16.67	750	64	--	--	-----	H-Nb_2O_5 + 1:2
				800	113	Not melted	1:6 + H-Nb_2O_5 + TTBs
				880	20	Not melted	TTBs + H-Nb_2O_5 + 1:6
				900	18.5	Not melted	"
		1000	69	--	--	-----	1:13 + TTBs
				1200	22	Not melted	"
80	20	750	64	--	--	-----	H-Nb_2O_5 + 1:2
				800	113	Not melted	1:6 + H-Nb_2O_5 + TTBs
				840	70	Not melted	TTBs + 1:6 + H-Nb_2O_5
				869	19	Not melted	"
				880	20	Not melted	"
				900	18.5	Not melted	"
				1000	67	Not melted	TTBs + 1:13
		1000	69	--	--	-----	"
				1200	22	Not melted	"
				1270	1	Not melted	-----
				1275	1.5	Not melted	-----
				1278	2.5	Partially melted	-----
77	23	870	91	--	--	-----	TTBs + H-Nb_2O_5 + 1:2
		1100	21	--	--	-----	TTBs + 1:13
		1100	44	--	--	-----	TTBs
				1238	19	-----	"
75	25	750	64	--	--	-----	H-Nb_2O_5 + 1:2
				800	113	Not melted	1:6 + TTBs + 1:2
				980	18.5	Not melted	TTBs
				1000	20	Not melted	"
		1000	69	--	--	Not melted	"
				1200	21	Not melted	"
				1270	1	Not melted	-----
				1275	1.5	Not melted	-----
				1278	2.5	Completely melted	-----
				1280	1	Completely melted	-----
		1200	21	800	115	Not melted	TTBs
		900	62	--	--	-----	-----
		1000	96	--	--	Not melted	TTBs
				1225	1	Not melted	"
				1225	5	Not melted	"

72.92	27.08	900	19	--	--	-----	TTBs + 1:2 + H-Nb_2O_5
		900	135	--	--	-----	TTBs + 1:2
				950	91	-----	"
		1100	44	--	--	Not melted	TTBs (+ 1:1 ?) [e]
				1238	19	Not melted	-----
				1249	3.5	Partially melted	-----
				1255	16.5	Partially melted	-----
70	30	750	64	--	--	-----	1:2 + 1:1 + H-Nb_2O_5
		1000	69	--	--	Not melted	1:2 + TTBs (+1:1) [e]
				1000	20	Not melted	"
				1200	22	Not melted	TTBs (+1:1 ?) [e]
66.67	33.33	800	62	--	--	-----	-----
		900	93	--	--	Not melted	-----
				950	93	Not melted	1:2
		800	62	--	--	-----	-----
		1100	62	--	--	Not melted	TTBs + 1:1
				975	21	Not melted	1:2
				985	22	Not melted	1:2 (+TTBs + 1:1) trace
		800	89	--	--	-----	1:2
				985	45	Not melted	1:2 (+1:1 + TTBs) trace
				1000	169	Not melted	TTBs + 1:1
				1073	67	Not melted	"
				1200	21	Not melted	"
65	35	750	64	--	--	-----	1:2 + 1:1 + H-Nb_2O_5
				1241	19	Not melted	-----
				1254	19	Partially melted	-----
		1000	69	--	--	Not melted	1:2 + 1:1
				1250	21	Partially melted	TTBs + 1:1 (?)
60	40	750	64	--	--	-----	1:2 + 1:1
				1241	19	Not melted	1:1 + TTBs
				1245	65	Partially melted	-----
				1254	19	Partially melted	-----
		1000	69	--	--	Not melted	1:2 + 1:1 (+TTBs) [e]
				1200	21	Not melted	1:1 + TTBs
				1250	21	Partially melted	"
55	45	750	64	--	--	-----	1:1 + 1:2
				1241	19	Not melted	1:1 + TTBs
				1245	65	Partially melted	-----
				1254	19	Partially melted	-----
		1000	69	--	--	Not melted	1:1 + 1:2
50	50	750	64	--	--	-----	1:1
		1000	69	--	--	Not melted	1:1

[a] For ease and accuracy of weighing Na_2O was added to Nb_2O_5 as $NaNbO_3$ not as the oxide end member.

[b] All specimens were initially calcined in Pt crucibles at the indicated temperatures and time.

[c] All subsequent heat treatments were quenched in sealed Pt tubes from the indicated temperature.

[d] All phases identified are given in order of amount present at room temperature (greatest amount first). The phases are not necessarily those present at the temperature to which the specimen was heated.

H-Nb_2O_5 - The high temperature form of Nb_2O_5
1:13 - $NaNb_{13}O_{33}$
1:6 - $NaNb_6O_{15}(OH)$. The presence of this phase indicates that the specimen has reacted with atmospheric moisture.
TTBs - A nonstoichiometric solid solution having an orthorhombic distortion of a tetragonal tungsten bronze-type lattice with superstructure indicating a tripled unit cell.
1:2 - $Na_2Nb_4O_{11}$
1:1 - $NaNbO_3$

[e] The presence of a small amount of either 1:1 or TTBs in equilibrium with a large amount of the other cannot be determined because of a complete overlap of all of the strongest peaks.

TABLE 4: EXPERIMENTAL DATA FOR THE SYSTEM Ta_2O_5-$NaTaO_3$

Composition Mole % a/		Initial Heat Treatment b/		Final Heat Treatment c/		Results of Physical Observation	Results of X-Ray Diffraction Analyses d/
Ta_2O_5	Na_2O	Temp. °C	Time Hrs.	Temp. °C	Time Hrs.		
95	5	1000	109	--	--	-----	L-Ta_2O_5 + 1:2
				1328	16.00	Not melted	-----
				1549	16.00	Not melted	H-Ta_2O_5 (tri.) + TTBs
				1648	0.08	Not melted	-----
				1653	0.08	Partially melted	-----
				1664	0.08	Partially melted	-----
				1679	0.08	Partially melted	-----
83.33	16.67	1000	109	--	--	-----	-----
				1328	16.00	Not melted	TTBs + L-Ta_2O_5
				1527	16.00	Not melted	TTBs + L-Ta_2O_5ss
				1625	41.00	Not melted	TTBs + H-Ta_2O_5
				1643	0.08	Not melted	-----
				1658	0.08	Partially melted	-----
				1670	0.08	Partially melted	-----
80	20	1000	109	--	--	---	1:2 + L-Ta_2O_5
				1195	552.00	No melting	"
				1270	360.00	No melting	TTBs + L-Ta_2O_5
				1329	64.00	No melting	"
				1527	16.00	No melting	TTBs
				1577	19.00	No melting	"
				1623	17.00	No melting	"
				1643	0.16	No melting	-----
				1654	0.16	Partially melted	-----
				1660	0.08	Completely melted	-----
				1670	0.08	Completely melted	-----
		1527	16	1195	552.00	No melting	TTBs + L-Ta_2O_5
				1270	360.00	No melting	"
77.78	22.22	800	112	--	--	-----	-----
				1350	48.00	Not melted	TTBs
				1527	16.00	Not melted	-----
				1642	0.16	Not melted	-----
				1654	0.16	Completely melted	-----
75	25	1000	109	--	--	-----	1:2 + L-Ta_2O_5
				1195	552.00	Not melted	1:2 + L-Ta_2O_5 + TTBs (tr)
				1270	360.00	Not melted	TTBs + 1:2
				1329	64.00	Not melted	"
				1527	6.00	Not melted	TTBs
				1613	17.00	Not melted	"
				1643	0.25	Completely melted	-----
				1722	0.08	Completely melted	-----
		1527	6	1195	552.00	Not melted	TTBs + 1:2 (tr)
				1270	360.00	Not melted	"
		1722	0.08	1576	16.00	Not melted	TTBs
70	30	1000	109	--	--	-----	-----
				1580	64.00	Not melted	1:2 + TTBs
				1612	0.08	Not melted	-----
				1627	0.08	Completely melted	-----
66.67	33.33	1000	109	--	--	Not melted	1:2
				1329	64.00	Not melted	"
				1524	7.00	Not melted	"
				1601	1.00	Not melted	-----
				1620	0.75	Not melted	-----
				1633	0.08	Not melted	-----
				1655	0.08	Completely melted	-----
				1698	0.08	Completely melted	-----
				1750	0.08	Completely melted	-----
				1805	0.08	Completely melted	-----

60	40	1000	109	--	--	-----	-----
				1602	5.00	Not melted	1:2 + 1:1
				1617	0.08	Not melted	-----
				1628	0.08	Not melted	-----
				1632	0.08	Partly melted	-----
				1664	0.08	Partly melted	-----
				1685	0.08	Partly melted	-----
				1690	0.08	Partly melted	-----
				1722	0.08	Partially melted	-----
				1737	0.08	Completely melted	-----
50	50	600	4	--	--	-----	1:1
				1328	16.00	Not melted	-----
				1527	0.50	Not melted	-----
				1622	0.50	Not melted	-----
				1676	0.08	Not melted	-----
				1782	0.08	Not melted	-----
				1800	0.08	Not melted	-----
				1821	0.08	Completely melted	-----

a/ For ease and accuracy of weighing Na_2O was added to Ta_2O_5 as $NaTaO_3$ not as the oxide end member.

b/ All specimens were initially calcined in Pt crucibles at the indicated temperatures and time.

c/ All subsequent heat treatments below about 1650° were quenched in sealed Pt tubes from the indicated temperatures. Experiment above about 1650° were performed in an inductively heated Ir crucible using sealed 80/20 Pt/Rh tubes.

d/ All phases identified are given in order of amount present at room temperature (greatest amount first). The phases are not necessarily those present at the temperature to which the specimen was heated.

L-Ta_2O_5 - The low temperature polymorph of Ta_2O_5
H-Ta_2O_5 - The high temperature polymorph of Ta_2O_5
ss - Solid solution
tri - Triclinic
tr - Trace
TTBs - A nonstoichiometric solid solution having an orthorhombic distortion of a tetragonal tungsten bronze-type lattice with superstructure indicating a tripled cell.
1:2 - $Na_2Ta_4O_{11}$
1:1 - $NaTaO_3$

TABLE 5: EXPERIMENTAL DATA FOR THE SYSTEM Nb_2O_5-$KNbO_3$

Composition Mole % [a]		Initial Heat Treatment [b]		Final Heat Treatment [c]		Results of Physical Observation	Results of X-Ray Diffraction Analyses [d]
Nb_2O_5	K_2O	Temp. °C	Time Hrs.	Temp. °C	Time Hrs.		
95	5	750	69	--	--	-----	H-Nb_2O_5 + 1:3
		1000	69	--	--	No melting	H-Nb_2O_5 + TTBs
				1100	114	No melting	"
				1200	69	No melting	"
				1275	20	No melting	H-Nb_2O_5 + GTB
				1350	20	Partially melted (?)	"
90.54	9.46	800	62	--	--	-----	-----
		1000	96	--	--	No melting	H-Nb_2O_5 + TTBs
				1305	140	No melting	GTB (+H-Nb_2O_5 ?)
				1315	46.5	Partially melted	H-Nb_2O_5 + HTB + ?
				1325	17	Partially melted	H-Nb_2O_5 + GTB + HTB + ?
90	10	750	69	--	--	-----	H-Nb_2O_5 + 1:3
		1000	69	--	--	No melting	TTBs + H-Nb_2O_5
				1100	23	No melting	"
				1200	69	No melting	"
				1250	40	No melting	GTB + H-Nb_2O_5 (+TTBs ?)
				1275	20	No melting	GTB + H-Nb_2O_5 (trace)
				1290	16	No melting	"
				1350	20	Partially melted	H-Nb_2O_5 + GTB + TTBs (?) + HTB (?)
				1360	20	Partially melted	H-Nb_2O_5 + TTBs + ?
				1375	40	Partially melted	H-Nb_2O_5 + HTB
88.5	11.5	800	62	--	--	-----	-----
		1000	96	--	--	No melting	TTBs + H-Nb_2O_5
				1200	66	No melting	TTBs + H-Nb_2O_5
				1300	18	No melting	GTB
				1515	1	Completely melted	-----
		1300	18	--	--	-----	GTB
				1190	18	No melting	-----
				1200	18	No melting	-----
				1200	66	No melting	GTB
				1210	71	No melting	GTB
				1230	71	No melting	GTB
				1325	17	Partially melted	TTBs + H-Nb_2O_5 + ?
				1335	70.5	Partially melted	-----
				1350	43	Partially melted	-----
		1515	1	--	--	Melted	-----
				1300	72	Not melted	GTB
88	12	750	69	--	--	-----	H-Nb_2O_5 + 1:3 + 1:1
		1000	69	--	--	No melting	TTBs + H-Nb_2O_5
				1100	45	No melting	"
				1200	69	No melting	"
				1275	20	No melting	GTB + TTBs
				1330	18	Partially melted	GTB
				1335	71	Partially melted	H-Nb_2O_5 + HTB + ?
				1350	20	Partially melted	GTB + H-Nb_2O_5 (?)
				1360	20	Partially melted	-----
				1375	40	Partially melted	H-Nb_2O_5 + HTB
86	14	975	23	--	--	-----	H-Nb_2O_5 + TTBs + 1:3
		1250	91	--	--	Not melted	TTBs + GTB
				1275	19	Not melted	-----
				1310	19	Partially melted (?)	GTB + TTBs
				1332	18	Partially melted	TTBs + H-Nb_2O_5 + ?
				1335	120	Partially melted	-----
				1355	125	Partially melted	-----
				1515	1	Completely melted	-----
85	15	975	23	--	--	-----	H-Nb_2O_5 + TTBs + 1:3 + 2:3 hyd.
		1250	91	--	--	Not melted	TTBs + GTB
				1275	19	Not melted	-----
				1310	19	Partially melted	GTB + TTBs
				1325	16	Partially melted	-----
				1335	19	Partially melted	H-Nb_2O_5 + TTBs + ?
				1335	125	Partially melted	-----
				1515	1	Completely melted	-----
84	16	975	23	--	--	-----	H-Nb_2O_5 + TTBs + 1:3 + 2:3 hyd.
		1250	91	--	--	Not melted	TTBs + GTB (?)
				1275	19	Not melted	-----
				1310	19	Partially melted	GTB + TTBs
				1335	19	Completely melted	-----
				1515	1	Completely melted	-----

83.66	16.34	750	69	--	--	-----	-----
		1000	69	--	--	Not melted	TTBs
				1100	114	Not melted	"
				1176	24	Not melted	"
				1200	69	Not melted	"
				1275	21	Not melted	"
				1279	1	Not melted	-----
				1285	1	Partially melted	-----
				1287	1	Partially melted	-----
82	18	975	16	--	--	-----	H-Nb_2O_5 + TTBs + 1:3 + 2:3 hyd.
		1250	91	--	--	Not melted	-----
				1275	19	Not melted	-----
				1335	18	Completely melted	-----
81.25	18.75	800	62	--	--	-----	-----
		1000	96	--	--	Not melted	TTBs
				1225	5	Not melted	"
				1275	19	Partially melted (?)	-----
				1335	18	Completely melted	TTBs + HTB
80	20	750	69	--	--	-----	1:3 + H-Nb_2O_5
				1000	69	Not melted	TTBs + 1:3 + 2:3
				1100	114	Not melted	TTBs
				1200	69	Not melted	TTBs + 1:3
				1275	21	Partially melted	TTBs
				1279	1	Completely melted	-----
		900	24	--	--	-----	TTBs + 1:3 + H-Nb_2O_5
		1000	59	--	--	-----	TTBs
				775	42	-----	"
				800	65	-----	"
				850	40	-----	"
		(uncalcined)		775	42	-----	TTBs + 1:3 + H-Nb_2O_5
				800	65	-----	"
				850	40	-----	"
77.78	22.22	800	69	--	--	-----	-----
				1100	45	-----	TTBs + 1:3
				1200	69	Not melted	"
75	25	750	69	--	--	-----	1:3 + 2:3 + H-Nb_2O_5
		1000	69	--	--	Not melted	1:3 + TTB
				1100	114	Not melted	"
				1200	69	Not melted	1:3
74	26	800	45	--	--	-----	-----
				1000	45	Not melted	1:3 + 4:9
73	27	800	45	--	--	-----	-----
				1100	45	Not melted	1:3 + 4:9
72.2	27.8	800	62	--	--	-----	-----
		1000	96	--	--	Not melted	1:3 + 4:9
70	30	750	69	--	--	-----	4:9 + 1:3
		1000	69	--	--	Not melted	"
				1100	114	Not melted	-----
69.23	30.77	820	73	--	--	-----	-----
		1000	79	--	--	-----	-----
				1100	21	Not melted	4:9
				1100	45	Not melted	-----
				1188	43	Not melted	4:9
				1205	2	Not melted	"
68	32	800	45	--	--	-----	-----
				1100	45	Not melted	4:9 + TTB
66.67	33.33	800	89	--	--	-----	1:3 + 2:3
		1000	164	--	--	Not melted	TTB + 4:9
				975	21	Not melted	TTB + 4:9
				985	45	Not melted	TTB + 4:9
				1100	114	Not melted	"
				1195	20	Partially melted	4:9
65	35	750	64	--	--	-----	-----
		1000	69	--	--	Not melted	TTB
				1100	21	Not melted	TTB
				1195	18	Partially melted	TTB
				1215	0.17	Melted	-----
		1398	1	--	--	Melted	(?)
				1170	2	Not melted	TTB
				1170	19	Not melted	TTB
				1183	19	Partially melted	TTB + 4:9 + 2:3 hyd.
				1189	2	Partially melted	"
				1191	67	Partially melted	4:9 + 2:3 hyd.
		800	47	--	--	-----	-----
		1000	70	--	--	-----	TTB
				1125	8	Not melted	TTB

63.5	36.5	800	65	--	--	-----	-----
		1000	45	--	--	Not melted	TTB + 2:3 hyd.
				1143	2	Not melted	"
				1158	1	Not melted	"
				1165	1	Not melted	-----
				1170	2	Partially melted	TTB
				1180	2	Partially melted	(?)
				1200	0.5	Melted	TTB
62	38	800	65	--	--	-----	-----
		1000	45	--	--	Not melted	2:3 hyd. + TTB
				1130	16	Not melted	"
				1143	2	Not melted	-----
				1158	1	Not melted	-----
				1160	1	Not melted	-----
				1165	1	Not melted	-----
				1170	2	Completely melted	-----
				1180	2	Completely melted	-----
				1200	0.5	Completely melted	2:3 + TTB
60	40	750	69	--	--	-----	1:3 + 2:3 + 1:1
		1000	69	--	--	Not melted	2:3 + 2:3 hyd.
				1000	20	Not melted	2:3
				1143	2	Not melted	-----
				1158	1	Not melted	-----
				1165	1	Completely melted	-----
				1170	2	Completely melted	-----
				1172	2	Completely melted	-----
				1180	2	Completely melted	-----
55	45	750	69	--	--	-----	1:1 + 1:3 + 2:3
		1000	69	--	--	Not melted	1:1 + 2:3 + 2:3 hyd.
53.85	46.15	750	69	--	--	-----	1:1 + 2:3 + 1:3
		1000	69	--	--	Not melted	1:1 + 2:3 + 2:3 hyd.
				1000	20	Not melted	"
				1100	23	Partially melted	1:1 + 2:3
50	50	750	69	--	--	-----	1:1
		1000	69	--	--	Not melted	1:1

---

[a] For ease and accuracy of weighing K_2O was added to Nb_2O_5 as $KNbO_3$ not as the oxide end member.

[b] All specimens were initially calcined in Pt crucibles at the indicated temperatures and time.

[c] All subsequent heat treatments were quenched in sealed Pt tubes from the indicated temperatures.

[d] All phases identified were given in order of amount present at room temperature (greatest amount first). The phases were not necessarily those present at the temperature to which the specimen was heated.

H-Nb_2O_5 - The high temperature form of Nb_2O_5.

1:3 - $NaNb_3O_8$.

GTB - Gatehouse Tungsten Bronze - A nonstoichiometric solid solution having a large tetragonal unit cell with 7-sided tunnels first described by B. M. Gatehouse for a rubidium niobate of unknown composition.

TTBs - A nonstoichiometric solid solution having an orthorhombic distortion of a tetragonal tungsten bronze-type lattice with superstructure indicating a tripled cell.

4:9 - A compound having the apparent composition $4K_2O:9Nb_2O_5$ ($K_8Nb_{18}O_{49}$).

TTB - Tetragonal Tungsten Bronze - A nonstoichiometric solid solution having an undistorted tetragonal lattice with no superstructure.

2:3 - $K_4Nb_6O_{17}$.

2:3 hyd. - The hydrated form of $K_4Nb_6O_{17}$ in equilibrium with atmospheric moisture at room temperature.

1:1 - $KNbO_3$.

HTB - A phase resulting from a quenched liquid with an x-ray pattern resembling a hexagonal tungsten bronze.

? - An unknown phase which apparently results from quenching a liquid.

TABLE 6: EXPERIMENTAL DATA FOR THE SYSTEM Ta_2O_5-$KTaO_3$

Composition Mole % [a]		Initial Heat Treatment [b]		Final Heat Treatment [c]		Results of Physical Observation	Results of X-Ray Diffraction Analyses [d]
Ta_2O_5	K_2O	Temp. °C	Time Hrs.	Temp. °C	Time Hrs.		
95	5	1000	109	--	--	-----	L-Ta_2O_5 + 1:5 + TTBs
				1337	16	No melting	L-Ta_2O_5 + TTBs
				1549	16	No melting	H-Ta_2O_5 + GTB
				1602	16	No melting	"
90	10	900	168	--	--	-----	-----
				1466	168	No melting	TTBs + L-Ta_2O_5 + H-Ta_2O_5
				1500	17	No melting	TTBs + H-Ta_2O_5 + L-Ta_2O_5
				1553	1.0	No melting	-----
				1609	17	No melting	GTB + H-Ta_2O_5 (?)
				1715	1.5	Partially melted	-----
				1747	1.5	Partially melted	HTB + H-Ta_2O_5
				1795	1.5	Partially melted	HTB + H-Ta_2O_5 + L-Ta_2O_5
		1000	109	1521	44	No melting	-----
				1601	0.75	No melting	-----
				1619	64	No melting	GTB + H-Ta_2O_5
				1620	16	No melting	GTB + H-Ta_2O_5
		1609	17	1466	168	No melting	GTB + TTBs
				1500	17	No melting	-----
				1521	44	No melting	-----
				1624	0.17	No melting	-----
				1647	0.17	No melting	-----
				1657	0.17	Partially melted	-----
89	11	800	115	--	--	-----	1:5 + L-Ta_2O_5
				1600	12	No melting	GTB
87.5	12.5	900	216	--	--	-----	1:5 + L-Ta_2O_5
				1601	17	No melting	GTB + TTBs
				1640	19	Partially melted	GTB
83.33	16.67	800	192	--	--	-----	L-Ta_2O_5 + 1:2
		900	168	--	--	-----	1:5
				950	360	No melting	1:5 + TTBs (tr)
				1100	64	No melting	1:5 + TTBs + L-Ta_2O_5
		1000	109	--	--	-----	TTBs + 1:5 + L-Ta_2O_5
				1337	16	-----	TTBs
				1532	16	-----	TTBs
				1610	16	-----	TTBs
				1624	0.17	Not melted	-----
				1634	6.5	Partially melted	GTB + HTB
				1635	0.17	Partially melted	-----
				1647	0.17	Partially melted	-----
80	20	1000	109	--	--	-----	TTBs + 1:5
				1337	16	Not melted	TTBs
				1538	16	Not melted	TTBs + 9L
				1614	16	Not melted	HTB + TTBs
				1617	16	Not melted	"
				1618	16	Not melted	"
		1617	16	1325	168	Not melted	TTBs
		1618	16	1350	144	Not melted	"
78.25	21.75	800	91	1600	6	-----	HTB
77.78	22.22	900	168	--	--	-----	-----
				1549	1.0	Not melted	TTBs + 9L + HTB
				1571	1.0	Not melted	-----
				1575	10	Not melted	-----
				1581	19	Not melted	HTB
				1602	6.5	Not melted	HTB
				1607	0.5	Not melted	-----
				1620	16	Partly melted (?)	HTB + 9L
				1632	19	Partly melted	-----
		1581	19	1549	19	Not melted	HTB + TTBs
		1602	6.5	1549	1.0	Not melted	-----
				1571	1.0	Not melted	HTB + TTBs
				1603	0.17	Not melted	-----
				1613	0.17	Not melted	-----
				1624	0.17	Partly melted	-----

75	25	900	168	--	--	-----	1:2 + 1:5 + TTBs
				1304	96	Not melted	TTBs + TTB
				1340	19	Not melted	-----
				1579	16	Not melted	9L + HTB
				1600	68	Not melted	-----
				1692	2	Completely melted	11L + HTB
		1000	109	--	--	-----	TTBs + TTB + 3L
				1100	64	Not melted	TTBs + TTB
				1327	120	Not melted	TTBs + TTB
				1340	19	Not melted	9L + TTBs
				1340	72	Not melted	"
				1538	64	Not melted	"
				1575	10	Not melted	"
				1598	0.5	Not melted	-----
				1611	5.5	Not melted	9L + HTB
				1634	16	Melted	HTB + H-1:3
				1646	1.0	Melted	"
		1340	72	--	--	-----	-----
				1600	68	Not melted	9L + HTB
				1606	16	Not melted	9L + HTB
		1340	72				
		900	1.5	1610	--	Not melted	9L + HTB
		1000	109				
		1538	64	1528	72	Not melted	9L + TTBs
		1600	68	1603	0.25	Not melted	-----
				1613	0.25	Melted	-----
				1624	0.25	Melted	-----
73.85 [e]	26.15	1462	69	--	--	Not melted	9L
				1304	96	Not melted	9L + TTB
				1327	120	Not melted	9L + TTB
				1603	0.17	Not melted	-----
				1613	0.17	Partially melted	-----
73.67 [e]	26.33	1443	89	--	--	Not melted	9L + 16L
73.5 [e]	26.5	1466	64	--	--	-----	16L + 9L (tr)
				1400	48	Not melted	16L + 9L + 11L
				1574	0.5	Not melted	-----
				1574	16	Not melted	16L
				1586	16	Not melted	-----
				1594	4	Not melted	-----
				1603	0.17	Not melted	-----
72.73	27.27	1000	68	--	--	-----	-----
				1361	24	Not melted	9L + TTB
				1400	48	Not melted	"
				1573	0.17	Not melted	-----
				1573	16	Not melted	11L + 16L
				1589	0.17	Not melted	-----
				1629	0.17	Completely melted	-----
				1632	0.08	Completely melted	-----
71.43	28.57	1000	68	--	--	-----	TTBs + TTB + 1:2 + 1:5 + 3L
				1361	24	Not melted	9L + TTB
				1438	75	Not melted	16L + TTB
				1465	336	Not melted	11L
				1507	139	Not melted	11L
				1578	1.0	Not melted	-----
				1583	3.5	Not melted	11L + TTB
				1591	88	Not melted	11L
				1611	0.08	Not melted	-----
				1613	0.17	Not melted	-----
				1618	0.08	Not melted	-----
				1618	16	Not melted	-----
				1624	0.08	Melted	-----
				1626	1.5	Melted	-----
				1694	1.0	Melted	11L
		1575	10	--	--	-----	11L + TTB
		1583	3.5	1438	75	-----	11L + 16L + TTB
				1465	336	-----	11L
				1507	137	-----	11L
70	30	1000	68	--	--	-----	-----
				1361	24	Not melted	TTB + 9L
				1622	1.0	Melted	11L + TTB (tr)

66.67	33.33	800	192	--	--	-----	1:2 + 1:1 + L-Ta_2O_5
		900	168	--	--	-----	1:2
				950	360	Not melted	"
				1100	64	Not melted	TTB
		1000	109	--	--	-----	1:2 + TTB + 3L
				798	163	Not melted	"
				1340	19	Not melted	TTB
				1340	72	Not melted	"
				1515	64	Not melted	TTB + 11L
				1538	20	Partially melted	11L + TTB
				1616	1.0	Completely melted	11L + TTB + 9L
66	34	800	90	1400	10	Not melted	TTB
65	35	800	112	--	--	-----	1:1 + 1:2 + L-Ta_2O_5
				1350	66	Not melted	TTB (+1:1 ?)
60	40	1000	92	--	--	-----	TTB + 1:1
				1318	64	Not melted	TTB + 1:1
				1368	0.5	Not melted	-----
				1412	16	Partially melted	-----
55	45	1000	92	--	--	-----	1:1 + TTB
				1318	64	Not melted	"
				1368	0.5	Not melted	-----
				1480	18	Completely melted	-----
50	50	600	4	--	--	-----	1:1
				1340	19	Not melted	"
				1368	0.5	Not melted	-----
				1375	0.5	Completely melted	-----

[a] For ease and accuracy of weighing K_2O was added to Ta_2O_5 as $KtaO_3$ not as the oxide end member.

[b] All specimens were initially calcined in Pt crucibles at the indicated temperature and time.

[c] All subsequent heat treatments were quenched in sealed Pt tubes from the indicated temperatures.

[d] All phases identified are given in order of amount present at room temperature (greatest amount first). The phases are not necessarily those present at the temperature to which the specimen was heated.

L-Ta_2O_5 - The low temperature polymorph of Ta_2O_5.
H-Ta_2O_5 - The high temperature polymorph of Ta_2O_5.
1:5 - KTa_5O_{13} - An orthorhombic compound of undetermined structure.
GTB - Gatehouse Tungsten Bronze - A nonstoichiometric solid solution having a large tetragonal unit cell with 7-sided tunnels first described by B. M. Gatehouse for a rubidium niobate of unknown composition.
TTBs - A nonstoichiometric solid solution having an orthorhombic distortion of a tetragonal tungsten bronze-type lattice with superstructure indicating a tripled cell.
HTB - Hexagonal Tungsten Bronze - A nonstoichiometric solid solution with an x-ray pattern resembling a hexagonal tungsten bronze.
9-L - A hexagonal phase with a c-axis ∿ 9 x 4 Å.
16-L - A hexagonal phase with a c-axis ∿ 16 x 4 Å.
11-L - A hexagonal (rhombohedral) phase with a c-axis ∿ 11 x 4 Å.
3-L - An apparently metastable hexagonal phase with a c-axis ∿ 3 x 4 Å.
1:2 - $K_2Ta_4O_{11}$.
H-1:3 - A monoclinic phase which apparently results from quenching a liquid near the composition $K_2O:3Ta_2O_5$.
TTB - Tetragonal Tungsten Bronze - A nonstoichiometric solid solution having an undistorted tetragonal lattice with no superstructure.
1:1 - $KTaO_3$.

[e] Made from the 1000° calcines of the 75:25 and 72.73:27.27 mixtures.

TABLE 7

Summary of LeRC Measurements [a] of Dielectric Loss
on Polycrystalline NBS Samples

Composition		Frequency, Hz [b]				Resonance [c]
		10^3	10^4	10^5	10^6	
$6Li_2O:17TiO_2$	ε'	54	30	22	19	No Peaks
	ε"	622	67	9.8	1.9	
$K_{1.55}Li_{1.26}(LiTi)O_{16}$	ε'	796	418	225	132	No Peaks
	ε"	401	194	94	43	
$K_{1.6}Mg_{0.8}Ti_{3.8}O_8$	ε'	80	74	71	70	ΔE = 15.1 kcal/mole
	ε"	4.0	3.1	1.4	0.9	ρ_{25} = 2.7 x 10^9 Ω-cm
$5Li_2O:95Ta_2O_5$ [d]	ε'	64	59	57	58	No Peaks
	ε"	7	2	0.7	0.3	
$5Li_2O:95Ta_2O_5$		---	---	---	---	No Peaks
$Li_{1.8}Ta_{5.8}W_{0.2}O_{16}$	ε'	19	18	18	18	No Peaks
	ε"	0.3	0.02	< 0.002	0.05	
$Na_2O:13Nb_2O_5$	ε'	20	19	19	19	No Peaks
	ε"	0.9	0.4	0.3	0.2	
$NaNb_3O_8$		---	---	---	---	No Peaks
$Na_{10.8}Nb_{34}W_{1.8}O_{95.6}$		---	---	---	---	ΔE > 10 ρ_{25} ≈ 3 x 10^7 Ω-cm
$21Na_2O:79Ta_2O_5$	ε'	22	22	21	21	No Peaks
	ε"	0.3	0.2	0.1	0.2	
$7K_2O:13Nb_2O_5$		---	---	---	---	Slight Peaks ΔE = 5.6 to 6.8 ρ_{25} ∿ 1 to 5 x 10^4 Ωcm
$11.5K_2O:88.5Nb_2O_5$	ε'	25	---	---	---	No Peaks
	ε"	5.1	---	---	---	
$3K_2O:13Nb_2O_5$		---	---	---	---	No Peaks
KNb_3O_8 [e]	ε'	< 100	< 100	< 100	< 100	No Peaks, two orientations.
	ε"	< 2	< 0.1	< 0.1	< 0.1	
$K_4Nb_6O_{17}\cdot XH_2O$ [e]	ε'	536	264	102	64	No Peaks, two orientations.
	ε"	854	64	< 1	< 1	
$11K_2O:89Ta_2O_5$	ε'	52	43	38	36	High Temp. ΔE = 10.3 kcal/mole ρ_{25} = 2 x 10^8 Ω-cm
	ε"	6.1	4.7	2.6	1.1	Low Temp. ΔE = 8 kcal/mole ρ_{25} = 1 x 10^8 Ω-cm
$K_2O:5Ta_2O_5$	ε'	18	18	18	18	No Peaks
	ε"	0.03	0.01	0.01	0.1	
$K_2O:4Ta_2O_5$	ε'	22	---	22	---	No Peaks
	ε"	0.04	---	0.1	---	
$21.75K_2O:78.25Ta_2O_5$		---	---	---	---	ΔE = 7.9 kcal/mole ρ_{25} = 1 x 10^4 Ω-cm
$34K_2O:66Ta_2O_5$		---	---	---	---	ΔE ≈ 20 to 25 kcal/mole ρ_{25} = 6 x 10^{13} Ω-cm
$K_{0.51}Ta_{0.51}W_{0.49}O_3$		---	---	---	---	No Peaks.

[a] Measurements made by H. E. Kautz, LeRC.

[b] at 25°C.

[c] Values of ΔE obtained from ε vs temperature measurements.

[d] hot pressed specimen.

[e] Single crystal specimens, supplied by K. Nassau, BTL.

TABLE 8

ALKALI TANTALATE PELLET FABRICATION

Composition	Calcine	Forming	Sintering	X-Ray
5 Li_2O:95 Ta_2O_5	1000°C - 144 hours	Hot pressed[a/] 1200°C Hot pressed[a/] 1300°C	Refire 1500°C 16.5 hours Refire 700°C 18 hours	Low Ta_2O_5, crystallinity improved by refiring Low Ta_2O_5, crystallinity improved by refiring
Li_2O:3 Ta_2O_5 ($LiTa_3O_8$)	1000°C - 23 hours 1050°C - 44 hours	10,000 psi	1300°C - 22 hours air quenched	Single phase, $LiTa_6O_{15}F$-type
"Substituted $LiTa_3O_8$" $Li_{1.8}Ta_{5.8}W_{0.2}O_{16}$	1000°C - 23 hours 1050°C - 44 hours	10,000 psi	1400°C - 23 hours air quenched	Single phase, $LiTa_6O_{15}F$-type
"Tetragonal Bronze" 21 Na_2O:79 Ta_2O_5	1000°C - 23 hours 1050°C - 44 hours	10,000 psi	1400°C - 17 hours air quenched	Single phase bronze
11 K_2O:89 Ta_2O_5	800°C - 90 hours	10,000 psi	1600°C - 12 hours Removed at temperature and placed on chill block for rapid cooling	Single phase
K_2O:5 Ta_2O_5	800°C - 90 hours	10,000 psi	1500°C - 20 hours air quenched	Tetragonal bronze
K_2O:4 Ta_2O_5	800°C - 90 hours	10,000 psi	1400°C - 20 hours air quenched	Tetragonal bronze
21.75 K_2O:78.25 Ta_2O_5	800°C - 91 hours	10,000 psi	1600°C - 6 hours Pellet sealed in platinum, welded closed. Removed at temperature and water-quenched	After removal of surface layer by grinding, single phase hexagonal bronze
34 K_2O:66 Ta_2O_5	800°C - 90 hours	10,000 psi	1400°C - 10 hours Cooled at 120°C/hour	Single phase
$K_{.51}Ta_{.51}W_{.49}O_3$ (Pyrochlore)	800°C - 34 hours	10,000 psi	950°C - 27 hours Removed at temperature and placed in quartz tube, evacuated to $p \leq 10^{-5}$ Torr and sealed to prevent hydration	X-ray of pellet impregnated with silicone resin to prevent hydration showed single phase pyrochlore

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[a/] Hot pressing performed by the Haselden Co., San Jose, California.

TABLE 9

ALKALI NIOBATE PELLET FABRICATION

Composition	Calcine	Forming	Sintering	X-Ray
Li_2O:14 Nb_2O_5	1000°C - 18 hours 1250°C - 68 hours	10,000 psi	1250°C - 12 hours Cooled at 180°C/Hr.	Single phase N-Nb_2O_5 after surface grinding
Na_2O:13 Nb_2O_5	800°C - 114 hours	10,000 psi	1225°C - 8 hours Cooled at 180°C/Hr.	Single phase except for one line of phase next highest in Na_2O content.
$NaNb_3O_8$	800°C - 62 hours 1000°C - 96 hours	18,000 psi	1225°C - 1 hour air quenched	Single phase 1:3
$Na_{10.8}(NbO)_4(WO)_{1.8}Nb_{30}O_{90}$	800°C - 89 hours 1000°C - 70 hours	18,000 psi	1225°C - 3 hours air quenched	Single phase, pattern similar to $NaNb_3O_8$
11.5 K_2O:88.5 Nb_2O_5	800°C - 62 hours 1000°C - 96 hours	18,000 psi	1300°C - 6.5 hours air quenched. Specimens poorly sintered. Excessive grain growth under all conditions. Hot pressing in progress.	Gatehouse tungsten bronze
3 K_2O:13 Nb_2O_5	800°C - 62 hours 1000°C - 96 hours	18,000 psi	1225°C - 1 hour air quenched	Tetragonal tungsten bronze with superstructure.
7 K_2O:13 Nb_2O_5	800°C - 47 hours 1000°C - 70 hours	18,000 psi	1225°C - 1 hour air quenched	Tetragonal tungsten bronze without superstructure.

TABLE 10

ALKALI TITANATE PELLET FABRICATION

Composition	Calcine	Forming	Sintering	X-Ray
Ramsdellite 6 Li_2O:17 TiO_2 $[Li_{.9}(Li_{.3}Ti_{1.7})O_4]$	9 pbw $6Li_2O:17TiO_2$ calcined: 800°C - 2.5 Hr. 1050°C - 68.5 Hr. 1 pbw raw batch, 6 Li_2CO_3:17 TiO_2	10,000 psi	1200°C - 17 hours air quenched.	Single phase Ramsdellite
K_2O:MgO:4 TiO_2 $[K_{1.6}(Mg_{.8}Ti_{3.2})O_8]$	800°C - 18 hours 1000°C - 24 hours	10,000 psi 0.5 percent by weight stearic acid as binder.	1200°C - 13 hours air quenched	Single phase, "Cmcm-phase"

TABLE 11

Summary of Crystal Growth Experiments

System	Phase	Melt Composition	Method	Comments
$K_2O-Nb_2O_5$	7:13 (TTB)	$36.5K_2O:63.5Nb_2O_5$	TSSG*	Yield: 4:9 → small amount 7:13 → 2:3
	17.5:82.5 (TTBs)	$17.5K_2O:82.5Nb_2O_5$	TSSG	Yield: polycrystalline multiphase
	17.5:82.5 (TTBs)	$20.0K_2O:80.0Nb_2O_5$	TSSG	Yield: polycrystalline TTB
	12.5:81.5 (GTB)	$15.0K_2O:85.0Nb_2O_5$	TSSG	Yield: Nb_2O_5
$K_2O-Ta_2O_5$	1:2 (TTB)	$45K_2O:55Ta_2O_5$	TSSG	Yield: single phase
$Li_2O-Ta_2O_5$	1:3	$25Li_2O:75Ta_2O_5$	Czochralski	Yield: single crystals
	5:95 (L-Ta_2O_5)	$15Li_2O:85Ta_2O_5$	TSSG	Yield: single crystals
$Na_2O-Nb_2O_5$	1:3 (TTBs)	$25Na_2O:75Nb_2O_5$	Czochralski	Yield: single crystals
$Na_2O-Ta_2O_5$	21:79 (TTBs)	$25Na_2O:75Ta_2O_5$	Czochralski	Excessive vaporization of Na_2O

* Top seeded solution growth.

TABLE 12

Crystallographic Data for Phases in the Nb_2O_5-Alkali Niobate and Ta_2O_5-Alkali Tantalate Systems

System	Designation	Composition Mol %		Symmetry	Unit Cell Dimensions a Å	b Å	c Å	α	β	γ	Conditions Limiting Possible Reflections	Probable Space Groups
Nb_2O_5-$LiNbO_3$		Nb_2O_5	Li_2O									
	N-Nb_2O_5	93.33	6.67	Monoclinic	25.518	3.827	17.554	---	124°59.1'	---	hkℓ:h+k=2n	C2,Cm,C2/m
	1:3	75	25	Monoclinic	7.457	5.035	15.264	---	107°18.7'	---	h0ℓ:ℓ=2n 0k0:k=2n	$P2_1/c$
Ta_2O_5-$LiTaO_3$		Ta_2O_5	Li_2O									
	L-Ta_2O_5ss	95	5	Orthorhombic	6.198	40.29	3.888	---	---	---	None	pm,pq [1]
	L-1:3	75	25	Monoclinic	7.41	5.10	15.12	---	107°12'	---	h0ℓ:ℓ=2n 0k0:k=2n	$P2_1/c$
	M-1:3	75	25	Monoclinic	9.420	11.536	5.055	---	91°32'	---	hkℓ:h+k=2n h0ℓ:ℓ=2n	Cc,C2/c
	H-1:3	75	25	Orthorhombic	16.716	8.941	3.840	---	---	---	0kℓ:ℓ=2n	Pmma,$P2_1ma$, Pm2a
Nb_2O_5-$NaNbO_3$		Nb_2O_5	Na_2O									
	1:13	92.86	7.14	Monoclinic	22.40	3.834	15.37	---	91°28.2'	---	hkℓ:h+k=2n	C2,Cm,C2/m
	1:6**	80	20	Orthorhombic	∿14.7	∿10.2	∿3.9	---	---	---	hkℓ:h+k=2n	C222,Cm2m, Cmm2,Cmmm
	TTBs	75	25	Orthorhombic	12.364	36.992	3.955	---	---	---	0kℓ:k=2n h0ℓ:h=2n	Pbam,$Pba2_1$
	1:2	66.67	33.33	Monoclinic	10.840	6.162	12.745	---	106°13.2'	---	hkℓ:h+k=2n h0ℓ:ℓ=2n	Cc,C2/c
Ta_2O_5-$NaTaO_3$		Ta_2O_5	Na_2O									
	TTBs	80	20	Orthorhombic	12.397	37.34	3.903	---	---	---	h0ℓ:h=2n	Pmam,$P2_1am$, Pma2
	TTBs	75	25	Orthorhombic	12.398	37.28	3.899	---	---	---	h0ℓ:h=2n	" "
	1:2	66.67	33.33	Hexagonal	6.120	---	36.629	---	---	---	hkℓ:-h+k+ℓ=3n h0ℓ:ℓ=2n	R3c,$R\bar{3}c$
Nb_2O_5-$KNbO_3$		Nb_2O_5	K_2O									
	GTB	88.5	11.5	Tetragonal	27.518	---	3.9687	---	---	---	h00:h=2n	$P42_12$,$P42_1m$
	TTBs	83.33	16.67	Orthorhombic	12.519	37.558	3.952	---	---	---	h0ℓ:h=2n	Pmam,$P2_1am$, Pma2
	TTBs	80	20	Orthorhombic	12.545	37.636	3.957	---	---	---	"	" "
	HTB	Unknown*		Hexagonal	7.511	---	3.889	---	---	---	None	P6/mmm
	1:3	75	25	Orthorhombic	8.925	21.232	3.808	---	---	---	hkℓ:k+ℓ=2n h0ℓ:h=2n	Amam,$A2_1am$, Ama2
	4:9	69.23	30.77	Triclinic	13.353	13.915	15.022	82°11.8'	69°42'	89°4.3'	None	P_1,$P\bar{1}$
	TTB	65	35	Tetragonal	12.589	---	3.981	---	---	---	h0ℓ:h=2n	Pmam,$P2_1am$, Pma2
	2:3	60	40	Orthorhombic	7.822	33.019	6.481	---	---	---	h0ℓ:h+ℓ=2n hk0:k=2n	Pmnb,$P2_1nb$
	2:3 hyd.	60	40	Orthorhombic	7.824	38.073	6.485	---	---	---	h00:h=2n 0k0:k=2n 00ℓ:ℓ=2n	$P2_12_12_1$
Ta_2O_5-$KTaO_3$		Ta_2O_5	K_2O									
	GTB	88.5	11.5	Tetragonal	27.55	---	3.899	---	---	---	h00:h=2n	$P42_12$, $P42_1m$
	1:5	83.33	16.67	Orthorhombic	5.654	10.713	16.80	---	---	---	h0ℓ:ℓ=2n 0kℓ:k=2n	Pbcm,$Pbc2_1$
	TTBs	80	20	Orthorhombic	12.547	37.641	3.922	---	---	---	h0ℓ:h=2n	Pmam,$P2_1am$, Pma2
	HTB	78.25	21.75	Hexagonal	7.527	---	3.901	---	---	---	None	P6/mmm
	9L	73.85	26.15	Hexagonal	7.55	---	36.583	---	---	---	hhℓ:ℓ=2n	$P6_3mc$,$P\bar{6}2c$, $P6_3mmc$
	16L	73.5	26.5	Hexagonal	7.542	---	65.57	---	---	---	hhℓ:ℓ=2n	" "
	11L	71.43	28.57	Hexagonal	7.54	---	43.512	---	---	---	hkℓ:-h+k+ℓ=3n	R3,$R\bar{3}$,R32, R3m,$R\bar{3}m$
	1:2	66.67	33.33	Hexagonal	6.283	---	36.878	---	---	---	hkℓ:-h+k+ℓ=3n	" "
	TTB	66	34	Tetragonal	12.569	---	3.957	---	---	---	h0ℓ:h=2n	Pmam,$P2_1am$, Pma2
	3L*	75	25	Hexagonal	9.051	---	12.284	---	---	---	h0ℓ:ℓ=2n	$P6_3cm$,$P\bar{6}c2$, $P6_3mcm$
	H-1:3*	75	25	Monoclinic	14.615	3.774	6.557	---	98°30'	---	None	P2,Pm,P2/m

[1] Two dimensional plane groups.

* Metastable phase obtained from quenched liquid.

** Probably due to reaction with atmospheric moisture-$NaNb_6O_{16}(OH)$.

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