

Isothermal Compressibilities of Alkaline Earth Oxides at 21° C

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Compression measurements were made by the piston-displacement method on powdered alkaline earth oxides at 21° C at 1,000-atmosphere intervals for pressures between 2,000 and 10,000 atmospheres. Pressure volume data are linear within experimental error. Compressibilities, β , and standard deviations of compressibilities, σ , in units of 10^{-6} per atmosphere are as follows: BeO, $\beta=0.27$, $\sigma=0.04$; MgO, $\beta=0.60$, $\sigma=0.12$; CaO, $\beta=0.89$, $\sigma=0.04$; SrO, $\beta=0.84$, $\sigma=0.10$; BaO, $\beta=1.76$, $\sigma=0.05$. Some abnormality in compressibility behavior for CaO and SrO is noted. This is probably related to a similar abnormality in densities.

1. Introduction

In a recent study [1]¹ of the behavior of the binary alkaline earth borate glasses under high pressures, it was noted that data on the compressibilities of the alkaline earth oxides were largely unavailable. Bridgman [2] has reported data on the compressibility of a large crystal of MgO and on compacted powders of MgO and CaO. Measurements on the powders were made without a confining liquid, pressure being applied directly on the compacted powder. The result for powdered MgO was much greater than for the single crystal; thus, the validity of the data for powdered CaO is doubtful. Madelung and Fuchs reported earlier on MgO [3].

As all the alkaline earth oxides except BeO form cubic crystals, the system is of considerable theoretical interest and has been treated by Mayer and Maltbie [4], using the methods developed by Born and Mayer [5] and by Sherman [6]. Because compressibility data were unavailable, Mayer and Maltbie assumed a repulsion term similar to that found in the alkali halides [5]. Their calculations then led to negative electron affinities for oxygen and sulfur. Compressibility data on the alkaline earth sulfides, selenides, and tellurides, also generally cubic, have been reported by Bridgman [7].

The present report describes the results of measurements of compressibilities of the alkaline earth oxides at 21° C at pressures up to 10,000 atm.

2. Experimental Method and Materials

Methods used in measuring compressions have been described in detail in an earlier paper [8]. All oxides were in powder form and were contained in a small stainless-steel cylinder that was open at one end. The reference run was made using the same cylinder, containing a steel bar having a volume similar to that of the powdered oxides.

All oxides except BaO were prepared at temperatures of at least 1,000° C and were cooled in a sealed container to minimize absorption of moisture from the atmosphere. The weighed cylinder was packed with oxide in the partly opened container, and the oxide was compacted in the cylinder with a steel ram rod. Early attempts to perform these operations in a dry box showed that the necessary manipulations could not be conveniently carried out under such conditions. The tube was reweighed after packing with oxide and immediately subjected to a vacuum (approximately 0.1 mm of Hg) produced by a mechanical pump. Following at least 4 hr under vacuum, a sufficient quantity of a light petroleum distillate (Varsol) to completely cover the tube was admitted to the evacuated system. The liquid used had previously been dried with the particular oxide under study. The specimen was permitted to remain under liquid for 1 hr at 1 atm, to assure penetration of the voids by the liquid before compression measurements were conducted. Following compression, the tube and contents were weighed in dry liquid to permit calculation of the volume of the powder. Each oxide was studied in at least two separate measurements, using freshly prepared material for each run.

Immediately after the cylinder had been packed with the compression specimen, a portion of the residual oxide was taken for quantitative analysis for anion impurities. This specimen was expected to contain more moisture and CO₂ than the one used for compression, because it was exposed for a longer period. Analyses on all specimens were conducted volumetrically. Approximately 0.1 g of oxide was weighed out and treated with 100 ml of water. Excess standard sulfuric acid was added and the mixture digested several days on a steam bath with frequent agitation, more acid being added if required to maintain an acid solution. Following digestion the excess acid was back titrated with standard alkali and the weight of the specimen as oxide was calculated. The ratio of calculated to measured weights was considered to give an estimate of the purity.

¹ Figures in brackets indicate the literature references at the end of this paper.

2.1. Preparation and Analysis of Oxides

BeO—Beryllium oxide was a commercial material of fluorescent grade and was fired at 1,000° C for 16 hr in platinum prior to use. No analysis was performed because of the high purity of this specimen and the relative inertness of BeO toward water and carbon dioxide.

MgO—Reagent grade MgO was fired at 1,000° C for 16 hr in platinum. Analysis showed 97.5 percent of MgO.

CaO—Reagent grade CaCO₃ was fired at 1,200° C for 24 hr in platinum to prepare CaO. Analysis showed 97.8 percent of CaO.

SrO—Strontium oxide was prepared by firing Sr(IO₃)₂ for 1 week in porcelain. Starting temperature was 600° C and the final firing was at 1,000° C for 72 hr. Sr(IO₃)₂ was prepared from reagent grade SrCl₂ and I₂O₅. Analysis gave 98.0 percent of SrO. One impurity was Sr(IO₃)₂ in very small quantity because the iodine liberated from excess KI by 0.2 g of the specimen was discharged by 1 drop of 0.1 N thiosulfate.

BaO—High-purity barium oxide was not prepared. All attempts to prepare this material gave relatively impure products originating from the attack of the highly corrosive barium compounds on the containers. The specimen studied was obtained commercially and was observed to contain small amounts of sulfides and colored cations. Analysis showed 98.4 percent of BaO.

3. Results and Discussion

The average experimental compression data for each oxide are given in table 1. Individual measure-

TABLE 1. Compression data for alkaline earth oxides

Pressure <i>atm</i>	Compression, $-\Delta V/V_0$				
	BeO ^a	MgO ^b	CaO ^a	SrO ^b	BaO ^a
10,000	0.00190	0.00614	0.00768	0.00666	0.01426
9,000	.00155	.00405	.00635	.00654	.01277
8,000	.00228	.00472	.00576	.00528	.01113
7,000	.00199	.00389	.00492	.00474	.00952
6,000	.00122	.00319	.00399	.00367	.00750
5,000	.00068	.00246	.00290	.00260	.00564
4,000	.00036	.00193	.00226	.00190	.00393
3,000	.00018	.00083	.00123	.00119	.00196
2,000	.00000	.00000	.00000	.00000	.00000

^a Average of 2 runs.

^b Average of 3 runs.

ments usually agreed to approximately ± 0.0004 in $-\Delta V/V_0$ [9] but many instances of deviations of greater magnitude were observed. These may be attributed to the small quantity of specimen used, approximately 4 cm³, and the relatively low compressibility of the specimens. In the more incompressible oxides, some tendency for compression values to decrease at the higher pressures is observed. A similar behavior is to be noted in the experimental data obtained on diamond by Adams [10], but the cause of this behavior is not known. It

is probably to be attributed to experimental errors inherent in measuring such small compressions.

Compressibilities were not determined from the average data of table 1, but were obtained by averaging the compressibilities, obtained from each measurement. To each set of experimental data a linear equation of the form $-\Delta V/V_0 = a + b(P - 2,000)$ was assumed to apply, and the value of b was determined by the method of least squares. A simple linear equation with no curvature term was considered to represent the data within the precision of the measurements. Individual values of b , the compressibility, were averaged for each oxide, and these results are shown in table 2 together with their standard deviations.

TABLE 2. Compressibilities of alkaline earth oxides

Oxide	Compressibility, average	Standard deviation of compressibility ^a
BeO	$b = 0.27 \times 10^{-6}$	0.04×10^{-6}
MgO	$b = .60$.12
CaO	$b = .89$.04
SrO	$b = .84$.10
BaO	$b = 1.76$.05

^a Computed from the formula $\sqrt{\Sigma(b-\bar{b})^2/(n-1)}$.

^b Average of 2 slopes.

^c Average of 3 slopes.

The only values in table 2 previously measured are those for MgO and CaO. Bridgman's value for single crystal MgO [2] is 0.59×10^{-6} /kg/cm² which agrees reasonably well with the value in table 2. However, his value of 4.57×10^{-6} /kg/cm² for compacted powdered CaO [2] is many times larger than that given in table 2. Madelung and Fuchs [3] reported 0.71×10^{-6} /megabar for MgO which is somewhat larger than found here. In general, it may be concluded that the low compressibilities shown in table 2 are what might be expected for these highly refractory oxides. The low compressibility of BeO is worthy of note. This low value is in concordance with the hardness of BeO as tabulated by Norton [11]. The compressibility of BeO is only slightly greater than diamond [10] and less than that of sapphire [12].

Mayer and Maltbie [4] in their discussion of the lattice energies of the alkaline earth oxides and sulfides concluded that the only available compressibility data for the oxides at that time [3] produced a repulsive exponent, ρ , which was somewhat too high. Accordingly they used a value of $\rho = 0.345 \times 10^{-8}$ cm, which had been found by Born and Mayer [5] as the average value for the alkali halides. Born and Mayer, using an exponential repulsion term, deduced the following relationship for determining ρ :

$$-a \left(1 + \frac{c_1}{c_2} e^{-2\delta/\rho} \right) \frac{M' c_2}{2M} e^{\left(\frac{\delta}{r_0} + 1 - a \right) \frac{r_0}{\rho}} = \frac{\frac{r_0}{\rho} \tau - 1}{\rho \sigma} = \frac{\frac{r_0}{\rho} \tau - 1}{a \frac{r_0}{\rho} \tau - 1} \quad (1)$$

where a is the ratio of the distances of the next nearest to the nearest neighbors, c_1 and c_2 are constants in the repulsion potential defined by the equations

$$c_1 = 1 + \frac{2Z_1}{N_1} \text{ and } c_2 = 1 - \frac{2Z_2}{N_2}$$

where Z_1 and Z_2 are the electronic charges on the positive and negative ions and N_1 and N_2 the number of electrons in the exterior shells of positive and negative ions respectively, M' the number of nearest neighbors and M the number of next nearest neighbors, r_o is the lattice separation of the ions, δ is the difference in ionic radii ($r_- - r_{++}$), and τ and σ are defined by the equations

$$\tau = r_o \frac{dA(r_o)}{dr} - \frac{3T}{N\beta} \left(\frac{\partial V}{\partial T} \right)_P \quad (2)$$

and

$$\sigma = -r_o^2 \frac{d^2A(r_o)}{dr^2} + \frac{9V}{N\beta} \left[1 + \frac{T}{\beta} \left(\frac{\partial \beta}{\partial T} \right)_P + \frac{T}{\beta^2 V} \left(\frac{\partial V}{\partial T} \right)_P \left(\frac{\partial \beta}{\partial P} \right)_T + \frac{2T}{3V} \left(\frac{\partial V}{\partial T} \right)_P \right] \quad (3)$$

In eq (2) and (3), in addition to the customary terms, $A(r_o)$ is the coulomb attractive potential energy, N is Avogadro's number, β is the compressibility, and V is the molar volume. For these oxides $1/\beta(\partial\beta/\partial T)_P$ and $1/V(\partial V/\partial T)_P$ are all very small, and the last three terms in the bracket of eq (3) are neglected in comparison with unity. Using known values for the Madelung constant in $A(r_o)$, the values of β in table 2, and available values for the expansivities [13,14], τ and σ can be calculated. These values were substituted in eq (1), which was solved graphically to give the values for ρ shown in table 3. In solving eq (1), the ionic radii of Pauling [15] were used together with NBS values for the quantity r_o [16,17] for all oxides except BaO, for which data of Wyckoff were taken [18].

TABLE 3. Values of the repulsive exponent ρ

Oxide	ρ
	<i>cm</i>
MgO.....	0.425×10^{-8}
CaO.....	.407
SrO.....	.337
BaO.....	.515
Avg.....	.421

Except for the value for SrO, the data for ρ in table 3 deviate considerably from the 0.345×10^{-8} cm assumed by Mayer and Maltbie [4]. However, the total repulsion energy of the crystals is rather small [4], and recalculation with the present data is not expected to change the data of Mayer and Maltbie [4] in any material manner.

Examination of the compressibilities of table 2 reveals an unexpected anomaly associated with CaO or SrO. It is anticipated that with increased atomic volume of cation, the compressibility should increase provided the anion remains constant and the crystals are isomorphous. Although the standard deviations of table 2 preclude an unequivocal conclusion that SrO is less compressible than CaO, it is certain that some irregularity in behavior exists. This irregularity is probably associated with an unexpectedly low density for CaO [16] compared with that of the other oxides [16,17]. Bridgman's earlier data on the sulfides [2] are also indicative of some nonuniformity in behavior, while Madelung and Fuch's [3] data on the compressibility of the isomorphous sulfates of calcium, strontium, and barium also show a minimum compressibility associated with strontium sulfate.

That an anomaly exists is shown by the fact that a similar minimum in density occurs at calcium throughout the isomorphous series of oxides, sulfides, selenides, and tellurides of the alkaline earths. That this behavior is in some manner associated with the position of calcium in the periodic system is indicated by the fact that a similar minimum density occurs for all alkaline earth sulfides, all alkali chlorides and all potassium halides. The sulfide, chloride, calcium, and potassium ions are all iso-electronic. The very high compressibility of potassium metal has been attributed by Bridgman [19] to an unusually open electronic structure. Presumably a similar explanation is to be sought for the ion itself and the other ions of an isoelectronic nature.

4. References

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