

Short Communications

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The optical properties and structures of $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$ and $\text{SrO} \cdot 2\text{Al}_2\text{O}_3$. By E. R. BOYKO* and L. G. WISNYI, *Knolls Atomic Power Laboratory*†

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Introduction

In 1937 two independent publications appeared in the literature describing a new compound, $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$. Tavasci (1937) found the compound to be uniaxial positive while Lagerqvist *et al.* (1937) concluded from X-ray studies that it was monoclinic. The first mention in the American literature was made by Goldsmith (1948) who suggested that a further study be initiated in an effort to resolve the conflicting data. Goldsmith stated that X-ray diffraction shows $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$ to be monoclinic, but that at the same time, optical properties alone indicate that the compound should be either hexagonal or tetragonal. Filonenko & Laurov (1950) then reported that $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$ crystallizes in the tetragonal system, while Gorla & Burdese (1951) published X-ray data confirming it to be monoclinic, but stating that they had found the optical properties to be the same as those reported by Shepherd *et al.* (1909) for the unstable phase of $3\text{CaO} \cdot 5\text{Al}_2\text{O}_3$.

This paper is presented in an effort to clarify the situation. The authors will not discuss the existence or non-existence of a $3\text{CaO} \cdot 5\text{Al}_2\text{O}_3$ phase, which, for many years, has been confused with $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$.

Optical study

In order to simplify the X-ray analysis, it was decided to work with both $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$ and the isomorphous compound $\text{SrO} \cdot 2\text{Al}_2\text{O}_3$. Single crystals of these compounds were obtained from melts which were also used to determine the melting points. The raw materials, alkaline earth carbonate plus alumina, were mixed, calcined, and heated in a molybdenum crucible to above the melting point and allowed to cool slowly. The thermal arrest at the melting point was determined through the use of a calibrated tungsten-molybdenum thermocouple.‡ Chemical analysis verified the stoichiometry of the resulting melts. The melting points were observed to be:

$$\begin{aligned} \text{CaO} \cdot 2\text{Al}_2\text{O}_3, & 1745 \pm 15^\circ \text{C}; \\ & \text{and } \text{SrO} \cdot 2\text{Al}_2\text{O}_3, 1770 \pm 15^\circ \text{C}. \end{aligned}$$

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‡ A complete discussion of the high temperature thermal analysis and the calibration of the tungsten-molybdenum thermocouple will be presented in a future paper by L. G. Wisnyi.

In discussing the optical properties of the compound $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$, it should be noted that these determinations were made at the School of Ceramics, Rutgers University, where the most accurate petrographic equipment was available, including a five-axis universal stage. The compound $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$ was observed as being biaxial positive with

$$\begin{aligned} \gamma &= 1.6516 \pm 0.0003, \quad \beta = 1.6184 \pm 0.0003, \\ \alpha &= 1.6178 \pm 0.0003, \end{aligned}$$

and

$$2V = 12^\circ \pm 1^\circ.$$

With ordinary petrographic equipment such a small difference between α and β could not be detected, and consequently the crystal would appear to be uniaxial.

Comparison of the optical properties reported for the compound $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$

Present authors	Gorla & Burdese and Shepherd <i>et al.</i>	Goldsmith and Tavasci
	$\gamma = 1.6516 \pm 0.0003$	1.674 ± 0.002
$\beta = 1.6184 \pm 0.0003$	1.671 ± 0.002	
$\alpha = 1.6178 \pm 0.0003$	1.662 ± 0.002	$\omega = 1.617 \pm 0.002$
$2V = 12 \pm 1^\circ$	$2V = 35^\circ \pm 5^\circ$	
Biaxial positive	Biaxial negative	Uniaxial positive

The refractive indices of the compound $\text{SrO} \cdot 2\text{Al}_2\text{O}_3$, however, are only reported to ± 0.002 units since in this case only ordinary petrographic equipment was used. It is biaxial negative with:

$$\alpha = 1.620 \pm 0.002, \quad \beta = 1.636 \pm 0.002, \quad \gamma = 1.644 \pm 0.002.$$

$2V$ is rather large and was estimated to be between 20° to 30° .

X-ray analysis

Lagerqvist *et al.* (1937) studied both the calcium and strontium compounds by X-ray diffraction. They measured the lattice parameters, and from the observed density of $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$ calculated that there were four formula weights in the unit cell. They concluded from systematic absences that the space group was either C_3^4-Cc or C_{2h}^2-C2/c . The authors chose the same axes as Lagerqvist and determined the lattice parameters to be:

$\text{CaO} \cdot 2\text{Al}_2\text{O}_3$	$\text{SrO} \cdot 2\text{Al}_2\text{O}_3$
$a = 12.89 \text{ \AA}$	$a = 13.04 \text{ \AA}$
$b = 8.88 \text{ \AA}$	$b = 9.01 \text{ \AA}$
$c = 5.45 \text{ \AA}$	$c = 5.55 \text{ \AA}$
$\beta = 107^\circ 3'$	$\beta = 106^\circ 31'$

Weissenberg photographs (three films) using copper radiation were taken around the b and c axes of the strontium compound and around the c axis of the calcium compound. Intensities for the zero levels were obtained from the films by the visual method. Since the crystals were dendritic in growth, it was impossible to grind them into either a cylindrical or spherical shape, and consequently no correction for absorption was made. Absorption anomalies could be seen on the films and in order to minimize these errors, the intensity of each reflection was measured more than once.

A Patterson projection along the c axis was computed for the strontium compound, and it was quite easily interpreted on the basis of the centrosymmetric space group C_{2h}^2-C2/c . The x and y coordinates of the Sr and the two Al atoms in the asymmetric zone were obtained, and since the Sr was in a special position $(0, y, \frac{1}{4})$, its z coordinates was also determined. The signs of the observed structure factors were determined using these parameters, and electron-density projections along the b and c axes were computed which clearly showed the Sr and Al positions. The four O atoms in the asymmetric zone were then placed in such a way as to be always on or near regions of high electron density which surrounded the two Al atoms. One O atom must be in a special position, and this was found to be $(0, y, \frac{1}{4})$. By correlating the peaks on the two projections, the (x, y, z) parameters of all the atoms in the asymmetric zone were determined. The special positions $(0, y, \frac{1}{4})$ can also be taken to be $(0, \bar{y}, \frac{1}{4})$, since the $(hk0)$ and $(h0l)$ reflections do not distinguish between them. The choice of the y values were made on the basis of bond lengths. Fourier projections were then computed until the shifts in the atomic parameters gave rise to no significant sign changes in the calculated structure factors. The atomic coordinates were then further refined by a modified least-square method, and the final parameters are given in Table 1.

Table 1. Atomic parameters

Atom	Parameters		
	x	y	z
Sr	0	0.810	0.250
Al ₁	0.169	0.086	0.295
Al ₂	0.122	0.441	0.257
O ₁	0	0.526	0.250
O ₂	0.117	0.048	0.544
O ₃	0.127	0.260	0.175
O ₄	0.188	0.447	0.598

General position:

$$0, 0, 0; \frac{1}{2}, \frac{1}{2}, 0+; x, y, z; \bar{x}, \bar{y}, \bar{z}; \bar{x}, y, \frac{1}{2}-z; x, \bar{y}, \frac{1}{2}+z.$$

Special position:

$$0, 0, 0; \frac{1}{2}, \frac{1}{2}, 0+; 0, y, \frac{1}{4}; 0, \bar{y}, \frac{1}{4}.$$

A plot of $\ln F_c/F_o$ versus $\sin^2 \theta$ gave no assembly of points through which a reasonably good straight line with positive slope could be drawn. Consequently the compound's isotropic temperature factor was simply taken to be zero. The reliability indices for this structure are $R(h0l) = 0.15$ and $R(hk0) = 0.22$. Using the coordinates determined from the strontium compound, structure factors for $\text{CaO} \cdot 2 \text{Al}_2\text{O}_3$ were calculated for the $(hk0)$ reflections. A comparison with the observed structure factors gave $R = 0.22$, which shows the existence of a high degree of isomorphism between the two compounds.

The aluminum atoms are in tetrahedral coordination, and in Table 2, the bond distances and angles are listed.

Table 2. Bond distances and angles in AlO_4 -tetrahedra

Bond lengths	Å	Bond angles	Degrees
Al ₁ -O ₂	1.74	O ₂ -Al ₁ -O ₃	109
Al ₁ -O ₃	1.73	O ₂ -Al ₁ -O ₄ *	108
Al ₁ -O ₄ *	1.82	O ₃ -Al ₁ -O ₄ *	117
Al ₁ -O ₂ †	1.82	O ₂ †-Al ₁ -O ₂	110
		O ₂ †-Al ₁ -O ₃	107
		O ₂ †-Al ₁ -O ₄ *	105
Al ₂ -O ₁	1.76	O ₁ -Al ₂ -O ₄	100
Al ₂ -O ₃	1.70	O ₁ -Al ₂ -O ₄ †	108
Al ₂ -O ₄	1.84	O ₄ †-Al ₂ -O ₄	111
Al ₂ -O ₄ †	1.72	O ₄ †-Al ₂ -O ₃	111
		O ₁ -Al ₂ -O ₃	121
		O ₄ -Al ₂ -O ₃	105

The superscript on oxygen atoms indicates the position the oxygen atom is in with respect to the positions given in Table 1.

* Position $\frac{1}{2}-x, \frac{1}{2}-y, \bar{z}$.

† Position $x, \bar{y}, \frac{1}{2}+z$.

One oxygen (O₄) is found to be at the corner of three tetrahedra. This arises from the 7:4 oxygen to aluminum ratio in the compound. In order to have a complete network of AlO_4 tetrahedra in which each oxygen atom is bonded to only two aluminum atoms, a 2:1 ratio would be required.

The somewhat high R values lower the confidence in the accuracy of the atomic parameters, and consequently, one should be cautious in considering the reality of any apparent distortions of the tetrahedra. These high R values, for the most part, are probably due to the nature of the data itself, but there is also the possibility that the structure has not yet been fully refined. The time allotted for this problem, however, did not permit any investigation of this possibility.

Conclusions

The compound $\text{CaO} \cdot 2 \text{Al}_2\text{O}_3$ has been shown to be biaxial positive with the difference in α and β so small as to be imperceptible with ordinary petrographic equipment. The structure determination of the isomorphic $\text{SrO} \cdot 2 \text{Al}_2\text{O}_3$ defines the complete nature of the phase, and proves the early work of Lagerqvist *et al.* (1937) to be entirely correct.

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