JOURNAL OF SOLID STATE CHEMISTRY **75**, 197–200 (1988)

BRIEF COMMUNICATIONS

Structure Refinement of $CaO \cdot 6Al_2O_3$

A. UTSUNOMIYA, K. TANAKA, H. MORIKAWA, AND F. MARUMO

Research Laboratory of Engineering Materials, Tokyo Institute of Technology, Nagatsuta 4259, Midori-ku, Yokohama 227, Japan

AND H. KOJIMA

Institute of Inorganic Synthesis, Faculty of Engineering, Yamanashi University, Takeda 4-3-11, Kofu 400, Japan

Received July 30, 1987; in revised form January 4, 1988

The crystal structure of $CaO \cdot 6Al_2O_3$ at 294 K was investigated by X-ray diffraction and refined to an R value of 0.025 for 2735 reflections (1492 independent reflections). It belongs to the space group $P6_3/mmc$ with $a = 5.5587(1)$, $c = 21.8929(3)$ Å, $V = 585.83(1)$ Å^3, and $Z = 2$, $D_x = 3.79$ g/cm^3, and $\mu(\text{Mo}K\alpha) = 15.86$ cm^{-1}. Three different models are refined for the bipyramidal Al^{3+} ions: (1) the central atom model, (2) the central atom model with anharmonic vibration, and (3) the split atom model. The results indicate that the split atom model where the Al^{3+} ion occupies statistically one of two equivalent sites is the real structure at room temperature.

Introduction

The crystal structure of $CaO \cdot 6Al_2O_3$ was studied by Kato and Saalfeld (*1*), and confirmed to be isostructural with the mineral magnetoplumbite. The structure belongs to the hexagonal space group $P6_3/mmc$. In this structure Al atoms are distributed over three crystallographically independent octahedral sites, one tetrahedral site, and one trigonal bipyramidal site. However, an ambiguity remains about the exact location of the Al atom in the trigonal bipyramidal site. Namely, there are at least two probable models; in one model, a five-coordinated Al atom locates at the 2b site on the mirror plane of the trigonal bipyramid (central atom model) and, in the other, two half-atoms locate at two equivalent 4e sites (split atom model) displaced from the mirror plane.

This report describes a result of structure refinement on $CaO \cdot 6Al_2O_3$ carried out to elucidate the precise structural features of the bipyramidal cation.

Experimental and Results

A single crystal was grown by the traveling solvent floating zone method using two halogen lamps as the heat source. The solvent with composition of $CaO \cdot 4Al_2O_3$ was used between a sintered rod and a seed crystal. A sintered rod with composition of $CaO \cdot 6Al_2O_3$ was used as the seed crystal. The growth rate was 1.5 mm/hr.

0022-4596/88 $3.00

A hexagonal platy crystal with thickness of 0.12 mm and hexagonal edge length of 0.13 mm was picked out from the crushed pieces of the grown crystal and used for intensity measurements. It was transparent and colorless. The space group $P6_3/mmc$ was confirmed with Weissenberg photographs. Intensities were measured on a four-circle diffractometer (Rigaku AFC-5UD) with Mo*Kα* radition (λ = 0.71069 Å) monochromated with pyrolytic graphite at 294 K. The ω-scan mode was employed with a scanning speed of 2°/min. Scan widths were determined according to the formula $(1.4 + 0.5 \tan \theta)°$. The intensities were corrected for Lorentz-polarization factors and for absorption effects, taking the crystal shape into consideration.

The 2625 reflections which satisfied the condition $|F_o| \geqq 3\sigma(|F_o|)$ were obtained within the range $2\theta \leqq 120°$, $0 \leqq h \leqq 13$, $0 \leqq k \leqq 13$, and $-53 \leqq l \leqq 0$ (3520 reflections were measured, of which 731 were unobserved; there were 1492 unique observed reflections). In addition, 110 strong reflections were measured in the full reciprocal space to correct anisotropic extinction effects. A total of 2735 reflections were used for the subsequent refinements. The cell parameters were determined from 144 reflections in the range $71.2 \leqq 2\theta \leqq 85.8°$ by the least-squares procedure. They are a = 5.5587(1) and c = 21.8929(3) Å.

Atomic scattering factors for Ca^{2+} and Al^{3+} ions and dispersion correction factors were taken from "International Tables for X-ray Crystallography" (*16*). The scattering factor given by Tokonami (*2*) was used for O^{2-} ions. The structure was refined with a modified version of the full-matrix least-squares program LINKT85, which has a function for extinction correction after Becker and Coppens (*3*) and also has a function for anharmonic vibration refinement by Tanaka and Marumo (*4*). The refinement was carried out on two models. The first refinement was carried out on the central atom model, starting from the atomic parameters given for $BaO \cdot 6Fe_2O_3$ by Obradors *et al.* (*5*). The least-squares calculations assuming an anisotropic type I extinction effect gave a little smaller R (= 0.039) and R_w (= 0.036) values than those (0.042 and 0.038) assuming an anisotropic type II extinction effect after some cycles of refinement. Therefore, further refinement was continued on the assumption of the type I extinction effects and gave the final R and R_w values of 0.028 and 0.027, respectively. The second refinement was carried out on the split atom model, like Obradors *et al.* tried on $BaO \cdot 6Fe_2O_3$, assuming the anisotropic extinction effects of type I. The least-squares calculations for this model gave the final R and R_w values of, respectively, 0.025 and 0.026, which are little smaller than those for the central atom model. Final parameters of the split atom model are given in Table I.

Discussions

The refinements with the bipyramidal Al(2) atom in the 2b site (central atom model) gave a U_{33} value of 0.0489 Å^2 for Al(2) atom, which is extremely larger than those for the other Al atoms. The difference Fourier map of this model showed a negative peak with the depth of -1.96 e/Å^3 at Al(2) site and two positive peaks with heights of 1.73 e/Å^3 at 0.2 Å apart from Al(2) site along the c axis. On the other hand, the refinements with the bipyramidal Al(2) atom in the 4e sites (split atom model) reduced the U_{33} value for Al(2) atom to 0.0110 Å^2, though the value is still larger than those for the other Al atoms. The difference Fourier map gave only quite small residual densities in this case. The negative peak at Al(2) site reduced the depth to -0.07 e/Å^3 and two positive peaks with heights of 0.10 e/Å^3 were observed at 0.4 Å apart from Al(2) site along the c axis.

The peaks on the difference Fourier map

TABLE I

POSITIONAL AND THERMAL ($\times 10^5$) PARAMETERS

Atom	Position	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}
Ca	2d	$\frac{2}{3}$	$\frac{1}{3}$	$\frac{1}{4}$	1273(12)	U_{11}	1353(20)	0
Al(1)	2a	0	0	0	335(13)	U_{11}	256(20)	0
Al(2)	4e	0	0	0.25771(7)	265(16)	U_{11}	1098(71)	0
Al(3)	4f	$\frac{1}{3}$	$\frac{2}{3}$	0.02808(3)	276(9)	U_{11}	395(14)	0
Al(4)	4f	$\frac{1}{3}$	$\frac{2}{3}$	0.19102(3)	327(9)	U_{11}	333(14)	0
Al(5)	12k	0.16855(3)	0.33710(7)	−0.10914(1)	306(6)	262(8)	435(8)	23(6)
O(1)	4e	0	0	0.14907(5)	326(17)	U_{11}	509(30)	0
O(2)	4f	$\frac{2}{3}$	$\frac{1}{3}$	0.05461(5)	392(17)	U_{11}	319(26)	0
O(3)	6h	0.18107(10)	0.36214(19)	$\frac{1}{4}$	712(20)	337(24)	485(22)	0
O(4)	12k	0.15505(7)	0.31010(13)	0.05213(3)	395(11)	303(15)	394(14)	−23(12)
O(5)	12k	0.50325(7)	1.00650(14)	0.14912(3)	358(11)	420(17)	509(15)	138(13)

Note. The thermal parameters are of the form: $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$; $2U_{12} = U_{22}$; $2U_{13} = U_{23}$.

for the central atom model may be ascribed to an anharmonic thermal vibration of Al(2) atom. Refinement was, therefore, carried out by introducing anharmonic potential parameters. The site symmetry of Al(2) atom is $\bar{6}m2$ and the temperature factor including anharmonic terms up to the fourth order was given by Tanaka and Marumo (*4*). The number of parameters increased is 6 in comparison with the simple central atom model. The final R and R_w values were 0.025 and 0.026 with this refinement, respectively. The difference Fourier map showed a negative peak with the depth of −0.65 e/Å^3 at Al(2) site and two positive peaks with heights of 0.24 e/Å^3 at 0.2 Å from Al(2) site along the c axis. Although refinement on the central atom model allowing anharmonic thermal vibration for Al(2) atom gave the same R value as the split atom model, the former evidently gave larger peaks on difference density maps than the latter. Thus the present study seems to support that the split atom model where Al(2) atom occupies statistically one of two equivalent sites in the 4e positions is the real structure of $CaO \cdot 6Al_2O_3$ at room temperature.

Table II lists interatomic distances within AlO_5 trigonal bipyramids observed in magnetoplumbite-type (*6–11*) and andalusite-type structures (*12, 13*). The corresponding distances in $BaO \cdot 6Fe_2O_3$ are also given for comparison. Mössbauer measurements for $BaO \cdot 6Fe_2O_3$ (*14*) revealed that the Fe^{3+} ion at the bipyramidal site occupies one of two equivalent positions of the 4e site at temperatures below 80 K and that it jumps between the two 4e sites at higher temperatures than about 80 K. The FeO_5 bipyramid in $BaO \cdot 6Fe_2O_3$ is slightly larger than the AlO_5 bipyramid in the aluminates and the equatorial O–O distances in $BaO \cdot 6Fe_2O_3$ are also longer than those in the aluminates by about 0.2 Å. This O–O separation acts as a potential barrier when the split ion jumps between the two sites. In the case of $BaO \cdot 6Fe_2O_3$, the opening of the oxygen equilateral triangle has a size of 0.47 Å, if the O^{2-} ions are assumed to be rigid spheres with radii of 1.39 Å. Since O(3) atom is shared by five cations, this value is expected for O(3) ion as the effective ionic radius (*15*). Similarly the size of the opening is calculated to be 0.35 Å for $CaO \cdot 6Al_2O_3$. Since the ionic radius of Al^{3+} ion (0.48 Å for fivefold coordination) is smaller than that for Fe^{3+} ion (0.58 Å) by

TABLE II

Comparison of the Atomic Distances (Å) in AlO_5 Trigonal Bipyramid

Sample	Average Al–O distance	Al to oxygen on the mirror plane distance	O–O distance of oxygen triangle on the mirror plane	Separation of Al–Al	Remarks	References
$CaO \cdot 6Al_2O_3$	1.934	1.751	3.020	0.338	Split atom model	Present study
$CaO \cdot 6Al_2O_3$	1.919	1.740	3.015		Central atom model	*(1)*
$SrO \cdot 6Al_2O_3$	1.949	1.755	3.040		Central atom model	*(6)*
$La_2O_3 \cdot 2MgO \cdot 11Al_2O_3$	1.938	1.762	3.051		Central atom model	*(7)*
$La_2O_3 \cdot 2MnO \cdot 11Al_2O_3$	1.945	1.763	3.028	0.445	Split atom model	*(8)*
$La_2O_3 \cdot 0.75CoO \cdot 11Al_2O_3$	1.966	1.809	3.100	0.519	Split atom model	*(8)*
$La_2O_3 \cdot 11Al_2O_3$	1.939	1.732	2.970	0.490	Split atom model	*(9)*
$Nd_2O_3 \cdot 11Al_2O_3$	1.943	1.755	3.014	0.457	Split atom model	*(10)*
$Nd_2O_3 \cdot Na_2O \cdot 23Al_2O_3$	1.927	1.748	3.013	0.383	Split atom model	*(11)*
$BaO \cdot 6Fe_2O_3$	2.039[a]	1.867[a]	3.220	0.340[a]	Split atom model	*(5)*
$2B_2O_3 \cdot 9Al_2O_3$	1.88	1.80[b]	3.05[b]		(andalusite type)	*(12)*
$SiO_2 \cdot Al_2O_3$	1.836	1.822[b]	3.137[b]		(andalusite type)	*(13)*

[a] Fe–O or Fe–Fe distance.

[b] Average value.

about 0.10 Å, the Al^{3+} ions in bipyramidal sites for $CaO \cdot 6Al_2O_3$ are probably not at rest in a statical disorder configuration but dynamically change their sites. However, in order to get further information about the dynamical character of Al(2) atom, it is necessary to analyze the structure at various temperatures including temperatures below 80 K.

References

1. K. Kato and H. Saalfeld, *Neues Jahr. Mineral. Abh.* **109,** 192 (1968).

2. M. Tokonami, *Acta Crystallogr.* **19,** 486 (1965).

3. P. J. Becker and P. Coppens, *Acta Crystallogr. Sect. A* **31,** 417 (1975).

4. K. Tanaka and F. Marumo, *Acta Crystallogr. Sect. A* **39,** 631 (1983).

5. X. Obradors, A. Collomb, M. Pernet, D. Samaras, and J. C. Joubert, *J. Solid State Chem.* **56,** 171 (1985).

6. A. J. Lindop, C. Matthews, and D. W. Goodwin, *Acta Crystallogr. Sect. B* **31,** 2940 (1975).

7. A. Kahn, A. M. Lejus, M. Madsac, J. Thery, D. Vivien, and J. C. Bernier, *J. Appl. Phys.* **52,** 6864 (1981).

8. M. Gasperin, M. C. Saine, A. Kahn, F. Laville, and A. M. Lejus, *J. Solid State Chem.* **54,** 61 (1984).

9. N. Iyi, Z. Inoue, S. Takekawa, and S. Kimura, *J. Solid State Chem.* **54,** 70 (1984).

10. N. Iyi, Z. Inoue, and S. Kimura, *J. Solid State Chem.* **54,** 123 (1984).

11. A. Kahn and J. Thery, *J. Solid State Chem.* **64,** 102 (1986).

12. M. Ihara, K. Imai, J. Fukunaga, and N. Yoshida, *J. Japan. Ceram. Soc.* **88,** 77 (1980). [In Japanese]

13. R. L. Ralph, L. W. Finger, R. M. Hazen, and S Ghose, *Amer. Mineral.* **69,** 513 (1984).

14. E. Kreber, U. Gonser, A. Trautwein, and F. Harris, *J. Phys. Chem. Solids* **36,** 263 (1975).

15. R. D. Shannon, *Acta Crystallogr. Sect. A* **32,** 751 (1976).

16. J. A. Ibers and W. C. Hamilton, "International Tables for X-ray Crystallography," Vol. 4, Kynoch Press, Birmingham (1974).