The refined structure of SrO.2Al₂O₃.

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An X-ray analysis of $SrO.2Al_2O_3$ has been performed, from which a fully refined structure has been derived with a reliability index $R=0.075$. A comparison was made with the published structure of $CaO.2Al_2O_3$, which indicated that the two compounds were isomorphous.

Recently there has been interest in the mixed oxides of alkali earths with alumina (Lindop, Barton & Goodwin, 1972; Goodwin & Lindop, 1972) for the purpose of finding suitable host lattices for the trivalent neodymium ion, which forms the basis of a number of powerful lasers near $1.06\mu m$ (Nd:YAG, Geusic, Marcos & Van Uitert, 1964; Nd:YAlO₃, Massey & Yarborough, 1971). A paper by Goodwin & Lindop (1970) referred to as paper I, confirmed the structure of the compound $CaO.2Al_2O_3$ as being monoclinic with space group $C2/c$. According to Boyko & Wisnyi (1958), referred to as B.W., the strontium and calcium compounds $SrO.2Al_2O_3$ and $CaO.2Al_2O_3$ are structurally isomorphous, and so it was decided to check this conclusion and fully refine the structure of $SrO.2Al_2O_3$ with a view to performing accurate point-change crystal-field calculations.

The linear absorption coefficient of $SrO.2Al_2O_3$ for Mo $K\alpha$ radiation turned out to be 94 cm⁻¹, which made corrections for absorption of X-rays essential for an accurate structure determination. Consequently small cubes of size ~0.7 mm were cut from a large single crystal grown by Czochralski techniques (Cockayne, 1966). These cubes were then ground into spheres of ~0.6 mm diameter by continuous agitation with jets of air inside a specially constructed cylinder lined with abrasive paper. After approximately ten days, nearly spherical crystals were formed, from which one with diameter 0.575 ± 0.045 mm was chosen for data collection. Further agitation was not considered useful in view of clear anisotropy in the crystal hardness, showing up as a uniform shape developed by crystals of all sizes. The absorption factor for the chosen sample was $\mu R = 2.70\pm0.20$.

Initial alignment and measurements of the unit cell were performed on a precession camera with Fe $K\alpha$ radiation. Following this, accurate data were collected using a Hilger & Watts four-circle computer-controlled diffractometer and Mo $K\alpha$ radiation. Integrated X-ray intensities were obtained by performing a combined ω and θ step scan over all possible reflexions within an angle 2θ from 0 to 60°. After averaging over four sets of equivalent reflexions to minimize the errors due to a non-spherical sample, 902 reflexions remained. Each reflexion was then corrected for absorption, by applying the appropriate absorption correction factor $A^*(\theta)$ for a sphere having $\mu R = 2.70$, as listed in *International Tables for X-ray Crystallography* (1965, Vol. II). These were then converted to structure amplitudes in the normal way.

The measured structure amplitudes were then used in a least-squares refinement of the structure with a much modified version of the program of Busing, Martin & Levy (1962). The starting point for the refinement was chosen as the structure parameters for the atoms of $CaO.2Al_2O_3$ given in paper I, with the appropriate ionic scattering factors for Al^{3+}, Sr^{2+} and O^{2-} taken from *International Tables*

for *X-ray Crystallography* (1965, Vol. III). This starting structure refined satisfactorily using isotropic temperature factors to give a residual $R(hkl)=0.083$. On conversion to anisotropic temperature factors and using a Cruickshank weighting scheme, further refinement yielded a final R value of 0.075, at which point parameter variations were very much less than their estimated errors. All calculations were performed with a set of standard computer programs for the ICL 4130 computer at the University of York.

The final low value of R compares well with the value $R=0.064$ previously found for $CaO.2Al_2O_3$, and confirms that the two compounds are isomorphous with space group $C2/c$. The final values for the unit-cell parameters and the original values given by B.W. are shown in Table 1, where the errors quoted are about three times the standard deviations from a least-squares fit. The refined atomic parameters in terms of fractions of the unit-cell dimensions, plus the anisotropic temperature factors are shown in Table 2.

Table 1. *Unit-cell parameters of* $SrO.2Al_2O_3$

	This work	B.W.
a	13.0389 ± 0.0090 Å	13.04 Å
b	9.0113 ± 0.0045	9.01
c	5.5358 ± 0.0027	5.55
β	$106°7'$	$106°31'$

From the measured structure it is clear that each unit cell contains four formula units $SrO.2Al_2O_3$ in a volume 624.88 Å³, giving a density 3.268 gm cm⁻³. If the structure is compared with $CaO.2Al_2O_3$ as given in paper I, the aluminum sites Al(1) and Al(2) remain virtually unchanged with only a 0.2% increase in the Al–O bond length for the four nearest neighbours, on changing from Ca to Sr. In addition the bond angles subtended by these neighbours at the aluminum atoms do approach those of a perfect tetrahedron with an average value of 109.40° for both sites in $SrO.2Al_2O_3$. However at the alkali-earth sites the four nearest oxygen atoms are about 0.19 Å more distant in the Sr relative to the Ca compound, reflecting the increase in ionic radius from 1.06 to 1.27 Å on changing from Ca^{2+} to Sr^{2+}. This point might be significant since the radius of Nd^{3+} is 1.15 Å, and might be expected to fit into the alkali-earth site in $SrO.2Al_2O_3$ more readily because of the reduced distortion it would induce in the lattice. It is hoped that this point can be confirmed by comparing the crystal-field calculation based on this structure with e.p.r. and optical experiments currently in progress.

Table 2. *The atomic positional and thermal parameters of* $SrO.2Al_2O_3$

Positional error: ± 0.0010. Temperature factor error: ± 0.002.

	Sr	O(1)	Al(1)	Al(2)	O(2)	O(3)	O(4)
X	0	0	0·1686	0·1212	0·1188	0·1246	0·1899
Y	0·8099	0·5253	0·0873	0·4400	0·0374	0·2582	0·4446
Z	0·25	0·25	0·2939	[0·2644	0·5442	0·1703	0·5965
β_{11}	0·00192	0·00151	0·00127	0·00138	0·00197	0·00260	0·00200
β_{22}	0·00332	0·00209	0·00267	0·00267	0·00363	0·00234	0·00451
β_{33}	0·00969	0·01169	0·00788	0·00852	0·00759	0·00698	0·00646
β_{12}	0	0	0·00018	−0·00001	0·00066	−0·00015	0·00012
β_{13}	0·00054	0·00051	0·00035	0·00072	0·00123	−0·00094	0·00062
β_{23}	0	0	0·00012	−0·00063	0·00050	−0·00074	−0·00052

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An X-ray study of the low temperature form of MgSiF6.6H2O and the relation between the crystal lattices of low- and high-temperature forms.

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A phase transition was found in $MgSiF_6.6H_2O$ at about 25°C. The crystal lattices of the low- and high-temperature forms are closely related, and the space groups are $P2_1/c$ and $R\bar{3}m$ respectively. The crystal structure of the low-temperature form is presented.

Introduction

A number of hexahydrates of the type $MGX_6.6H_2O$ have been reported to have a CsCl-like structure with one formula unit in the rhombohedral cell (Wyckoff, 1965), but atomic coordinates have been given for only $NiSnCl_6.6H_2O$ (Pauling, 1930) and $FeSiF_6.6H_2O$ (Hamilton, 1962). For the latter the crystal symmetry observed was $R\bar{3}m$, in contrast to $R\bar{3}$ for the former, and was interpreted by Hamilton to be a result of disorder on a microscopic scale.

A phase transition in this series has been found by optical methods for $MnSiF_6.6H_2O$ (Tsujikawa & Couture, 1955) and a monoclinic symmetry has been suggested for the low-temperature form of Mn– and $CoSiF_6.6H_2O$ on the basis of the X-ray photographs taken at liquid nitrogen temperatures (Kodera, Torii, Osaki & Watanabé, 1972).

A description of some extra reflexions in an early report by Hassel & Salvesen (1927) led us to study $MgSiF_6.6H_2O$ in detail, in the hope of finding a low-temperature form existing even at room temperature.

Structure of the low-temperature form

Crystals of the low-temperature form were obtained by adding powdered $MgCO_3$ to an aqueous solution of H_2SiF_6 and evaporating the solution at about 20°C. Most of them were twinned, and the single crystals used for the X-ray analysis were first selected under a polarizing microscope and then checked by taking Weissenberg photographs. The single crystals became twinned very easily with the application of small uneven pressure and had to be handled with particular care.

Crystal data; $MgSiF_6.6H_2O$, space group $P2_1/c$, lattice constants, $a = 6·460$, $b = 9·524$, $c = 8·460$ Å (all $\pm 0·005$ Å), $\beta = 99°24' \pm 3'$, $D_o = 1·77$, $D_c = 1·780$ g.cm^{-3}, $Z = 2$.

Intensities recorded with Cu $K\alpha$ radiation on Weissenberg photographs taken about the b axis (0 to 6 layers) were estimated visually. An absorption correction ($\mu r = 2·0$) was applied assuming a spherical shape for the crystal. The number of independent reflexions obtained was 709.

The structure was solved using three-dimensional Patterson and Fourier syntheses and was refined by full-matrix least-squares calculations to an R value of 0·138, at which stage the refinement was terminated because of the unfavourable shape of the crystals used. The structure obtained consists of octahedral ions $[Mg(H_2O)_6]^{2+}$ and $[SiF_6]^{2-}$ arranged in a slightly distorted CsCl structure. Fig. 1 shows the arrangement of the two ions in the b-axis projection. The atomic coordinates are given in Table 1 and correspond closely to those given for $FeSiF_6.6H_2O$ by Hamilton if the