

A Comparison of Three Sets of Diffraction Data for $\text{Al}_2\text{Y}_4\text{O}_9$: X-Ray Synchrotron Powder Data, X-Ray Single Crystal Data from $\text{Ag } K_\alpha$ Radiation, and Neutron Single Crystal Data from 1.01 Å Neutrons

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$\text{Al}_2\text{Y}_4\text{O}_9$ is monoclinic, space group $P2_1/c$ (No. 14) with $a = 7.375(1)$, $b = 10.507(2)$, $c = 11.113(1)$ Å, $\beta = 108.58(2)^\circ$, $Z = 4$ and $d_x = 4.52 \text{ g cm}^{-3}$. Two yttrium atoms are coordinated with six, and two with seven, oxygen atoms. The two aluminium atoms are coordinated with four oxygen atoms. Single crystals of the compound were made from a melt of $\text{Al}_2\text{Y}_4\text{O}_9$. Three sets of diffraction data are compared: (i) X-ray synchrotron powder data where the pattern had contributions from 574 reflections, (ii) single crystal X-ray data from $\text{Ag } K_\alpha$ radiation with 1540 independent reflections and (iii) single crystal neutron diffraction data with 1.01 Å neutrons and 984 independent reflections. The precision of the atomic coordinates from the synchrotron X-ray powder diffraction data is comparable with or slightly lower than that for the coordinates from the two single crystal data sets.

Synchrotron X-radiation offers new research possibilities in structure analysis of solids. Measurements that were previously impossible or very tedious to make with the use of traditional X-ray sources are now possible. One of the new areas is crystallographic studies by synchrotron X-ray powder diffractometry, where solution of structures as well as refinements of crystal structure models are reported.¹ It would be of interest to know the precision of such a structure investigation made from synchrotron X-ray powder diffraction data and to compare it with the precision obtained by single crystal diffractometry using traditional X-ray tubes as well as neutron diffractometry. To study this problem, the previously reported structure of $\text{Al}_2\text{Y}_4\text{O}_9$ from synchrotron X-ray powder diffraction¹ is compared below with single crystal diffractometer investigations of the structure using $\text{Ag } K_\alpha$ X-radiation and 1.01 Å neutrons.

The compounds $\text{Al}_2\text{RE}_2\text{O}_9$ exist for the series of rare earths (RE) from Sm to Lu; they are all isostructural, and $\text{Al}_2\text{Y}_4\text{O}_9$ has the same structure.^{2,3} Aluminium has a tetrahedral coordination in the structure; two yttrium atoms are in a sixfold and two in a sevenfold coordination. Two of the oxygen atoms are coordinated with three metal atoms, and the remaining oxygen atoms are in a tetrahedral coordination. The compound $\text{Al}_2\text{Y}_4\text{O}_9$ was chosen for the synchrotron X-ray powder diffraction investigation because it has a monoclinic unit cell with a volume of 816 Å³ and the powder pattern would thus contain a great number of reflections.

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Experimental

Chemistry. The compound $\text{Al}_2\text{Y}_4\text{O}_9$ was made from analytical grade oxides, Y_2O_3 (Fluka) and Al_2O_3 (Merck). The oxides were kept at 1000°C for 24 h in platinum crucibles before a stoichiometric mixture was made of the oxides. This mixture was pressed isostatically to a rod that was placed in a MgO crucible and kept at 1340°C for 24 h. The rod was finally melted in a crystal furnace.

The experiment sketched in Fig. 1 was used in growth of single crystals sufficiently large for single crystal X-ray diffraction analysis. A hanging drop of the melt at the end of the preform is slowly frozen by a programmed reduction of the RF power of the heating coil, and in this way a larger number of X-ray-size single crystals are produced. The method is convenient for the growth of small single crystals of binary oxides with high melting points, as no crucible is used in the growth process. The preform of the oxide cannot couple with the RF power of the heating coil. A susceptor was inserted between the heating coil and the preform. This susceptor was a ring of graphite. The RF power will couple to the ring, which will act as a resistance heating element.

Fig. 2 is a sketch of floating zone growth with the use of a susceptor. The preform moves downwards relative to the susceptor, and the figure illustrates a situation where almost all of the preform has passed through the susceptor. This growth mode has been used for floating zone growth of single crystals of $\text{Al}_2\text{Y}_4\text{O}_9$ large enough for the single crystal neutron diffraction investigation.

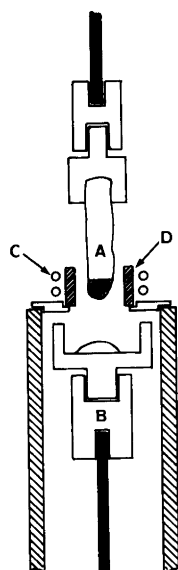


Fig. 1. A ceramic rod of $\text{Al}_2\text{Y}_4\text{O}_9$ (A) is mounted in a BN holder and a small table of BN is placed in a holder (B) under the rod. The RF coil (C) transmits power to a graphite ring (D) that melts the end of the rod by thermal radiation. When the power is reduced slowly, small single crystals of $\text{Al}_2\text{Y}_4\text{O}_9$ grow from the molten drop at the end of the ceramic rod. The diameter of the ceramic rod is ca. 10 mm.

X-Ray diffraction. Guinier photographs of $\text{Al}_2\text{Y}_4\text{O}_9$ were taken with Si ($a = 5.43050 \text{ \AA}$) as an internal standard and $\text{Cu } K_{\alpha 1}$ radiation ($\lambda = 1.5440598 \text{ \AA}$). The positions of the diffraction lines were measured on a double-beam photometer, and from the indexed powder pattern the unit cell parameters were refined by a least-squares procedure using the program CELLKANT.⁴ The values obtained were $a = 7.375(1)$, $b = 10.507(2)$, $c = 11.113(1) \text{ \AA}$, $\beta = 108.58(2)^\circ$, space group $P2_1/c$.

A single crystal of $\text{Al}_2\text{Y}_4\text{O}_9$ with the dimensions $0.374 \times 0.175 \times 0.056 \text{ mm}$ was used in the single crystal structure investigation. A four-circle diffractometer (Huber) using $\text{Ag } K_{\alpha}$ radiation ($\lambda = 0.5608 \text{ \AA}$) and the ω - 2θ step-scan technique was used in the data collection. The total scan width in 2θ was $2.0^\circ + 0.9 \tan \theta$, and the extent of a reflection was decided by the minimum $\sigma(I)/I$ method.⁵ A total of 9520 reflections were measured, including two standard reflections for every 50 reflections, corrected for absorption ($\mu = 161 \text{ cm}^{-1}$), and averaged to give 1540 independent reflections with $I > 4\sigma(I)$ used in the structure refinements. The R -values on averaging the reflections were $R = 12.2\%$ and $R_w = 9.2\%$, where $R = 100 \times \Sigma |F - F_{av}| / \Sigma F$ and $R_w = 100 \times \Sigma |F_w - F_{w,av}| / \Sigma F_w$. The transmission range of the absorption corrections was 0.004–0.013.

Neutron diffraction. A single crystal with the dimensions $1.5 \times 2.2 \times 3.2 \text{ mm}$ was used in the data collection with a four-circle diffractometer at DR3, Risø, using 1.01 \AA neutrons and the ω - 2θ scan technique. Prior to the measure-

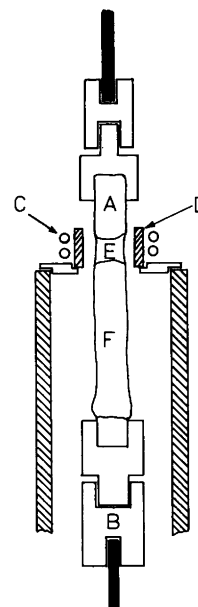


Fig. 2. Diagram showing RF heating with the use of a susceptor ring for floating zone growth. (A) Preform mounted in a BN holder on upper shaft; (B) BN holder on lower shaft for the grown crystal (F); (C) Heating coil, (D) susceptor ring supported as in Fig. 1; (E) molten zone. The diameter of crystal is ca. 10 mm.

ments the intensities of the reflections out to $\sin \theta/\lambda = 0.81$ were calculated using the program LAZY PULVERIX.⁶ A selection of the strong reflections were measured, including two standard reflections for every 50 reflections. The reflections were measured twice, giving a total of 3107 measured reflections. The R -values on averaging the reflections were $R = 4.0\%$ and $R_w = 5.8\%$. No absorption corrections were made ($\mu = 0.019 \text{ cm}^{-1}$). The number of independent reflections used in the structure refinements was 984.

Structure refinement with X-ray data

The set of atomic coordinates found in the synchrotron X-ray powder investigation (Table 1) was used as starting parameters in the structure refinement. The atomic scattering curves reported by Cromer and Mann⁷ were used, and the yttrium scattering contributions were corrected for the anomalous dispersion.⁸ The least-squares program LINUS⁹ was used in the refinement, and the values of the positional parameters refined at a conventional R -value of 9.1% are listed in Table 1. The structure factors were weighted using the standard deviations of the reflections. The parameters refined were a scale factor and an extinction parameter, and for each atom three positional parameters. For the metal atoms six anisotropic temperature factor parameters were refined, and for the oxygen atoms an isotropic temperature factor was refined. Fig. 3 shows the coordination polyhedra of the metal atoms made from the model deduced from the single crystal X-ray diffraction investigation.

Table 1. Atomic coordinates for $\text{Al}_2\text{Y}_4\text{O}_9$ from three sets of diffraction data. For each atom the coordinates listed are from X-ray synchrotron powder data, from X-ray single crystal data and from neutron single crystal data.

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Y(1)	0.5244(6)	0.1081(6)	0.7864(5)
	0.5231(5)	0.1095(2)	0.7852(2)
	0.5194(9)	0.1076(7)	0.7873(7)
Y(2)	0.0221(7)	0.0944(5)	0.8066(4)
	0.0233(5)	0.0959(2)	0.8055(2)
	0.0269(9)	0.0953(7)	0.8064(8)
Y(3)	0.3390(7)	0.1276(5)	0.4370(5)
	0.3394(6)	0.1272(2)	0.4369(2)
	0.3455(9)	0.1281(7)	0.4357(7)
Y(4)	0.8382(7)	0.1206(6)	0.4173(5)
	0.8378(5)	0.1214(2)	0.4163(2)
	0.8303(9)	0.1211(8)	0.4160(8)
Al(1)	0.2300(16)	0.1818(15)	0.1323(12)
	0.2156(18)	0.1801(7)	0.1277(7)
	0.2123(26)	0.1829(18)	0.1244(19)
Al(2)	0.6544(20)	0.1808(15)	0.1170(12)
	0.6555(16)	0.1775(8)	0.1127(7)
	0.6650(20)	0.1757(15)	0.1205(15)
O(1)	0.7816(38)	0.2341(31)	0.7454(26)
	0.7846(39)	0.2353(18)	0.7497(18)
	0.7773(18)	0.2346(13)	0.7592(13)
O(2)	0.2228(37)	0.2391(29)	0.7642(25)
	0.2313(35)	0.2369(16)	0.7659(16)
	0.2304(18)	0.2361(13)	0.7567(13)
O(3)	0.2151(37)	0.0182(27)	0.1559(24)
	0.2128(44)	0.0186(19)	0.1588(19)
	0.2008(14)	0.0174(11)	0.1471(11)
O(4)	0.0741(33)	0.2372(23)	0.9822(20)
	0.0716(38)	0.2349(17)	0.9804(17)
	0.0804(16)	0.2338(12)	0.9715(12)
O(5)	0.4286(42)	0.2308(21)	0.1107(24)
	0.4294(39)	0.2394(14)	0.1145(17)
	0.4325(15)	0.2357(8)	0.1188(11)
O(6)	0.6519(32)	0.2372(24)	0.9577(20)
	0.6386(35)	0.2320(15)	0.9618(16)
	0.6414(16)	0.2320(12)	0.9711(12)
O(7)	0.6884(38)	0.0049(28)	0.1615(26)
	0.6939(46)	0.0168(20)	0.1619(20)
	0.7067(13)	0.0217(10)	0.1677(10)
O(8)	0.0829(54)	0.0045(27)	0.3938(30)
	0.0802(49)	-0.0042(18)	0.3907(21)
	0.0814(12)	-0.0006(8)	0.3988(9)
O(9)	0.5676(50)	0.0061(27)	0.4014(28)
	0.5627(48)	0.0052(16)	0.3900(21)
	0.5607(15)	0.0018(10)	0.3861(12)

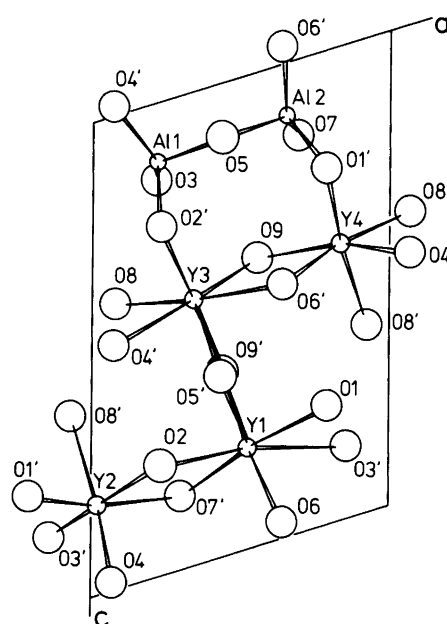


Fig. 3. Coordination polyhedra of the metal atoms listed in Table 1.

Structure refinement with neutron data

As starting parameters in the structure refinements, the atomic coordinates found in the single crystal X-ray investigation were used. The program LINUS⁹ was used in the least-squares refinements with scattering contributions from Ref. 10. A conventional *R*-value of 10.9% was obtained with the positional parameters listed in Table 1. The standard deviations of the reflections were used in the weights of the structure factors. The parameters refined were a scale factor and, for each atom, three positional parameters and an isotropic temperature factor. No extinction corrections were made. Fig. 4 shows a stereoscopic drawing of the structure made from the model obtained with the neutron single crystal diffraction data.

Discussion

The atomic coordinates for the three sets of data are all listed in Table 1. The standard deviations of the positional parameters for the metal atoms are all larger for the neutron single crystal data set than for the X-ray single crystal data set, and some of the coordinates deviate significantly (more than three standard deviations) between the two sets of data. This is to be expected for two reasons. The average scattering contribution for the metal atoms is greater in the case of X-ray diffraction than for neutron diffraction, and the number of independent reflections in the X-ray diffraction data set is greater than the number of reflections in the neutron diffraction data set.

The standard deviations of the positional parameters of the yttrium atoms obtained from the single crystal neutron

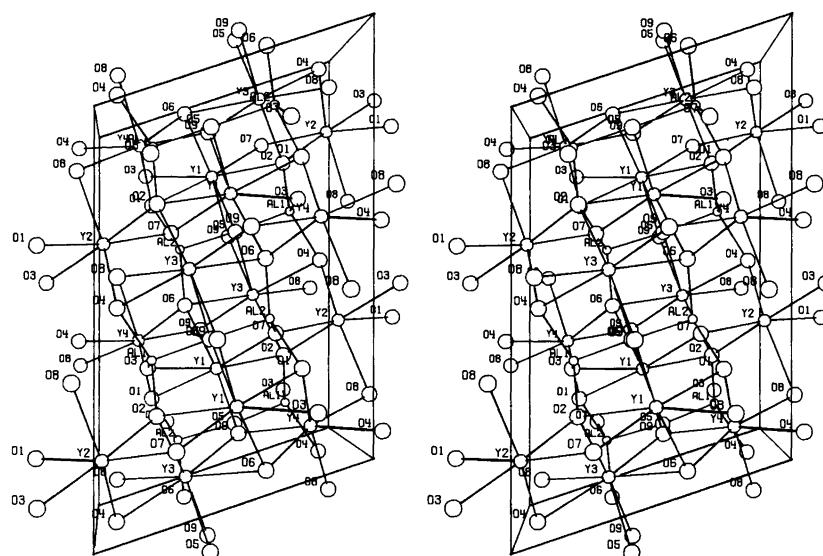


Fig. 4. Projection of the structure of $\text{Al}_2\text{Y}_4\text{O}_9$ along [010].

diffraction data are comparable with and slightly larger than the corresponding values obtained from the synchrotron X-ray powder diffraction data. The standard deviations of the positional parameters of the aluminium atoms are comparable with or slightly larger for the single crystal neutron diffraction data than for the synchrotron powder diffraction data, and this is most likely due to the low scattering contribution from aluminium in the neutron diffraction case.

The standard deviations of the positional parameters of the oxygen atoms are all smaller for the neutron diffraction single crystal data set than for X-ray single crystal data and the synchrotron X-ray powder diffraction data. The coordinates of the oxygen atoms do not deviate significantly between the three sets of data, mostly owing to the high values of the standard deviations of the coordinates for the two X-ray diffraction data sets.

The standard deviations of the coordinates from the synchrotron X-ray powder diffraction data are slightly higher than the corresponding values obtained from the X-ray single crystal data taken with $\text{Ag } K_\alpha$ radiation, and the two sets of coordinates do not differ significantly from each other, except for atom Al(1). The precision of the coordinates obtained from the synchrotron X-ray powder diffraction data is thus comparable with or slightly lower than that of the coordinates obtained from the two single crystal data sets. The time required to obtain the diffraction data was 35 min for the synchrotron X-ray powder data, one week for the X-ray single crystal data and six weeks for the neutron single crystal data. Taking this into consideration, together with the acceptable precision of the structural model calculated from the synchrotron X-ray powder diffraction data, well-resolved synchrotron X-ray powder diffraction data measured out to high $\sin \theta/\lambda$ values may be comparable with single crystal diffraction data in refine-

ments of crystal structures. In the present investigation the synchrotron X-ray powder data compete fairly well with the two sets of single crystal data with respect to the precision of the positional parameters of the structure. By improving the counting statistics and recording out to higher values of $\sin \theta/\lambda$, the precision could certainly be improved. However, accurate values of temperature factor parameters are not easy to obtain from powder diffraction data. For this reason a comparison of temperature factor parameters for the three sets of data has been omitted.

$\text{Al}_2\text{Y}_4\text{O}_9$ is isostructural with $\text{Al}_2\text{Eu}_4\text{O}_9$. The standard deviations of the positional parameters of the yttrium and aluminium atoms from the single crystal neutron diffraction set of $\text{Al}_2\text{Y}_4\text{O}_9$ are higher than the corresponding values for the europium and aluminium atoms for the structure of $\text{Al}_2\text{Eu}_4\text{O}_9$, based on 3184 X-ray single crystal reflections. However, the standard deviations of the positional parameters of the oxygen atoms for the neutron diffraction data set of $\text{Al}_2\text{Y}_4\text{O}_9$ are comparable with, or in most cases smaller than, those of the oxygen atoms of $\text{Al}_2\text{Eu}_4\text{O}_9$. Some of the positional parameters deviate significantly between the two sets of data.

Table 2 lists interatomic distances calculated from the neutron diffraction single crystal data for $\text{Al}_2\text{Y}_4\text{O}_9$. The atoms Y(2) and Y(4) are coordinated in octahedra, and Y(1) and Y(3) are coordinated with seven oxygen atoms in a coordination polyhedron often found for yttrium and RE metals in coordination with oxygen. The average interatomic distances in the YO_6 and YO_7 coordination polyhedra are 2.296(7) and 2.374(7) Å, respectively, and the AlO_4 tetrahedra have average distances of 1.748(9) Å, calculated from the single crystal X-ray diffraction data, and average values of 2.292(4), 2.377(4) and 1.741(7) Å, respectively, calculated from the single crystal neutron diffraction data. These results are in good agreement with the

Table 2. Interatomic distances in $\text{Al}_2\text{Y}_4\text{O}_9$ in Å, from single crystal neutron diffraction data.^a

Y(1)–O(9)	2.158	Y(3)–O(9)	2.268
Y(1)–O(7)	2.325	Y(3)–O(8)	2.298
Y(1)–O(6)	2.349	Y(3)–O(9)	2.322
Y(1)–O(3)	2.357	Y(3)–O(2)	2.377
Y(1)–O(5)	2.422	Y(3)–O(5)	2.401
Y(1)–O(1)	2.425	Y(3)–O(6)	2.556
Y(1)–O(2)	2.451	Y(3)–O(4)	2.565
Y(2)–O(3)	2.245	Y(4)–O(1)	2.247
Y(2)–O(7)	2.257	Y(4)–O(9)	2.284
Y(2)–O(4)	2.276	Y(4)–O(6)	2.290
Y(2)–O(1)	2.278	Y(4)–O(8)	2.308
Y(2)–O(2)	2.293	Y(4)–O(4)	2.319
Y(2)–O(8)	2.381	Y(4)–O(8)	2.326
Al(1)–O(2)	1.670	Al(2)–O(7)	1.699
Al(1)–O(5)	1.736	Al(2)–O(6)	1.718
Al(1)–O(4)	1.752	Al(2)–O(1)	1.771
Al(1)–O(3)	1.762	Al(2)–O(5)	1.821

^aY–O and Al–O standard deviations are 0.015 and 0.020 Å, respectively.

average yttrium–oxygen distance of 2.284(4) Å found in Y_2O_3 ¹¹ and the average aluminium–oxygen distances of 1.74(2) and 1.742(2) Å, respectively, found in $\text{Al}_2\text{Eu}_4\text{O}_9$ ² and in $\text{LiAlSiO}_4 \cdot \text{D}_2\text{O}$.¹²

The compound $\text{Al}_2\text{Y}_4\text{O}_9$ melts congruently at 2020 °C.¹³ The crucible-free method of preparation used in this work is fast and convenient for the preparation of small single crystals for X-ray crystallographic investigations, and much faster than the preparation of single crystals by solid-state sintering reactions.¹⁴

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