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CRYSTAL STRUCTURE REFINEMENT OF $YAlO_3$, A PROMISING LASER MATERIAL

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ABSTRACT

Yttrium orthoaluminate, $YAlO_3$, has a perovskite-like orthorhombic crystal structure ($a = 5.330(2)$ Å, $b = 7.375(2)$ Å, $c = 5.180(2)$ Å; space group $Pnma\text{-}D_{2h}^{16}$). The structure has been refined from 880 independent X-ray reflections to $R = 0.075$. The oxygen coordination around Al^{3+} remains nearly cubic whereas the YO_{12} - and YAl_8-polyhedra are rather distorted.

Introduction

Yttrium orthoaluminate, $YAlO_3$, is known to have a perovskite-like crystal structure (1). It is therefore usually termed YAP (Yttrium-Aluminium-Perovskite) in analogy to YAG (Yttrium-Aluminium-Garnet). Its potential as an efficient laser host has been extensively studied in the past (2-7). Polarized laser action in $Nd:YAlO_3$ has been observed at room temperature at five wave length between 1.06 and 1.10 µm and at two lines near 1.34 µm.

The main disadvantage of YAP in laser application is that $YAlO_3$-single crystals usually exhibit a brownish coloration after the growing procedure (8). This can be reduced by annealing. But despite of the thermal treatment even clear crystals become inevitably coloured when irradiated with the pump light and lasing can no longer be achieved. A rather broad absorption band with a maximum at about 0.45 µm has been reported (3). Attempts to elucidate the nature of this absorption have been undertaken only recently (9, 10). Schirmer et al. (10) suggest it to be caused by optical absorption of bound small polarons. In order to facilitate the discussion on the defects responsible for the absorption exact structural information is required. So we decided to perform a complete crystal structure analysis of $YAlO_3$ by X-ray methods.

Experimental

The specimen to be investigated was taken from a colourless undoped Czochralski-grown single crystal of $YAlO_3$. The sample was ground to a sphere of radius 235 µm in an air operated crystal grinder. The sphere was mounted on a Nonius CAD-4 automatic single crystal diffractometer with kappa-geometry. A total of 880 independent reflections up to $(\sin\Theta)/\lambda = 1.00$ Å^{-1} was measured with a scintillation counter (NaJ:Tl) using Zr-filtered MoK α -radiation ($\lambda = 0.7107$ Å). Long-time drift of the primary beam intensity was corrected measuring the intensities of the standard reflections (121) and (220) every twenty measurements. The integrated intensities were corrected for Lorentz, polarisation, and absorption factors. Standard deviations were obtained only from counting statistics. 411 reflections had an integrated intensity less than three times their standard deviations and were excluded from the structure refinement.

Crystal Data

A series of orthorhombic perovskite-like compounds has been investigated by Geller and Wood (1). Among other items lattice constants of the compounds and an explicit crystal structure of $GdFeO_3$ representing the structural type are reported. The space group is given as Pbnm-D_{2h}^{16} which is unfortunately not standardized in the International Tables (11). Conversion to the standardized space group Pnma is achieved by simply altering the (old) x-axis of Pbnm to the (new) z-axis of Pnma which is in matrix form:

$$\underset{\text{Pbnm}}{\begin{bmatrix}1&0&0\\0&1&0\\0&0&1\end{bmatrix}} \rightarrow \underset{\text{Pnma}}{\begin{bmatrix}0&1&0\\0&0&1\\1&0&0\end{bmatrix}} \qquad \underset{\text{Pnma}}{\begin{bmatrix}1&0&0\\0&1&0\\0&0&1\end{bmatrix}} \rightarrow \underset{\text{Pbnm}}{\begin{bmatrix}0&0&1\\1&0&0\\0&1&0\end{bmatrix}}$$

We shall base our structural work on the standardized space group Pnma.

For comparison, the lattice constants of $YAlO_3$ given in (1) and those we obtained by least-squares refinement from Guinier powder photographs taken with Ni-filtered CuK α_1-radiation ($\lambda = 1.5405$ Å) are compiled in Table 1. Other relevant items are also included.

The very high linear absorption coefficient μ is caused by Yttrium which is near the absorption edge for MoK α -radiation. This results in a μR (R = radius of the single crystal sphere) of 7. The measured density Dm was obtained by weighing a crystal block of 0.60 x 0.58 x 0.55 cm^3.

Figure 1 shows the relation of the monoclinic perovskite-like pseudocell to the orthorhombic unit cell. The great number of unobserved reflections mentioned above is due to this pseudocell.

Refinement of the Crystal Structure

The crystal structure of YAlO was refined using the atomic

TABLE 1

Crystal Data

Geller & Wood (1)		present study		Dm	Z	FW
a	5.179 Å		5.330(2) Å	5.36 gcm^{-3}	4	163.88
b	5.329 Å		7.375(2) Å			
c	7.370 Å		5.180(2) Å	Dx	μ	F(000)
V	203.4 $Å^3$		203.62 $Å^3$	5.35 gcm^{-3}	297 cm^{-1}	304
SG	Pbnm		Pnma			e

coordinates of the $GdFeO_3$-lattice (1)[3] as starting parameters. Y^{3+} and O_I^{2-} are located at position 4c, Al^{3+} at 4b, and O_{II}^{2-} at 8d of the space group Pnma (11). The scattering factors for Y^{3+} and Al^{3+} were taken from (12), those of O^{2-} from (13). A full-matrix least squares refinement was carried out using the program CRYLSQ of the X-ray system (14). $\Delta f'$ and $\Delta f''$ corrections for anomalous dispersion in the neutral atom values (15) were applied. In the case of individual isotropic temperature motion, we obtained a final agreement index

$$R = \sum \left| \, |F_o| - |F_c| \, \right| / \sum F_o$$

of 0.080. Refinement with anisotropic temperature coefficients and isotropic extinction correction calculated with Larson's method (16) resulted in an extinction factor of 6×10^{-5}, an absolute scale of 5.156, and an R-value of 0.075. No weighting scheme was applied to the observed reflections. After the final refinement cycle shifts of all positional and temperature parameters were less than 1 % of the corresponding standard deviations. The final atomic coordinates are listed in Table 2, the anisotropic temperature coefficients in Table 3. For direct comparison with the $GdFeO_3$-structure the listing of the atomic positions corresponding to Pbnm (1) are also included in Table 2. The

TABLE 2

Atomic coordinates

Atom	Y^{3+}	Al^{3+}	O_I^{2-}	O_{II}^{2-}	
Pos.	4c	4b	4c	8d	
x	.0526(2)	0	.475(2)	.293(2)	
y	1/4	0	1/4	.044(2)	Pnma
z	.9896(2)	1/2	.086(2)	.703(2)	
x	-.0104(2)	1/2	.086(2)	-.297(2)	
y	.0526(2)	0	.475(2)	.293(2)	Pbnm
z	1/4	0	1/4	.044(2)	

F_o, F_c-listing is available from the authors.

The lattice constants given in the first row of Table 1 and the atomic coordinates of Table 2 were used to calculate interatomic distances and angles of the predominant coordination polyhedra in the $YAlO_3$-structure by means of the program BONDLA of the X-ray system (14). The relevant magnitudes are compiled in Table 4, the ionic charge symbols being omitted for simplicity. Whereas the AlO_6-octahedron remains nearly cubic the YO_{12}- and YAl_8-polyhedra are rather distorted. To get an idea of this distortion the coordination of Y^{3+} by its 12 O^{2-}-ligands is presented in Figure 2 calculated and drawn by means of the program ORTEP (17).

TABLE 3

Anisotropic temperature coefficients (x 10^2)

	Y^{3+}	Al^{3+}	O_I^{2-}	O_{II}^{2-}
U_{11}	.47(4)	.41(12)	1.02(38)	.68(21)
U_{22}	.42(4)	.39(12)	.39(29)	.88(22)
U_{33}	.75(4)	.70(13)	.41(27)	.37(18)
U_{12}	0	.06(10)	0	-.12(21)
U_{13}	.00(4)	.23(13)	.17(27)	.07(19)
U_{23}	0	-.05(13)	0	.23(19)

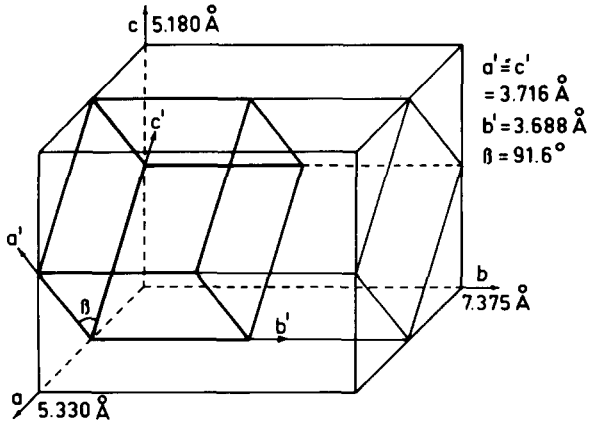

FIG. 1
Relationship between the orthorhombic unit cell and the monoclinic pseudocell in $YAlO_3$

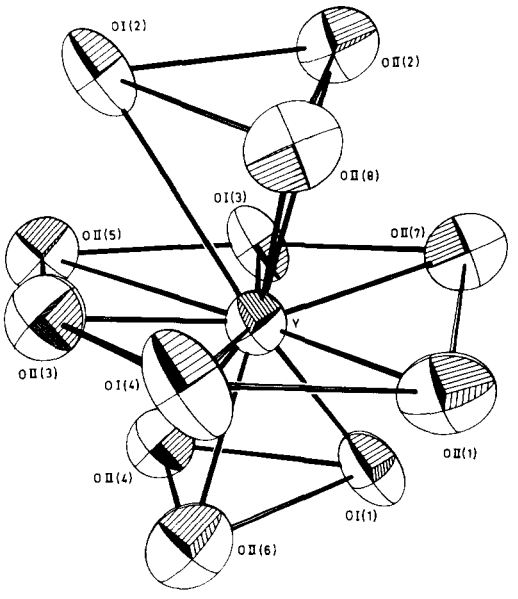

FIG. 2
YO_{12}- polyhedron

TABLE 4

Interatomic distances (Å) and angles (o)

coordinates of bonding ions

Y (see table 2)

Al (1) (see table 2)
(2) (x , y , z+1)
(3) (x+1/2, y+1/2, z+1/2)
(4) (x-1/2, y+1/2, z+1/2)
(5) (x , y+1/2, z+1)
(6) (x , y+1/2, z)
(7) (x+1/2, y , z+1/2)
(8) (x-1/2, y , z+1/2)

OI (1) (x , y , z+1)
(2) (x-1 , y , z+1)
(3) (x-1/2, y , 3/2-z)
(4) (x-1/2, y , 1/2-z)
(5) (1/2-x, y , z+1/2)

OII (1) (see table 2)
(2) (x , y , 2-z)
(3) (x-1/2, 1/2-y, 3/2-z)
(4) (1/2-x, y+1/2, z+1/2)
(5) (x , y+1/2, 2-z)
(6) (x , 1/2-y, z)
(7) (1/2-x, y , z+1/2)
(8) (x-1/2, y , 3/2-z)
(9) (x , y , 1-z)
(10) (1/2-x, y , z-1/2)

Y - Y 3.642(2)

Al- Al 3.687(1)

YAl_8-hexahedron

Y-Al	(1) (6)	3.148(1)
	(2) (5)	3.236(1)
	(3) (7)	3.015(1)
	(4) (8)	3.475(1)

Al (1)-Y-Al (6) 71.71(4)
Al (1)-Y-Al (7) 74.14(2)
Al (1)-Y-Al (8) 68.05(2)
Al (2)-Y-Al (5) 69.48(4)
Al (2)-Y-Al (7) 72.87(2)
Al (2)-Y-Al (8) 67.14(2)
Al (3)-Y-Al (7) 75.41(4)
Al (4)-Y-Al (8) 64.08(3)

AlO_6-octahedron

Al-OI	(4) (5)	1.901(2)
-OII	(1) (9)	1.911(7)
	(8) (10)	1.921(7)

OII (1)-Al-OI (4) 91.18(39)
OII (1)-Al-OII (10) 90.02(29)
OI (4)-Al-OII (10) 90.98(27)

YO_{12}-polyhedron (see Fig. 2)

Y-OI	(1)	2.306(11)
	(2)	3.119(11)
	(3)	2.237(10)
	(4)	3.010(10)
Y-OII	(1) (6)	2.480(7)
	(2) (5)	3.262(7)
	(3) (8)	2.283(7)
	(4) (7)	2.570(7)

OII (1)-Y-OI (4) 58.53(22)
OII (1)-Y-OII (7) 64.88(22)
OI (3)-Y-OII (7) 68.69(19)
OI (3)-Y-OII (5) 54.24(20)
OII (3)-Y-OII (5) 55.16(20)
OII (3)-Y-OI (4) 58.98(21)
OI (1)-Y-OII (6) 67.99(24)
OII (4)-Y-OII (4) 66.08(19)
OII (2)-Y-OII (8) 55.16(20)
OI (2)-Y-OII (8) 58.12(21)
OI (2)-Y-OII (2) 50.52(16)

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