Zeitschrift für Kristallographie 172, 129–133 (1985)

A Pb/Nd-stabilized mullite of the composition $Al_{5.03}Ge_{0.97}$ $Pb_{0.15}Nd_{0.06}O_{9.71}$

H. Saalfeld and K. H. Klaska

Mineralogisch-Petrographisches Institut der Universität Hamburg,
Grindelallee 48, D-2000 Hamburg 13, Federal Republic of Germany

Received: April 5, 1985

Mullite / Flux growth / Crystal structure refinement / Non-stoichiometric compound

Abstract. In a PbO/PbF_2 flux (1400 °C) a new (Al,Ge)-mullite was grown incorporating Pb^{2+} and Nd^{3+} ions. the needle like crystals (about 2 mm in length) are orthorhombic: $P2_12_12$, $a = 7.6648(4)$, $b = 7.7914(3)$, $c = 2.9213(1)$ Å, $V = 174.46(1)$ Å^3, $Z = 1$, $D_x = 3.79$ g cm^{-3}. Final $R = 0.0211$ for 297 observed reflections. Pb^{2+} and Nd^{3+} are located in the vacancies that are formed by omission of O(3)-atoms.

Introduction

(Al,Ge)-mullite of the composition $3\,Al_2O_3 \cdot 2GeO_2$ is well known from the structural point of view (Durovič and Fejdi, 1976). There exists a close relationship to the corresponding silicon-mullite $3Al_2O_3 \cdot 2\,SiO_2$. In contrast to the (Al,Si)-mullites it was not possible so far to grow (Al,Ge)-mullites with a more extended solid solution range. Recently the synthesis of an (Al,Ge)-mullite was successful in a flux containing Pb- and Nd-ions. This mullite has a Al/Ge ratio of nearly 5:1 (exactly $2.6\,Al_2O_3 \cdot 1\,GeO_2$), but it always contains a certain amount of Pb- and Nd-ions that are considered necessary for the stabilization of this mullite.

Experimental

The crystal growth of the (Al,Ge)-mullite was carried out using PbO/PbF_2 flux solvent and Nd_2O_3, Al_2O_3, GeO_2 as feed nutrients. The crystals were

---

Author's address: Prof. Dr. H. Saalfeld (responsible for correspondence), Dr. K. H. Klaska, Mineralogisch-Petrographisches Institut der Universität Hamburg, Grindelallee 48, D-2000 Hamburg 13, Federal Republic of Germany

Table 1. Microprobe analysis of (Al, Ge)-mullite. Results in wt%

Al_2O_3	64.06
GeO_2	25.34
PbO	8.20
Nd_2O_3	2.40

Table 2. Positional parameters of the average structure in ($\times 10^4$). Standard deviations are given in parentheses

Atom	Mult	$x(\Delta x)$	$y(\Delta y)$	$z(\Delta z)$
Al(1)	0.5	0	0	52(15)
Al(2)	0.55	3500(1)	1618(1)	5012(10)
Al*	0.2	2315(6)	2987(5)	4866(52)
Ge	0.243	3500(1)	1618(1)	5012(10)
Pb(1)	0.03063	1182(6)	3666(6)	4810(59)
Pb(2)	0.01937	4543(12)	621(14)	4934(96)
O(1)	1.0	3717(2)	2878(2)	−90(34)
O(2)	1.0	3621(2)	5788(2)	4913(25)
O(3)	0.23066	5000	0	4339(55)
O*	0.19684	472(16)	4429(15)	5373(86)

grown by slowly cooling of the melt from 1400 °C. They were recovered by leaching from any residual flux by diluted nitric acid. The needle-like crystals attained a length of 1 – 2 mm. Various single crystals were chemically analyzed by electron microprobe technique. The individual results showed no significant differences, and the mean values given in Table 1 led to the formula

$$[Al_{5.03}Ge_{0.97}]Pb_{0.15}Nd_{0.06}O_{9.71} .$$

This is in very good agreement with the result of the structure refinement.

Single crystal photographs confirmed a mullite of good quality. Moreover reflections could be detected that are not in accordance with the usual space group *Pbam*. So the space group of the lower symmetry $P2_12_12$ was used for the structure refinement. A single crystal (0.041 × 0.041 × 0.069 mm) was selected for the measurement of the lattice parameters and the intensities on an automatic four-circle diffractometer (SYNTEX $P2_1$) with graphite monochromatized Mo$K\alpha$-radiation. The refined unit-cell parameters are given in the Abstract. A data set of 336 unique reflections was measured up to $2\vartheta_{max} = 60°$. The intensities were corrected for Lorentz and polarisation factors. Corrections for absorption and extinction were applied. The atomic coordinates of $3Al_2O_3 \cdot 2GeO_2$-mullite published by Durovič and Fejdi (1976) were used as starting values for the crystal structure refinement. The atomic scattering factors were taken from the International Tables for X-ray Crystallography, vol IV (1974). After some cycles a difference synthesis was calculated in order to locate the (Pb, Nd)-positions. Including these atoms with their occupancies further cycles of refinement with anisotropic temperature coefficients reduced R_W to 0.0211 for all 297 observed reflections with $I > 3\,\sigma(I)$ and 39 unobserved reflections.

Positional parameters are given in Table 2. Lists of interatomic distances and bond angles, details of procedure, structure factors and anisotropic temperature coefficients have been deposited at the Mineralogisch-Petrographisches Institut der Universität Hamburg, and are available on request.

Discussion

The cell content of the (Al, Si)-mullites can be expressed by the formula $Al_2[Al_{2+2x}Si_{2-2x}]O_{10-x}$ where x gives the number of oxygen atoms missing per average unit cell (Cameron, 1977). Sintered silicon-mullites have the composition $3\,Al_2O_3 \cdot 2\,SiO_2$ whereas melt-crystallized mullites in general can be described by the composition $2\,Al_2O_3 \cdot 1\,SiO_2$. Both mullites exhibit certain groups of diffuse reflections proving the existence of incommensurate modulated structures. On the basis of the sharp reflections the average structure with the space group *Pbam* could be determined (Burnham, 1963; Durovič, 1969; Saalfeld and Guse, 1981). In the case of (Al, Ge)-mullite only the composition $3\,Al_2O_3 \cdot 2\,GeO_2$ was found with no evidence of extended solid solution (Miller et al. 1967; Prochazka, 1982). The structure analysis by Durovič and Fejdi (1976) showed that the atomic arrangement is isostructural with mullite $3\,Al_2O_3 \cdot 2\,SiO_2$. The present investigation has proved the existence of an (Al, Ge)-mullite with a ratio $2.6\,Al_2O_2 \cdot 1\,GeO_2$ and a cell content $Al_2[Al_{3.03}Ge_{0.97}]Pb_{0.15}Nd_{0.06}O_{9.71}$. The number of vacancies is $x = 0.29$. This value is lower than expected by the Al/Ge-ratio (0.515) and caused by the (Pb, Nd)-balance of valency. This composition seems to be possible only in the presence of incorporated Pb^{2+} and Nd^{3+} ions. The space group is now $P2_12_12$. The mirror planes have disappeared and some atoms are no longer in special positions.

The positions of the Pb^{2+} and Nd^{3+} ions could be clearly detected in the large vacancies of the mullite structure (it was not possible, however, to distinguish between these ions). Fig. 1 shows part of the real structure with possible (Pb, Nd)-positions. Two different kinds of vacancies can be seen: vacancies that are terminated by three linked tetrahedra over O(3) coordinating Pb(2) and those terminated by three linked tetrahedra over 0^+ coordinating Pb(1). The Pb – O-coordination is in both cases irregular. Eight Pb(1) – O-distances range between 2.249 and 3.189 Å (Table 3). Pb(2) is coordinated by nine oxygens in distances ranging from 2.368 to 3.371 Å. This variation of Pb – O-distances is in good agreement with that in other

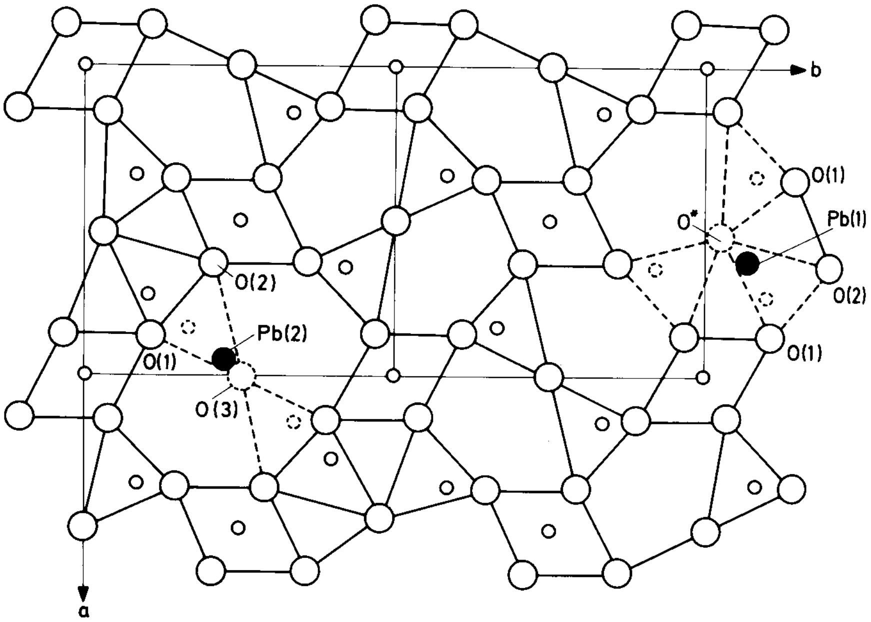

Fig. 1. Part of the real mullite structure with the locations of (Pb,Nd)-ions

Table 3. Interatomic distances of the Pb-polyhedra; e.s.d.'s in parentheses

Pb(1)–polyhedron		Pb(2)–polyhedron	
Pb(1)–O(2)	2.249 Å	Pb(2)–O(1)	2.368 Å
Pb(1)–O(1)	2.490	Pb(2)–O(1)	2.376
Pb(1)–O(2)	2.496	Pb(2)–O(2)	2.429
Pb(1)–O(1)	2.525	Pb(2)–O(3)	2.812
Pb(1)–O(1)	2.630	Pb(2)–O(2)	3.132
Pb(1)–O(1)	2.719	Pb(2)–O(3)	3.152
Pb(1)–O*	2.872	Pb(2)–O(2)	3.313
Pb(1)–O*	3.189	Pb(2)–O(1)	3.365
		Pb(2)–O(1)	3.371

Pb^{2+}-containing oxygen-compounds. The occupation factors show a clear preference for the Pb(1)-position.

Like all mullites this Pb-containing (Al,Ge)-mullite shows diffuse reflections due to the incommensurate character of the crystal structure. However, it was not the intention of this study to describe and analyse these very diffuse satellite reflections.

Further work will be necessary to clarify the mechanism by which larger cations are incorporated in the vacancies of the lattice. Moreover the question arises whether the silicon-mullites are also capable to incorporate larger cations and how the properties are influenced by this penetration.

Acknowledgement. The authors thank Dr. G. Adiwidjaja for collecting the diffractometer data.

References

Burnham, C. W.: Crystal structure of mullite. Carnegie Inst. Washington Year book **63**, 223–227 (1963)
Cameron, W. E.: Mullite: a substituted alumina. Am. Mineral. **62**, 747–755 (1977)
Durovič, S.: Refinement of the crystal structure of mullite. Chem. Zvesti **23**, 113–128 (1969)
Durovič, S., Fejdi, P.: Synthesis and crystallochemical parameters of D-mullities. Silikáty c **2**, 97–112 (1976)
Miller, J. L., McCormick, G. R., Ampian, S. G.: Phase equilibria in the system GeO_2–Al_2O_3. J. Am. Ceram. Soc. **50**, 268–269 (1967)
Prochazka, S.: Sintering and properties of dense aluminium germanate. Proceedings of the 5th CIMTEC (1982)
Saalfeld, H., Guse, W.: Structure refinement of 3:2-mullite ($3Al_2O_3 \cdot 2SiO_2$). Neues Jahrb. Mineral. Monatsh. 145–150 (1981)