Zeitschrift für Kristallographie 195, 65–73 (1991)
 – 0044-2968/91 $ 3.00 + 0.00

Solid solution and optical properties of (Al, Ge)-mullites

H. Saalfeld and H. Gerlach

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

Dedicated to Prof. K. Fischer on occasion of his 65th birthday anniversary

Received: September 24, 1990; in revised form: October 18, 1990

(Al, Ge)-*mullite* / *Flux synthesis* / *Optical properties*

Abstract. With the flux-technique single crystals of (Al, Ge)-mullites have been synthesized in the range of 1.28 $Al_2O_3 \cdot 1\ GeO_2$ to 1.93 $Al_2O_3 \cdot 1\ GeO_2$. Chemical and optical (microrefractometer spindel-stage) data of the solid solution series have been collected. The results of a structure refinement of the mullite 1.93:1 are compared with those of a refinement of the mullite 1.50:1 (Neumann, 1984).

Introduction

The (Al, Si)-mullites represent a solid solution series with the general composition $Al_{4+2x}Si_{2-2x}O_{10-x}$ where x is the number of oxygen atoms missing per unit cell (Cameron, 1977). The reduction of oxygens is due to the substitution of Si^{4+} by Al^{3+}. The crystal structure of mullite consists of $[AlO_6]$-octahedra running parallel to the c-axis. These octahedra are crosslinked by double-chains of (Al, Si)-tetrahedra (Burnham, 1963, 1964). Two types of these double-chains exist: one type is identical with that found in sillimanite, in the other the tetrahedra are linked in such a way that vertices also point in opposite direction (new positions Al* and O*) producing six-membered rings (Saalfeld, 1979). In this arrangement vacancies are generated whose number increases with growing Al_2O_3-content. Ordering of these double-chains exists in small domains (Nakajima et al., 1975; Saalfeld, 1979; Ylä-Jääski and Nissen, 1983). Disorder and incommensurate character of the mullite structure can be seen in the appearance of diffuse reflections and satellites. A structure determination on the bases of the sharp reflections only reveals the 'average structure' (Fig. 1). Important

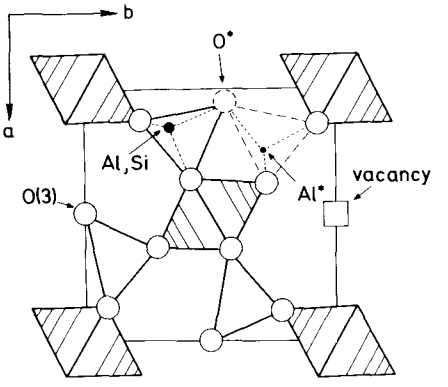

Fig. 1. Scheme of the average structure of mullite (*a*, *b*-plane) with location of a vacancy.

members of the series are the mullite 1.5 $Al_2O_3 \cdot 1\ SiO_2$ ($x = 0.25$) that forms by sinter processes and the fused mullite 2 $Al_2O_3 \cdot 1\ SiO_2$ ($x = 0.4$).

Complete substitution of SiO_2 and GeO_2 in the structure leads to the (Al, Ge)-mullites with the same atomic arrangement (Gelsdorf et al., 1958; Durovič and Fejdi, 1976; Prochazka, 1982; Schneider and Werner, 1982; Neumann, 1984). The ratio Al_2O_3:GeO_2 was found to vary in a small region about 1.5:1. Only in one case a ratio 2.6:1 was observed (Saalfeld and Klaska, 1985). But here the incorporation of Pb^{2+} and Nd^{3+} ions may be responsible for the change of composition. It is the aim of the present investigation to find the limits of the solid solution series of the (Al, Ge)-mullites and to describe their influence on optical and structural properties.

Synthesis of the (Al, Ge)-mullites

The flux method was successfully applied to grow the (Al, Ge)-mullites. In a Pt/Au crucible mixtures of PbO and MoO_3 as flux solvent and Al_2O_3 and GeO_2 as feed nutrients were heated in the temperature range 1185–1380° C. After some hours the crucible was cooled (rate of cooling: 160–5° C/h) and the reaction product treated with a mixture of nitric acid and acetic acid. The remaining crystals proved to be needles of (Al, Ge)-mullite. The largest crystals have a length up to 5 mm and a diameter of 0.1 mm. The morphology is a combination of the planes {110} and {001}. Nearly 40 syntheses have been carried out with different proportions of Al_2O_3 and GeO_2. A solid solution series could be established ranging from 1.23 $Al_2O_3 \cdot 1\ GeO_2$ to 1.96 $Al_2O_3 \cdot 1\ GeO_2$. In no case the Ge-analogue of sillimanite or andalusite was observed, only Ge-kyanite occurs under special experimental conditions (Gerlach et al., 1989).

Table 1. Some representative members of the series $Al_{4+2x}Ge_{2-2x}O_{10-x}$.

Al_2O_3	GeO_2	PbO	MoO_3	sum	Al_2O_3/GeO_2	x
wt.%						
55.03	45.88	0.13	0.03	101.07	1.23:1	0.13
56.23	43.69	0.09	0.02	100.03	1.32:1	0.18
59.57	41.16	0.21	0.07	101.01	1.48:1	0.24
60.48	38.73	0.26	0.03	99.50	1.60:1	0.29
65.09	34.11	0.29	0.03	99.52	1.96:1	0.39

Table 2. Optical data of the (Al, Ge)-mullites ($\lambda = 589.3$ nm).

Nr.	Al_2O_3:GeO_2	$2V$ (°)	n_x	n_y	n_z	$n_z - n_x$
1	1.28:1	52.9(9)	1.6965	1.6979	1.7016	0.0051
2	1.32:1	51.3(6)	1.6952	1.6958	1.7001	0.0049
3	1.48:1	51.0(9)	1.6910	1.6931	1.6980	0.0070
4	1.52:1	49.6(7)	1.6898	1.6918	1.6979	0.0081
5	1.55:1	49.4(8)	1.6900	1.6908	1.6971	0.0071
6	1.60:1	48.2(5)	1.6887	1.6908	1.6959	0.0072
7	1.62:1	46.8(8)	1.6891	1.6895	1.6981	0.0090
8	1.73:1	47.0(6)	1.6896	1.6903	1.6976	0.0080
9	1.80:1	47.3(6)	1.6880	1.6889	1.6960	0.0080
10	1.93:1	48.0(4)	1.6882	1.6896	1.6953	0.0071

Chemical composition

The chemical analyses were obtained by a micro-beam apparatus (Cameca) using as standards Al_2O_3, PbS, Ge, Mo. Table 1 summarizes the composition of some representative mullites. The average composition was recorded with five data points for each crystal. PbO and MoO_3 are regarded as impurities absorbed on the surface of the crystals.

Optical properties

The optical properties of the (Al, Ge)-mullites were determined by the microrefractometer spindel-stage (Medenbach, 1980). 10 crystals with different Al_2O_3/GeO_2-ratio were selected for the measurements. Chemical analyses and optical examination were carried out on the same crystals. The optical measurement had to be performed prior to the chemical analyses because the evaporated carbon film necessary for the microprobe analysis influences the optical results. In Table 2 optical data of the crystals

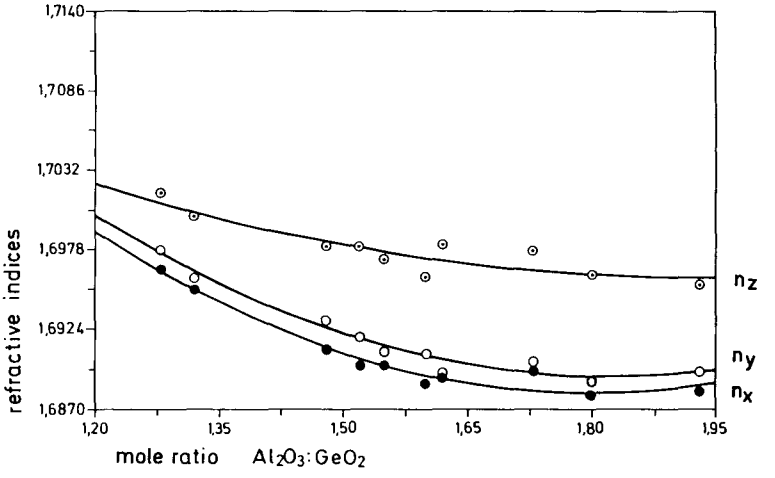

Fig. 2. Refractive indices of (Al, Ge)-mullites as function of the mole ratio Al_2O_3/GeO_2 ($\lambda = 589.3$ nm).

Table 3. Optical data of the (Al, Ge)-mullite 1.93:1.

Orientation:	$x = a$, $y = b$, $z = c$
Axial angle:	$(+)\ 2V = 48.0(4)^\circ$
$\lambda = 589.3$ nm, 20° C	
Chromatic dispersion:	$r < v$ weak

Refractive indices (wavelengths corresponding to the Fraunhofer lines):

	C 656.3	D 589.3	F 486.1 nm
n_x	1.6832	1.6882	1.7004
n_y	1.6843	1.6896	1.7027
n_z	1.6897	1.6953	1.7090
$n_z - n_x$	0.0065	0.0071	0.0086

Wavelength of absorption band maximum: $\lambda_i = 128.2$ nm
Integrated absorbance: $I_i = 17.5$

measured with $\lambda = 589.3$ nm are given. The refraction indices show variations due to experimental conditions but with distinct tendency to lower values with increasing Al_2O_3-content. The error of n is nearly $\Delta n = \pm 0.0005$. Fig. 2 shows the variation of the refractive indices as function of the mole ratio Al_2O_3/GeO_2. The reason of the slope is the decrease in Ge^{4+}-ions and the growing number of vacancies in the crystal structure. In all cases n_z has the highest value due to the shortest O—O-distances of the stable $[AlO_6]$-octahedra running parallel to the c-axis of the crystal. The difference between n_x and n_y is small on account of the similarity of

Table 4. Lattice parameters (Å) and densities ($g \cdot cm^{-3}$) of three (Al, Ge)-mullites (e.s.d.'s are in parentheses).

	Al_2O_3/GeO_2		
	1.28:1	1.50:1*	1.93:1
a	7.632(2)	7.644	7.644(1)
b	7.777(2)	7.779	7.760(1)
c	2.924(1)	2.925	2.923(1)
V (Å^3)	173.55(7)	173.95	173.38(6)
D_x	3.790	3.688	3.563

* Neumann (1984), e.s.d.'s are not published.

Table 5. Fractional atom coordinates and isotropic thermal parameters for the 1.93:1-(Al, Ge)-mullite (1st line) $\times 10^4$. Standard deviations in parentheses. The coordinates for the 1.50:1 (Al, Ge)-mullite (Neumann, 1984) are given in each 2nd line.

Atom		Mult.	x	y	z	B (Å^2)
Al(1)		0.25	0	0	0	0.53
		0.25	0	0	0	–
(Al, Ge)	Al	0.2500				
		0.2585	3499(2)	1606(2)	5000	0.48
	Ge	0.1543	3505(1)	1605(1)	5000	–
		0.1791				
Al*	Al	0.0957				
		0.0540	2308(13)	2966(12)	5000	0.88
	Ge	–	2302(5)	2949(5)	5000	–
		0.0085				
O(1)		0.5	3708(6)	2875(5)	0	1.06
		0.5	3708(2)	2869(1)	0	–
O(2)		0.5	1369(6)	799(5)	5000	0.98
		0.5	1369(1)	795(1)	5000	–
O(3)		0.1065	0	5000	5000	1.03
		0.1563	0	5000	5000	–
O*		0.0957	437(28)	4547(30)	5000	1.02
		0.0625	467(17)	4510(15)	5000	–

the electron density behaviour in the axis directions a and b. The variation of 2V with the chemical composition is not so pronounced but a slight decrease with growing Al_2O_3-content is obvious (Table 2).

In Table 3 as example the complete optical data of a dispersion measurement of the 1.93:1 (Al, Ge)-mullite are given. The data of the other mullites are available on request from the authors.

Table 6. Selected interatomic distances (Å) and bond-angles (°) for 1.50:1 (Al, Ge)-mullite (Neumann, 1984) and 1.93:1 (Al, Ge)-mullite (this study) with e.s.d.'s in parentheses.

		1.50:1		1.93:1	
Octahedron	Al(1)–O(2)	4 × 1.902(2)		1.901(3)	
AlO_6	–O(1)	2 × 1.930(1)		1.922(3)	
	mean:	1.911(14)		1.908(10)	
	O(2)–O(2)	2 × 2.432(2)	79.48(5)	2.432(9)	79.52(21)
	O(2)–O(2)	2 × 2.925	100.52(5)	2.923	100.48(21)
	O(2)–O(1)	4 × 2.713(1)	90.12(5)	2.700(5)	90.13(12)
	O(2)–O(1)	4 × 2.706(1)	89.88(5)	2.708(6)	89.83(16)
Tetrahedron 1	(Al, Ge)–O(1)	2 × 1.769(1)		1.769(2)	
$(Al, Ge)O_4$	–O(2)	1.750(1)		1.745(5)	
	–O(3)	1.693(1)		1.694(1)	
	mean:	1.745(36)		1.744(31)	
	O(1)–O(1)	2.925	111.56(8)	2.923	111.39(23)
	O(1)–O(2)	2 × 2.817(1)	106.37(4)	2.816(6)	106.50(16)
	O(1)–O(3)	2 × 2.845(1)	110.52(4)	2.844(4)	110.38(14)
	O(2)–O(3)	2.844(1)	111.35(4)	2.844(5)	111.57(16)
Tetrahedron 2	(Al, Ge)–O(1)	2 × 1.769(1)		1.769(2)	
$(Al, Ge)O_4$	–O(2)	1.750(1)		1.745(5)	
	–O*	1.733(17)		1.731(23)	
	mean:	1.755(17)		1.754(17)	
	O(1)–O(1)	2.925	111.56(6)	2.932	111.39(23)
	O(1)–O(2)	2 × 2.817(1)	106.37(4)	2.816(6)	106.50(16)
	O(1)–O*	2 × 2.716(14)	101.71(17)	2.723(20)	102.16(41)
	O(2)–O*	3.140(15)	128.76(32)	3.121(21)	127.80(74)

		1.50:1		1.93:1	
Tetrahedron 3	(Al, Ge)–O(1)	2×1.769(1)		1.769(2)	
$(Al, Ge)O_4$	–O(2)	1.750(1)		1.745(5)	
	–O*	1.809(16)		1.793(23)	
	mean:	1.774(25)		1.768(17)	
	O(1)–O(1)	2.925	111.56(6)	2.923	111.39(23)
	O(1)–O(2)	2×2.817(1)	106.37(4)	2.817(6)	106.50(16)
	O(1)–O*	2×3.058(15)	117.51(13)	3.038(21)	117.06(28)
	O(2)–O*	2.617(16)	94.70(34)	2.628(23)	95.92(68)
Tetrahedron 4	(Al, Ge)–O(1)	2×1.816(2)		1.813(6)	
Al^*O_4	–O(2)	1.820(4)		1.829(10)	
	–O*	1.858(10)		1.884(23)	
	mean:	1.827(20)		1.835(30)	
	O(1)–O(1)	2.925	107.31(20)	2.923	107.47(50)
	O(1)–O(2)	2×2.817(1)	101.55(15)	2.816(6)	101.28(38)
	O(1)–O*	2×3.145(10)	118.01(25)	3.174(19)	118.27(44)
	O(2)–O*	2.973(11)	107.83(55)	2.995(23)	107.50(88)

Crystallographic data

All members of the solid solution series crystallize in the space group *Pbam*. In contrast to the (Al, Si)-mullites there exist no remarkable change in the lattice constants because the ionic radii of Al^{3+} and Ge^{4+} are nearly equal. Table 4 shows the lattice constants refined from single crystal measurements and the densities of three representative (Al, Ge)-mullites.

As dicussed below the average structures of the series have comparable atomic parameters. Only the positions Al*, O* and O(3) will differ in the site occupancies. An untwinned crystal of a 1.93:1 (Al, Ge)-mullite was measured with a four-circle diffractometer (CAD-4 Enraf Nonius) with AgK_α radiation. A total of 624 reflections has been measured by $\omega/2\vartheta$-scan technique. The number of independent reflections with $I > 3\sigma(I)$ was 207. The intensities were corrected for Lp-effects. The absorption (dimensions of the crystal: $0.21 \times 0.30 \times 0.30$ mm^3 with $\mu = 33.66$ cm^{-1}) was applied by using the program ABSCOR (Eck and Kato, 1975).

The structure was refined by full-matrix least-squares calculations with the program ORXFLS3 (Busing et al., 1971). Scattering curves for all atoms and anomalous dispersion terms were taken from 'International Tables for X-ray Crystallography' (1974). As starting values the atomic positional parameters determined for the 1.50:1 (Al, Ge)-mullite (Neumann, 1984) have been used. The R-value converged to 0.039 ($R_w = 0.041$) with isotropic temperature factors. The final positional parameters and equivalent temperature factors are given in Table 5. For comparison the corresponding parameters of the 1.50:1-mullite (Neumann, 1984) are added. The assumption of the nearly equal values of both mullites was confirmed. The occupancies of the positions Al*, O* and O(3) yield the number of vacancies with $x = 0.38$ (1.93:1-mullite) and $x = 0.25$ (1.50:1-mullite) in very good accordance with the chemical composition. It is noteworthy that the Al*-position of the 1.93:1-mullite does not contain any remarkable content of Ge^{4+}. The refinement proved to be insensitive to low contents of Ge^{4+}. A refinement of the 1.28:1-mullite is in progress to check the cation distribution in the (*)-positions. Interatomic distances and bond-angles for the 1.93:1-mullite are given in Table 6. A comparison with the corresponding values of the 1.50:1-mullite shows that no significant differences exist.

Conclusion

With the flux technique the syntheses of (Al, Ge)-mullites in the limits of 1.28:1 to 1.96:1 (Al_2O_3:GeO_2) was successful. The existence of a continuous solid solution series was confirmed. It is not yet sure whether the limits of this series of the (Al, Ge)-mullites found here are definitive. Substitutions and incorporations may extend the range of solid solution (Saalfeld and Klaska, 1985). The relation between the chemical composition and the

optical behaviour also confirms the character of a solid solution series. As assumed the crystal structures do not show significant differences with the exception of the site occupancies for the positions Al*, O*, O(3). The (Al, Ge)-mullites also show diffuse reflections. However, these reflections are rather weak and not so pronounced as in the case of the (Al, Si)-mullites. Additional studies with electron microscopy are planned to get further informations on domain patterns and disorder of the (Al, Ge)-mullites.

Acknowledgements. We wish to express our thanks to the Deutsche Forschungsgemeinschaft for financial support.

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