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BRIEF COMMUNICATION

Crystal Structure of a New Digermanate: $Al_2Ge_2O_7$

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The structure of $Al_2Ge_2O_7$ has been determined by using a single crystal. The symmetry is monoclinic ($C2/c$, $Z = 4$) with unit cell parameters $a = 7.132(1)$ Å, $b = 7.741(1)$ Å, $c = 9.702(2)$ Å, $\beta = 110.62(2)°$. The structure is characterized by digermanate groups (Ge_2O_7) and by AlO_5 bipyramids with two common edges forming $(AlO_3)_\infty$ chains. The relationship with the thortveitite structure is discussed in terms of coordination polyhedra. © 1986 Academic Press, Inc.

Introduction

As described in a previous paper, a new phase $Al_2Ge_2O_7$ has been prepared and identified in the Al_2O_3–GeO_2 system (*1*). Recently the stoichiometric composition has been confirmed and the unit-cell and crystal symmetry have been determined on single crystals grown by chemical vapor transport (*2*).

This paper reports on the full structural investigation of $Al_2Ge_2O_7$ achieved on a single crystal. The crystallographic description of this compound is given with regard to that of germanates with the thortveitite-type structure.

Experimental

Among the flat available crystals, one single crystal was selected. All experimental data are given in Table I. They were corrected for Lorentz-polarization and absorption effects. Scattering factors of Al^{3+}, Ge^{4+}, and O^{-2} ions came from Cramer and Waber's table (*3*).

In a first step, approximate atomic coordinates were determined from a Patterson map which clearly showed the Ge–Ge and Al–Ge vectors. A subsequent Fourier synthesis revealed the positions of the oxygen atoms. A few refinement cycles led to a final agreement factor $R = 0.051$ in the space group $C2/c$ (the space group Cc was excluded because of a higher R factor = 0.057).

All atomic parameters and thermal factors are gathered in Tables II and III.

Discussion of the structure

A projection of the structure on the (010) plane is shown in Fig. 1. It is characterized by well-defined Ge_2O_7 groups consisting of two tetrahedra with a common atom O(1). The variation of O–Ge–O angles in the tetrahedra is from 104.9° to 114.6° (average = 109.4°), which is close to the ideal value of 109.47°. Al^{3+} ions have five oxygen neigh-

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TABLE I

CRYSTALLOGRAPHIC DATA AND STRUCTURE REFINEMENT PARAMETERS

Crystal shape	Platelet (0.06 × 0.06 × 0.03 mm) limited with (001), (110), (111), (110) planes
Lattice parameters at 295 K	a = 7.132(1) Å b = 7.741(1) Å β = 110.62(2)° c = 9.702(2) Å Z = 4
Crystal symmetry	$C2/c$
Density	
Experimental	d = 4.0 ± 0.1 g/cm³
Theoretical	d = 4.06 g/cm³
Data collection	C.A.D. 3 Enraf-Nonius diffractometer with graphite monochromator λMo$K\alpha$ $\theta/2\theta$ scan $0° < \theta < 35°$ up to 9 scans on weak reflections $\sin\theta/\lambda_{max}$ = 0.82 $0 \le h \le 10$ $0 \le k \le 10$ $-12 \le l \le 12$ 900 reflections measured 540 reflections utilized ($I \ge 3\sigma(I)$)
Data corrections	Lorentz and polarization effects Absorption corrections based on the crystal morphology (μ = 58 cm^{-1})
Resolution of the structure	Patterson and Fourier synthesis. Atomic scattering factors from Cromer and Waber (Int. Tables for Crystallography, 1974, Vol. IV)
Agreement factor R	R = 0.051

bors, building a distorted trigonal bipyramid (Fig. 2). Those pyramids are linked by common edges O(3)–O(3′) and O(4)–O(4′) to form infinite $(AlO_3)_\infty$ chains, and these chains are linked to the (Ge_2O_7) groups by the O(2) oxygen atoms. Notice that O(1) and O(2) have only two cation neighbors and consequently they exhibit thermal factors higher than those of O(3) and O(4) which are linked to three cations.

TABLE II

POSITIONAL PARAMETERS AND ISOTROPIC THERMAL FACTOR FOR $Al_2Ge_2O_7$

Atom	X	Y	Z	B (Å²)
Ge	0.2414(1)	0.2488(1)	0.2945(1)	0.34(7)
Al	0.3290(4)	0.0764(5)	0.0211(3)	0.36(9)
O(1)	0	0.1694(18)	0.25	0.94(17)
O(2)	0.2891(11)	0.4310(11)	0.3982(7)	0.78(11)
O(3)	0.3972(10)	0.0834(11)	0.3973(7)	0.46(10)
O(4)	0.2887(10)	0.2739(10)	0.1292(7)	0.47(11)

TABLE III

REFINED TEMPERATURE FACTOR EXPRESSIONS ($\beta \times 10^4$)

Atom	$\beta(1,1)$	$\beta(2,2)$	$\beta(3,3)$	$\beta(1,2)$	$\beta(1,3)$	$\beta(2,3)$
Ge	31	0	13	4	4	2
Al	29	0	15	6	5	1
O(1)	46	14	45	−69	12	133
O(2)	46	14	28	19	21	−8
O(3)	39	0	19	−15	0	8
O(4)	44	5	9	−15	13	7

Main interatomic distances and angles for Al and Ge surroundings are given in Table IV.

Oxygen–oxygen distances in the Ge_2O_7 groups have values within 2.7–3.0 Å; in AlO_5 bipyramids, they are between 2.38 and 3.0 Å. Two very short O–O distances, 2.38 and 2.40 Å, account for high bond strength in the $(AlO_3)_\infty$ bipyramid chains. The same behavior is observed in andalusite, Al_2SiO_5, where half of the Al atoms are arranged in AlO_5 trigonal bipyramids linked in pairs by very short O–O edges (2.25 Å), forming (Al_2O_8) groups (*4*).

The structure of $Al_2Ge_2O_7$ is closely related to the thortveitite structure, although

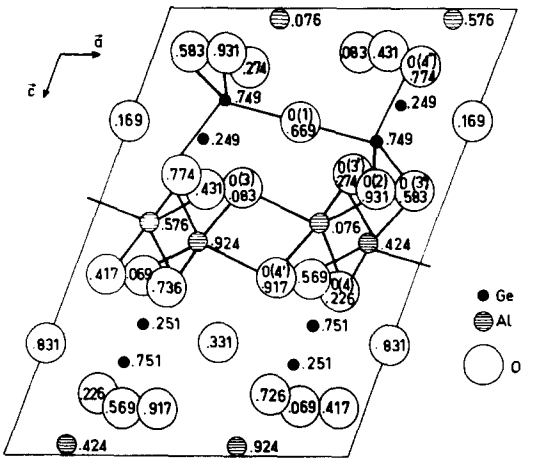

FIG. 1. Projection of $Al_2Ge_2O_7$ structure along the [010] direction. One Ge_2O_7 group is represented, as well as projection of chains consisting of distorted bipyramids AlO_5. Chains are running along [110] and [1$\bar{1}$0] directions.

TABLE IV

MAIN INTERATOMIC DISTANCES (Å) AND ANGLES (°) IN THE Ge_2O_7 AND AlO_5 POLYHEDRA

Ge–O(2) = 1.696(8)		
Ge–O(1) = 1.734(5)		
Ge–O(3″) = 1.757(7)	Ge–O(1)–Ge = 138.5(4)	
Ge–O(4″) = 1.762(8)	Ge–O(2)–Al = 140.7(5)	
Average d_{Ge-O} = 1.74		
	O(2)–Al–O(4) = 127.6(6)	Σ = 359.9
	O(2)–Al–O(3) = 115.7(5)	
	O(3)–Al–O(4) = 116.6(5)	
Al–O(2) = 1.748(9)	O(3′)–Al–O(4′) = 167.8(6)	
Al–O(4) = 1.820(7)		
Al–O(3) = 1.831(7)	O(4)–Al–O(4′) = 79.2(6)	
Al–O(3′) = 1.903(9)	O(3)–Al–O(4′) = 94.7(5)	
Al–O(4′) = 1.932(9)	O(2)–Al–O(4′) = 94.8(6)	
Average d_{Al-O} = 1.85	O(4)–Al–O(3′) = 93.4(6)	
	O(3)–Al–O(3′) = 79.7(5)	
	O(2)–Al–O(3′) = 97.5(6)	

it differs by the fivefold coordination of Al atoms. In thortveitite-type germanates ($In_2Ge_2O_7$ and $Sc_2Ge_2O_7$), infinite layers $(MO_3)_\infty$ of octahedra, instead of chains of bipyramids, are separated by Ge_2O_7 groups (*5, 6*). Another difference lies in the value of the Ge–O_1–Ge′ angle in the pyrogermanate group, which is 138.5° in $Al_2Ge_2O_7$ and 180° in thortveitite because of symmetry.

$Al_2Ge_2O_7$ belongs to the same family as several diphosphates and vanadates: $\alpha - Cu_2P_2O_7$ (*7*), $\alpha - Zn_2V_2O_7$ (*8, 9*), $\beta - Cu_2V_2O_7$ (*10*); but among the aluminum silicates or germanates it exhibits the specific character of having cations which are only four or fivefold coordinated.

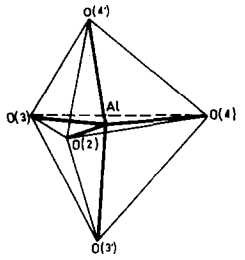

FIG. 2. Distorted trigonal bipyramid AlO_5.

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