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New Gallium Germanates with Tunnel Structures: α-Ga_4GeO_8 and $Ga_4Ge_3O_{12}$

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The structure of several gallium germanates has been established or confirmed (Ga_4GeO_8 α and β forms, Ga_2GeO_5, $Ga_4Ge_3O_{12}$). Among them, α-Ga_4GeO_8 exhibits a new type of tunnel structure resulting from an intergrowth of GeO_2 rutile elements in the β-gallia network. Large hexagonal tunnels take place at the junction of both lattices. This compound is the first term of a series having as general formula $Ga_4M_{2n-1}O_{4n+4}$. Several other compounds M = Ge (n = 1, 2), Ti (n = 2, 3, 11 . . .), and Sn (n = 1) belong to the same family.

Introduction

In a previous study on trivalent ion germanates, one of us determined the Ga_2O_3–GeO_2 phase diagram (*1*). As GeO_2 may adopt either quartz or rutile structure, some of the gallium germanates are isomorphous to silicates and some have new types of structures. Their crystal growth and characterization have been reported recently (*2*).

Two compounds with Ga_2GeO_5 formula are known and they are isostructural with aluminum silicates having andalusite and mullite structures. Three other phases have been identified but their structures were undetermined up to now due to the lack of single crystals: $Ga_4Ge_3O_{12}$ and two modifications of Ga_4GeO_8.

Structural data on these compounds are reported in this paper with the complete description of α-Ga_4GeO_8. No homologous compounds exit in the Ga_2O_3–SiO_2 system, but a series of parent phases were observed in the Ga_2O_3–TiO_2 system (*3–9*). A general model is proposed for the structure of these gallium germanates and titanates.

Structure of Ga_4GeO_8 Compounds

Two modifications are known for Ga_4GeO_8: the low temperature α-form and the β-form stable at $T \geq 1300$ K (*1*). Single crystals of both have been prepared from chemical vapor transport (*2*).

(*1*) β-Ga_4GeO_8

The X-ray study on a single crystal gave the lattice constants of a monoclinic unit cell with the unique space group $P2_1/c$, $Z = 4$. An indexed powder diagram of β-Ga_4GeO_8 is given in Table I. A metastable phase with Al_4GeO_8 composition had also been prepared (*1*). Its X-ray powder pattern can be interpreted with similar lattice constants.

It is likely that these two phases are isostructural with the mixed valence iron ger-

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TABLE I

DEBYE–SCHERRER POWDER PATTERN OF β-Ga_4GeO_8

d (Å)	I/I_1	$h\ k\ l$		
5.75	5	0 1 1		
5.46	5	1 1 0		
3.69	5	$\bar{2}$ 1 1	$\bar{2}$ 0 2	
3.66	90	2 0 0		
3.59	10	1 2 0		
3.37	10	$\bar{2}$ 1 2		
3.34	1	2 1 0		
3.03	80	1 2 1		
2.988	5	1 0 2		
2.915	5	$\bar{2}$ 2 1		
2.876	20	0 2 2		
2.826	20	$\bar{1}$ 1 3		
2.807	100	1 1 2		
2.734	10	2 2 0		
2.716	5	$\bar{3}$ 0 2		
2.582	10	$\bar{3}$ 1 2		
2.571	90	$\bar{3}$ 1 1	$\bar{1}$ 3 1	
2.368	5	$\bar{2}$ 2 3		
2.352	10	2 2 1		
2.337	50	1 3 1	3 1 0	
2.238	5	2 0 2		
2.133	15	1 1 3		
2.057	10	0 4 0		
2.011	15	0 0 4		
1.990	10	$\bar{1}$ 4 1	$\bar{2}$ 2 4	1 4 0
1.6066	5	1 2 4	1 5 0	
1.4784	15	3 3 2	$\bar{5}$ 2 4	
1.4385	50	0 4 4		
1.4356	30	$\bar{4}$ 4 3		
1.4331	20	4 0 2		
1.4300	10	$\bar{2}$ 5 3		

manate $Fe^{II}Fe^{III}_2Ge_2O_8$ the structure of which has been published recently (*10*) and which possesses the same space group $P2_1/c$ as β-Ga_4GeO_8. Unit-cell parameters for the three compounds are gathered in Table II. The structure refinement of β-Ga_4GeO_8 is now under way.

(*2*) α-Ga_4GeO_8

(*a*) *Structural determination.* This phase crystallizes with a new type of structure that we have completely determined on a single crystal. Experimental crystallographic data are given in Table III.

TABLE II

LATTICE CONSTANTS OF M_5O_8 COMPOUNDS (SPACE GROUP $P2_1/c$, $Z = 4$)

Compound	a (Å)	b (Å)	c (Å)	β (°)	V (Å^3)
Al_4GeO_8	8.007(5)	7.926(5)	8.809(5)	117.6(1)	498.6
Ga_4GeO_8-β	8.258(2)	8.226(2)	9.084(2)	117.63(2)	546.7
$Fe_3Ge_2O_8$ (*10*)	8.479	8.333	9.196	117.7	575.3

During the preliminary investigation of α-Ga_4GeO_8 crystals, the following relationships between this phase and β-gallia were observed:

$\mathbf{a} = \mathbf{a}'$

$\mathbf{b} = \mathbf{b}'$

$\mathbf{c} = -\frac{1}{3}\mathbf{a}' - \frac{5}{3}\mathbf{c}'$

a, **b**, **c**, unit-cell vectors of α-Ga_4GeO_8

a′, **b**′, **c**′, unit-cell vectors of β-Ga_2O_3

Two parameters are similar, especially the **b** vectors which have a very short length (~3 Å). Among the possible space group $C2/m$, $C2$, and Cm, we have first tried to solve the structure in the holohedral space group of β-gallia (*11*).

TABLE III

CRYSTALLOGRAPHIC AND EXPERIMENTAL DATA FOR α-Ga_4GeO_8 STRUCTURE REFINEMENT

Crystal size	Needle-shaped crystal 0.03 × 0.02 × 0.2 mm
Space group	$C2/m$
Lattice constants at 295 K	a = 12.169(3) Å b = 3.005(1) Å β = 125.06(2)° c = 9.414(2) Å Z = 2
Specific gravity	Measured 5.5(1) Mg/m3 Theoretical 5.6 Mg/m3
Experimental conditions	Nonius CAD 3 diffractometer Graphite monochromator λMoK_α radiation = 0.7107 Å $\theta/2\theta$ scan $3.5 < \theta < 37.0$ $\sin\theta/\lambda < 0.85$ $0 \le h \le 15$ $0 \le k \le 4$ $-12 \le l \le 12$
Number of reflections	603 measured 565 with $I > 3\sigma(I)$
Number of parameters	20
Corrections	Lorentz and polarization effects No absorption corrections μ = 90 cm^{-1}, $\mu R < 1$
Atomic scattering factors	Int. Tables for X-Ray Crystallography, 1974, Vol. IV (Cromer and Waber's table)
Refinement factor	R = 0.029

In the unit cell containing two Ga_4GeO_8 formulas, we have to place 16 anions and 10 *M* cations. These can be taken as equivalent since Ga^{3+} and Ge^{4+} are isoelectronic. Considering the available Wyckoff positions of multiplicity 2, 4, or 8, two of the cations necessarily are in a twofold position. This was confirmed on a Patterson map, together with two fourfold positions for the remaining cations. Then a Fourier map provided the positions of the oxygen atoms. Due to the short **b** axis, all atoms are constrained in two planes of the structure ($z = 0$ and $z = 0.5$).

Refinement of the structure using isotropic thermal coefficients rapidly converged to a satisfactory agreement factor $R = 0.029$. Final atomic parameters are given in Table IV. As previously mentioned, Ga and Ge ions are not discernible by X rays, but the probable distribution of cations on the *M* positions has been drawn from the values of M–O bond lengths (Table V).

Three cationic sites are present in the structure: M_3 is tetrahedral. M_2 and M_1 are octahedral positions. The mean value of M_3–O distances (1.83 Å) corresponds with no ambiguity to the usual Ga–O distance in a GaO_4 tetrahedron. For a GeO_4 tetrahedron, the Ge–O bond would be shorter (~1.74–1.79 Å). Germanium atoms are so found in octahedral sites only. It is reasonable to assume that Ge atoms are found in the octahedral sites M_1 with smaller size. Gallium atoms are thus in both tetrahedral and octahedral M_2 sites. This defines units made of two tetrahedra plus two octahedra, quite similar to the units of β-gallia.

TABLE IV

ATOMIC PARAMETERS AND THERMAL FACTORS IN α-Ga_4GeO_8

Atom	Wyckoff position	*x*	*y*	*z*	*B* (Å²)
M(1) = Ge	2a	0	0	0	0.29(2)
M(2) = Ga(1)	4i	0.7576(1)	0	0.3596(1)	0.40(1)
M(3) = Ga(2)	4i	0.4621(1)	0	0.2809(1)	0.38(1)
O(1)	4i	0.1627(5)	0	0.2183(7)	0.53(7)
O(2)	4i	0.6446(5)	0	0.4618(7)	0.49(7)
O(3)	4i	0.4403(6)	0	0.0738(7)	0.65(7)
O(4)	4i	0.8912(6)	0	0.3064(7)	0.65(8)

Note. Estimated standard deviations are given in parentheses.

TABLE V

MAIN INTERATOMIC DISTANCES (IN ANGSTROM) IN α-Ga_4GeO_8

Tetrahedral site			
M(3)–O(3)	1.810(8)		
M(3)–O(4)	2 × 1.816(5)		
M(3)–O(2)	1.867(4)		
Mean value = 1.83	in tetrahedra	Ge – O = 1.74	GeO_2 quartz(12)
		Ga – O = 1.82	β-Ga_2O_3(11)
Octahedral sites			
M(1)–O(1)	2 × 1.862(4)		
M(1)–O(3)	4 × 1.960(6)		
Mean value = 1.93	in octahedra	Ge – O = 1.90	GeO_2 rutile(13)
		Ga – O = 2.00	β-Ga_2O_3(11)
M(2)–O(1)	2 × 1.896(3)		
M(2)–O(4)	1.956(9)		
M(2)–O(2′)	2 × 2.050(3)		
M(2)–O(2)	2.083(8)		
Mean value = 1.99			
Vacant site in tunnels			
□–O(1)	2.32		
□–O(3)	3 × 2.32		
□–O(4)	2 × 2.59		
□–O(4)	2.68		

(b) Description of the structure. A projection of the α-Ga_4GeO_8 structure on the (010) plane is given on Fig. 1. As shown on the corresponding idealized model, the structure consists of β-gallia blocks linked by [010] chains of GeO_6 octahedra. Therefore, α-Ga_4GeO_8 can be described as β-gallia with insertion of rutile chains. This structural analysis confirms the model proposed by Bursill and Stone (*7, 9*) from a high-resolution electron microscopy study.

The anionic network of α-Ga_4GeO_8 is not close packed as it is in β-Ga_2O_3. It exhibits channels running along the [010] direction. One may consider that these tunnels result from the clustering of oxygen vacancies in (001) planes. As shown on Fig. 2, the idealized anionic sublattice of α-Ga_4GeO_8 can be obtained by the suppression of one every ninth (001) plane in β-Ga_2O_3 and a simulta-

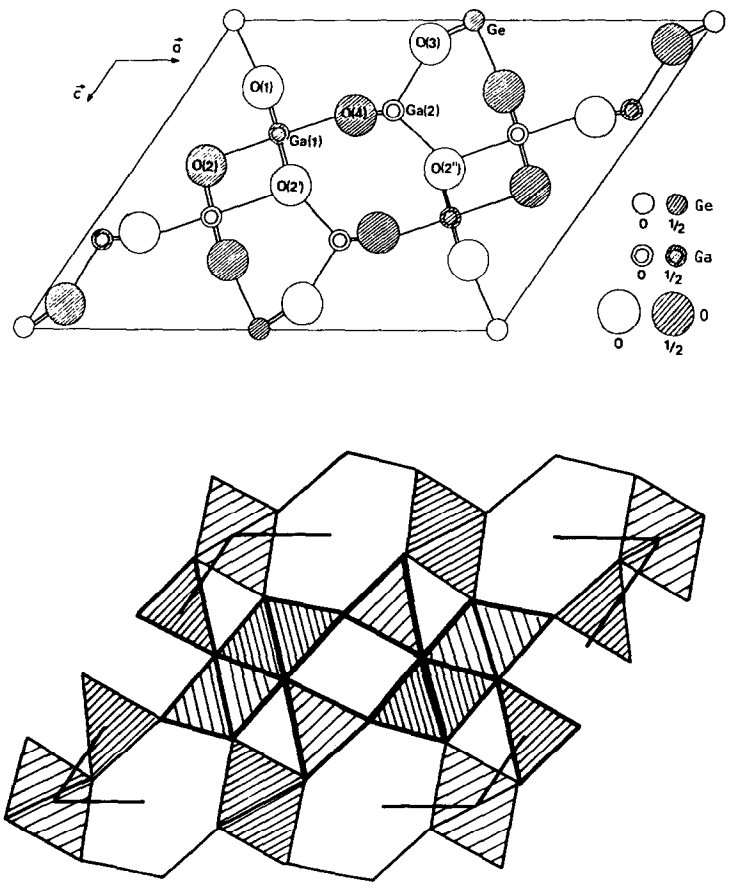

FIG. 1. Projection of the α-Ga_4GeO_8 structure on the (010) plane and the corresponding description in polyhedra.

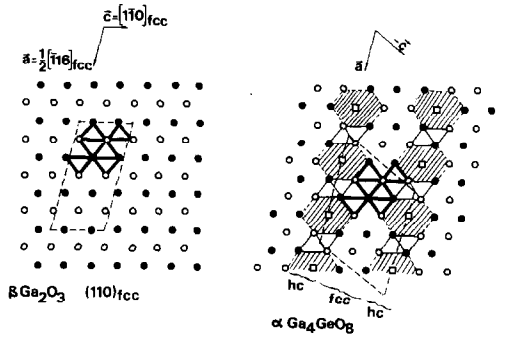

FIG. 2. Structural relationships between β-gallia and α-Ga_4GeO_8. Circles indicate oxygen positions in (010) planes (full circles, $Z = 0$; empty circles, $Z = 0.5$).

neous crystallographic shear with a $[\frac{1}{2}, 0, \frac{1}{2}]$ vector. A double chain (gallium octahedra plus tetrahedra) of β-gallia is substituted by a single chain of germanium octahedra to give the Ga_4GeO_8 composition. A schematic writing for these relations between the two structures would be

$$[Ga_3]_{oct}[Ga_3]_{tet}O_9 \rightarrow [Ga_2Ge]_{oct}[Ga_2]_{tet}O_8\square$$

Tunnels are limited by four chains of octahedra and two chains of tetrahedra. Their dimensions are quite comparable to that of some tungsten bronzes (*14, 15*). Bottlenecks in the tunnels are at $z = 0.25$. Large vacant sites with seven oxygen neighbors

are found at $z = 0$. Comparable sites with the same size (2.3–2.7 Å) and coordination (sevenfold) are occupied by Na^+ in $NaMoPO_6$, Ca^{2+} in $CaTiSiO_5$ (titanite), and Nd^{3+} in A-Nd_2O_3 (*16*). This channel structure could therefore be convenient for the insertion of middle-sized cations.

Intergrowth between β-Gallia and Rutile

In the Ga_2O_3–TiO_2 system, phases belonging to a series with general formula $Ga_4Ti_{2n-1}O_{4n+4}$ were observed (*3–9*). For the term $n = 11$, an X-ray structural determination was performed (*6*). For others, observations by high-resolution electron microscopy resulted in the same description as ours for α-Ga_4GeO_8, i.e., these phases are built by an intergrowth of β-gallia and rutile (*5, 9*). The (010) plane of β-gallia is parallel to the (001) plane of MO_2 and channels with hexagonal section are spaced along $[103]_{\beta\text{-gallia}} /\!/ [210]_{\text{rutile}}$ at ~10.3 Å.

In the Ga_2O_3–GeO_2 system, we have also obtained the term $n = 2$, $Ga_4Ge_3O_{12}$, but as powder sample only. Its powder diagram has been indexed with a monoclinic unit cell deriving from α-Ga_4GeO_8 by insertion of more rutile elements. We have also been able to characterize the structure of a previously prepared phase Ga_4SnO_8 (*17*): it is isomorphous to α-Ga_4GeO_8.

Then, our description of α-Ge_4GeO_8 provides the link for a general pattern of possible intergrowth between β-gallia and rutile structures with formation of hexagonal tunnels. The first term of the series $Ga_4M_{2n-1}O_{4n+4}$ has the structure of α-Ga_4GeO_8 and the last term is MO_2 rutile. According to the composition, β-gallia units are more or less diluted in rutile. Models for ordered phases with space group $C2/m$, $Z = 2$ are shown in Fig. 3, including the structure of $Ga_4Ti_{21}O_{48}$ determined by Lloyd *et al.* (*6*).

Lattice constants of phases identified in this series are gathered in Table VI. For the terms $n = 2, 3$, and 5 of titanates, parameters are deduced from values given by Bursill and Stone (*9*) assuming the structural model proposed in Fig. 3.

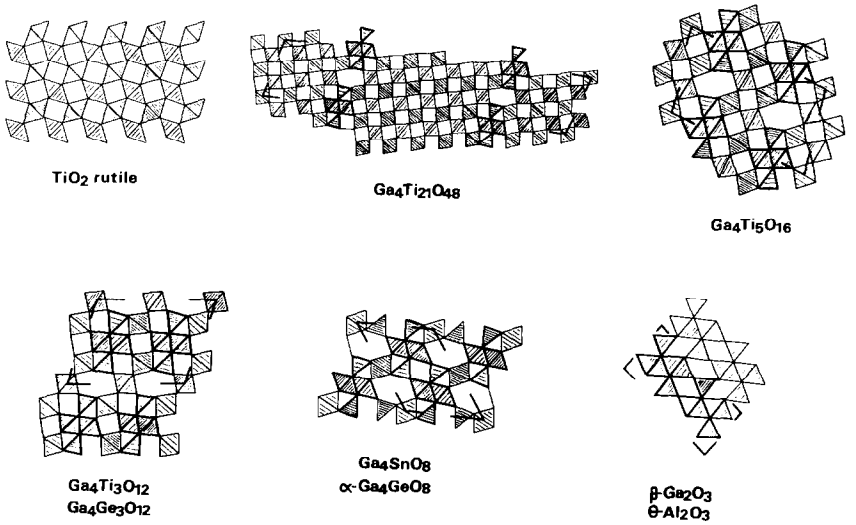

FIG. 3. Models for ordered structures $Ga_4M_{2n-1}O_{4n+4}$ with space group $C2/m$, $Z = 2$ resulting from intergrowth of rutile and β-gallia. Projection along the two-fold axis ($b \simeq 3$ Å).

TABLE VI

LATTICE CONTANTS OF COMPOUNDS IN THE SERIES $Ga_4M_{2n-1}O_{4n+4}$

n	Compound	a (Å)	b (Å)	c (Å)	β (°)	V (Å^3)
11	$Ga_4Ti_{21}O_{48}$	51.80	2.975	10.302	103.8	1541.8
5	$Ga_4Ti_9O_{24}$	25.32	2.96	10.3	90.0	772.0
3	$Ga_4Ti_5O_{16}$	17.76	2.96	10.3	103.2	525.8
2	$Ga_4Ti_3O_{12}$	14.16	2.96	10.3	105.2	416.6
2	$Ga_4Ge_3O_{12}$	13.69	2.890	10.09	106.5	382.8
1	Ga_4SnO_8	12.15	3.075	10.49[a]	130.7	297.1
1	Ga_4GeO_8	12.17	3.005	10.25[a]	131.26	281.8

[a] In order to make easier the comparison with other compounds, the c constant given for Ga_4MO_8 compounds corresponds to $(a + c)$ of the standard unit cell.

Conclusion

Among the several compounds of the Ga_2O_3–GeO_2 system which were obtained as single crystals, the structure of the two modifications of Ga_4GeO_8 are reported. The β-high temperature form is isostructural with $Fe_3Ge_2O_8$ (*10*). The α-form is a new structural type belonging, as well as $Ga_4Ge_3O_{12}$, to a general series.

The well-known Magneli phases MO_{2n-1} are a way to pass from MO_2 rutile to M_2O_3 corundum by a (121) crystallographic shear in the rutile structure. The series $Ga_4M_{2n-1}O_{4n+4}$ is another possibility to pass from MO_2 rutile to M_2O_3 by a (210) crystallographic shear and insertion of β-gallia units.

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