Polymorphism of Strontium Monogallate: The Framework Structures of β-SrGa$_2$O$_4$ and ABW-Type γ-SrGa$_2$O$_4$

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The crystal structures of two modifications of strontium monogallate have been investigated by single-crystal X-ray diffraction. A β-phase corresponding to the stable modification at room temperature and γ-SrGa$_2$O$_4$, a quenched high-pressure polymorph prepared at 1250°C and 2.5 GPa. β-SrGa$_2$O$_4$ is monoclinic, space group $P12_1/c1$, $a = 8.3770(3)$ Å, $b = 8.9940(2)$ Å, $c = 10.6800(4)$, $\beta = 93.932(2)°$, $V = 802.8(5)$ Å^3, $Z = 8$, $D_{calc} = 4.82$ g cm^{-3}, w$R2 = 0.083$ for 2351 reflections; γ-SrGa$_2$O$_4$ is monoclinic as well, space group $P12_1/n1$, $a = 8.1100(2)$ Å, $b = 10.7610(3)$ Å, $c = 9.0570(2)$ Å, $\beta = 91.569(1)°$, $V = 790.1(3)$ Å^3, $Z = 8$, $D_{calc} = 4.89$ g cm^{-3}, w$R2 = 0.068$ for 2300 reflections. The structures of both phases are characterized by layers of six-membered rings of GaO$_4$ tetrahedra perpendicular to the a axis. The stacking of the layers parallel to the a axis results in a three-dimensional framework containing channels that are occupied by the Sr cations for charge compensation. The two modifications differ with respect to the relative orientation of up (U) and down (D) pointing apices of adjacent tetrahedra within a single ring. The sequence of directedness is UUUDDD for γ-SrGa$_2$O$_4$ and UUDUDD for β-SrGa$_2$O$_4$, respectively. γ-SrGa$_2$O$_4$ belongs to the zeolite ABW-type structures and is apparently the only member with space group symmetry $P12_1/n1$ in combination with a doubled b axis compared to the ABW-aristotype (space group $Jmma$). It is the first member of this structure family with exclusively trivalent tetrahedral ions of only one chemical species and divalent nonframework cations within the channels. The compound is isotypic with the monclinic modification of CaGa$_2$O$_4$. © 2000 Academic Press

Key Words: SrGa$_2$O$_4$; ABW-type structure; polymorphism; high pressure phase; framework structure.

INTRODUCTION

The phase relationships in the system SrO–Ga$_2$O$_3$ have been investigated several times since the first study of Glasser and Dent Glasser (1). To date eight different double oxides have been reported: Sr$_4$Ga$_2$O$_7$ (2–5), Sr$_7$Ga$_4$O$_{13}$ (4), Sr$_3$Ga$_2$O$_6$ (3,4,6), Sr$_2$Ga$_2$O$_5$ (2,4), Sr$_3$Ga$_4$O$_9$ (2,4,5), SrGa$_2$O$_4$ (2–4), SrGa$_4$O$_7$ (2,4), and SrGa$_{12}$O$_{19}$ (4). According to Plakthii *et al.* (2) strontium monogallate occurs in two

different modifications: a monoclinic phase stable at room temperature (β-SrGa$_2$O$_4$) and a high-temperature form (α-SrGa$_2$O$_4$). Structural investigations have been limited to those compounds rich in Ga$_2$O$_3$, i.e., β-SrGa$_2$O$_4$ (7), SrGa$_4$O$_7$ (8), and SrGa$_{12}$O$_{19}$ (9,10).

As a part of an ongoing study of high-pressure calcium and strontium gallates, we have synthesized a new polymorph of SrGa$_2$O$_4$ (named γ-SrGa$_2$O$_4$) that is closely related in terms of its unit cell parameters to the β-form. The crystal structure of β-SrGa$_2$O$_4$ was determined by Schulze and Müller-Buschbaum (7) yielding extremely short Ga–O bond distances of 1.39 Å. This value is much lower than the distances usually observed in oxogallates and may indicate either that an incorrect space group symmetry was chosen or that wrong atomic positions were assigned.

The objectives of this study were twofold. First, a determination of the structure of γ-SrGa$_2$O$_4$ and second a reinvestigation of the crystal structure of β-SrGa$_2$O$_4$. We describe the similarities and differences in the structures of the two polymorphs and their structural relationships to other framework types.

EXPERIMENTAL DETAILS

Sample Preparation

The starting material for the high-pressure γ-phase was prepared by solid-state reactions, using SrCO$_3$ (Fluka, >98%) and Ga$_2$O$_3$ (Fluka, 99.99%) as reagents. The mixed powders were pressed into pellets and sintered in air at 1250°C for 24 h; this procedure was repeated twice. The sintered precursor material was reground and used for high-pressure experiments performed at the Bayerisches Geoinstitut. The experiments were carried out in a $\frac{1}{2}$-inch piston cylinder apparatus using talc–Pyrex cells with a tapered graphite heater. The samples were encapsulated in 1-cm long and 5-mm diameter welded Pt capsules. The experiments were performed at 2.5 GPa and 1250°C for 48 h. Pressure was calibrated against the quartz/coesite and kyanite/sillimanite transitions as well as the melting point of

diopside. A friction correction of 18% was applied to the nominal pressure on the basis of these calibration data. Temperature was measured with a Pt$_{90}$Rh$_{10}$-Pt thermocouple and controlled with an Eurotherm 818 controller. Temperatures are considered accurate within $\pm 10°C$ with a temperature gradient of about 5°C from the top to the middle of the capsule (Shaw and Fliervoet, unpublished data). The experiments were carried out using the hot-piston out technique. The samples were quenched isobarically by turning off the power of the furnace while maintaining pressure within 0.02 GPa of the run pressure. Quench rates were of the order of 75°C per second.

Single crystals of the β-phase were grown from a nonstoichiometric melt of composition 3SrO·2Ga$_2$O$_3$. One gram of mixed strontium carbonate and gallium oxide powder was placed in a covered 50-ml platinum crucible and heated in air from 100°C in 10 h to 1350°C. The mixture was held at this temperature for 8 days. It was then cooled down to 600°C at a rate of 5°C/h and finally quenched to room temperature.

X-Ray Single-Crystal Data Collection

Preliminary investigations included polarization microscopy and X-ray diffraction camera techniques. Precession and Laue photographs indicated monoclinic Laue symmetry $2/m$ for β- as well as for γ-SrGa$_2$O$_4$. The single-crystal diffraction data were collected from platy transparent optical-quality crystals using a Nonius Kappa-CCD diffractometer. Experimental details pertaining to data collection are given in Table 1. The morphology of the crystals was described by 7 and 9 external faces for β- and γ-SrGa$_2$O$_4$, respectively, and an analytical absorption correction based on the indexed faces was applied for both phases. Data reduction included Lorentz and polarization corrections.

Structure Solution and Refinement

The analysis of the systematic absences resulted in the assignment of the monoclinic space groups $P12_1/c1$ (for β-SrGa$_2$O$_4$) and $P12_1/n1$ for the γ-phase. The space group symmetry for the β-phase agrees with that proposed by Schulze and Müller-Buschbaum (7). Initial structural models that conform to these space group symmetries were found by direct methods, using the program SIR92 (11). The phase sets with the maximum combined figure of merit resulted in E maps, the most intense peaks of which could be interpreted in both cases as the atomic positions of tetrahedral framework structures. The subsequent refinements were carried out with the SHELXL-93 program (12). X-ray scattering factors for the different cations in their respective valence state, together with real and imaginary anomalous-dispersion coefficients, were taken from the "International Tables for X-ray Crystallography" (13); the values for O^{2-}

TABLE 1
Experimental Details for the X-Ray Data Collection and the Refinement of β- and γ-SrGa$_2$O$_4$

	β-SrGa$_2$O$_4$	γ-SrGa$_2$O$_4$
(A) Crystal-cell data		
a (Å)	8.3770(3)	8.1100(2)
b (Å)	8.9940(2)	10.7610(3)
c (Å)	10.6800(4)	9.0570(2)
β (deg)	93.932(2)	91.569(1)
V (Å^3)	802.8(5)	790.1(3)
Space group	$P12_1/c1$	$P12_1/n1$
Z	8	8
Formula	SrGa$_2$O$_4$	SrGa$_2$O$_4$
D_{calc} (g cm^{-3})	4.82	4.89
μ (cm^{-1})	277.7	282.2
(B) Intensity measurements		
Crystal size	$30 \times 70 \times 80\,\mu m^3$	$40 \times 85 \times 85\,\mu m^3$
Diffractometer	Nonius Kappa-CCD	
Monochromator	Graphite	
θ range	3.0°–30.0°	2.9°–30.0°
Reflection range	$-11 \le h \le 8$,	$0 \le h \le 11$,
	$\lvert k \rvert \leqslant 12$,	$\lvert k \rvert \le 15$,
	$-12 \le l \le 15$	$\lvert l \rvert \le 12$
No. of measured reflections	9334	4490
No. of unique reflections	2351	2300
No. of unique reflections $(l > 2\sigma(l))$	2215	1915
R_{int} for $2/m$	0.067	0.075
(C) Refinement of the structure		
No. of parameters used in the refinement	128	128
$R1$ $(F_0 > 4\sigma(F_0))$, $R1$ (all reflections)^a	0.031, 0.034	0.027, 0.034
$wR2$ $(F_0 > 4\sigma(F_0))$, $wR2$ (all reflections)^b	0.083, 0.084	0.068, 0.071
Weighting parameters a, b	0.025, 4.73	0.001, 0.00
Goodness-of-fit	1.17	0.91
Final $\Delta\rho_{min}$ (e$^-$/Å^3)	-1.32	-1.25
Final $\Delta\rho_{max}$ (e$^-$/Å^3)	1.44	1.16

^{a} $R1 = \sum \lVert F_0 \rvert - \lvert F_c \rVert / \sum \lvert F_0 \rvert$.
^{b} $wR2 = (\sum(w(F_0^2 - F_c^2)^2)/\sum(w(F_0^2)^2))^{1/2}$, $\quad w = 1/(\sigma^2(F_0^2) + (aP)^2 + bP)$, $P = (2F_c^2 + max(F_0^2, 0))/3$.

were taken from Hovestreydt (14). Each of the final least-squares calculations using anisotropic displacement parameters converged to $R1 = 0.034$ for 128 parameters for all independent reflections (cf. Table 1). The largest parameter shift in the final cycle was <0.001. The refined atomic coordinates, equivalent isotropic and anisotropic displacement factors as well as selected interatomic distances and angles are given in Tables 2 to 4. All atoms in both phases occupy general positions. Figures showing structural details were made using the programs STRUPLO (15) and ATOMS (16).

TABLE 2a
Atomic Coordinates and Equivalent Isotropic Displacement Factors for β-SrGa$_2$O$_4$

	x	y	z	$U(\text{eq})^a$
Sr1	−0.0350(1)	0.2389(1)	−0.3499(1)	0.010(1)
Sr2	0.4958(1)	0.2129(1)	−0.3696(1)	0.010(1)
Ga1	0.2806(1)	0.5647(1)	−0.3693(1)	0.007(1)
Ga2	0.2059(1)	0.3924(1)	−0.1203(1)	0.007(1)
Ga3	−0.1956(1)	0.4050(1)	−0.1103(1)	0.007(1)
Ga4	0.3213(1)	0.0562(1)	−0.1398(1)	0.007(1)
O1	0.0096(4)	0.3403(4)	−0.0681(3)	0.014(1)
O2	0.2399(4)	0.5853(4)	−0.5385(3)	0.012(1)
O3	0.5198(4)	−0.0101(4)	−0.1791(4)	0.013(1)
O4	0.1513(4)	0.4396(4)	−0.2858(3)	0.013(1)
O5	−0.2735(4)	0.2492(4)	−0.2072(3)	0.010(1)
O6	0.2831(4)	0.5640(4)	−0.0413(3)	0.010(1)
O7	0.2150(4)	0.0781(4)	−0.2969(3)	0.010(1)
O8	0.3466(4)	0.2434(4)	−0.0753(3)	0.012(1)

^{a} $U(\text{eq})$ is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

TABLE 2b
Atomic Coordinates and Equivalent Isotropic Displacement Factors for γ-SrGa$_2$O$_4$

	x	y	z	$U(\text{eq})^a$
Sr1	0.5034(1)	−0.3482(1)	−0.1996(1)	0.008(1)
Sr2	0.4942(1)	0.1095(1)	−0.2259(1)	0.010(1)
Ga1	0.8281(1)	0.1135(1)	0.0689(1)	0.007(1)
Ga2	0.2625(1)	−0.1134(1)	−0.4048(1)	0.007(1)
Ga3	0.7807(1)	−0.1378(1)	−0.0677(1)	0.007(1)
Ga4	0.6919(1)	−0.1350(1)	−0.4075(1)	0.007(1)
O1	0.1523(3)	−0.2581(3)	−0.4532(3)	0.008(1)
O2	0.7852(4)	−0.2185(3)	−0.2479(3)	0.009(1)
O3	0.1698(4)	−0.0349(3)	−0.2487(3)	0.012(1)
O4	0.9814(4)	−0.1348(3)	−0.0276(4)	0.011(1)
O5	0.7662(3)	0.2828(3)	0.0833(3)	0.008(1)
O6	0.7698(4)	0.0241(3)	−0.4232(4)	0.015(1)
O7	0.4795(4)	−0.1142(3)	−0.3402(4)	0.013(1)
O8	0.6924(4)	0.0192(3)	−0.0544(4)	0.013(1)

^{a} $U(\text{eq})$ is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

COMPARATIVE DESCRIPTION OF THE TWO MODIFICATIONS

For both modifications, pseudo-orthorhombic primitive unit cells of about $8 \times 9 \times 11$ Å^3 can be chosen (cf. Table 1). This points to a possible structural relationship between the two phases. Both β- and γ-SrGa$_2$O$_4$ belong to the group of stuffed framework structures consisting of sequences of tetrahedral layers. Each layer perpendicular to [100] is composed of trigonally shaped six-membered rings (S6R) of GaO$_4$ tetrahedra forming honeycomb-like nets. Figure 1 shows a projection parallel to [100] of one of the tetrahedral sheets in γ-strontium monogallate compared with a corresponding sheet in β-SrGa$_2$O$_4$. The single layers can be described as being built by condensation of two different types of unbranched vierer single chains via common corners: slightly folded chains (type I) and chains with a more pronounced degree of folding (type II). Linkage of the fundamental chains of type I yields straight zweier double chains with all S6R centers aligned parallel to the chain direction. Condensation of the vierer single chains of type II results in a zigzag pattern of the S6R. The equatorial oxygen atoms of the layers are not strictly coplanar. The tilting angle in the corrugated layers between the normal to the plane defined by the three basal O atoms of the tetrahedra and the [100] direction varies between 7° and 32° for γ-SrGa$_2$O$_4$ and between 19° and 30° for the β-phase, respectively. Subsequent layers are connected by bridging apical

TABLE 3a
Anisotropic Displacement Parameters (Å$^2 \times 10^3$) for β-SrGa$_2$O$_4$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Sr1	7(1)	12(1)	10(1)	−3(1)	1(1)	0(1)
Sr2	9(1)	11(1)	10(1)	1(1)	0(1)	1(1)
Ga1	7(1)	8(1)	6(1)	0(1)	2(1)	0(1)
Ga2	7(1)	8(1)	7(1)	0(1)	1(1)	0(1)
Ga3	8(1)	8(1)	6(1)	0(1)	2(1)	0(1)
Ga4	7(1)	8(1)	6(1)	0(1)	1(1)	0(1)
O1	8(2)	20(2)	16(2)	7(1)	4(1)	0(1)
O2	17(2)	12(2)	8(2)	−1(1)	−1(1)	6(1)
O3	7(2)	12(2)	19(2)	−4(1)	0(1)	−2(1)
O4	15(2)	16(2)	9(2)	4(1)	0(1)	−8(1)
O5	15(2)	8(2)	7(2)	−2(1)	−1(1)	−2(1)
O6	12(2)	11(2)	8(2)	−2(1)	4(1)	−4(1)
O7	13(2)	7(2)	8(2)	−1(1)	−2(1)	1(1)
O8	12(2)	8(2)	15(2)	−2(1)	−3(1)	2(1)

Note. The anisotropic displacement factor exponent takes the form $-2\pi^2[h^2a^{*2}U_{11} + \cdots + 2hka^*b^*U_{12}]$.

TABLE 3b
Anisotropic Displacement Parameters (Å$^2 \times 10^3$) for γ-SrGa$_2$O$_4$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Sr1	9(1)	8(1)	7(1)	0(1)	−2(1)	−1(1)
Sr2	11(1)	9(1)	11(1)	−2(1)	−4(1)	2(1)
Ga1	9(1)	5(1)	5(1)	0(1)	−1(1)	−1(1)
Ga2	9(1)	6(1)	6(1)	0(1)	−1(1)	−1(1)
Ga3	9(1)	6(1)	6(1)	0(1)	−2(1)	0(1)
Ga4	10(1)	5(1)	5(1)	1(1)	−1(1)	0(1)
O1	12(1)	5(1)	8(1)	−3(1)	−1(1)	−1(1)
O2	16(1)	7(1)	5(1)	−1(1)	−1(1)	2(1)
O3	21(2)	8(1)	6(1)	1(1)	1(1)	7(1)
O4	6(1)	18(2)	9(2)	2(1)	−3(1)	−1(1)
O5	12(1)	7(1)	5(1)	1(1)	1(1)	3(1)
O6	28(2)	9(2)	7(2)	3(1)	−5(1)	−7(1)
O7	10(1)	14(2)	14(2)	−6(1)	1(1)	0(1)
O8	13(2)	7(2)	17(2)	−4(1)	−9(1)	2(1)

Note. The anisotropic displacement factor exponent takes the form $-2\pi^2[h^2a^{*2}U_{11} + \cdots + 2hka^*b^*U_{12}]$.

TABLE 4

Selected Bond Distances (Å) and Angles (deg) for β- and γ-SrGa$_2$O$_4$

β-SrGa$_2$O$_4$		γ-SrGa$_2$O$_4$	
Ga1–O2	1.825(4)	Ga1–O4	1.811(3)
–O4	1.835(3)	–O3	1.834(3)
–O3	1.843(3)	–O8	1.849(3)
–O5	1.852(3)	–O5	1.895(3)
Mean	1.839	Mean	1.847
Ga2–O8	1.827(3)	Ga2–O3	1.827(3)
–O1	1.833(3)	–O7	1.840(3)
–O4	1.845(4)	–O1	1.841(3)
–O6	1.855(3)	–O6	1.842(3)
Mean	1.840	Mean	1.838
Ga3–O5	1.836(3)	Ga3–O4	1.821(3)
–O1	1.841(3)	–O8	1.841(3)
–O6	1.843(3)	–O2	1.851(3)
–O7	1.846(3)	–O1	1.864(3)
Mean	1.842	Mean	1.844
Ga4–O8	1.826(3)	Ga4–O6	1.832(3)
–O2	1.832(3)	–O2	1.846(3)
–O3	1.842(3)	–O7	1.856(3)
–O7	1.856(3)	–O5	1.862(3)
Mean	1.839	Mean	1.849
Sr1–O4	2.453(3)	Sr1–O4	2.479(3)
–O1	2.489(4)	–O3	2.488(3)
–O2	2.566(3)	–O6	2.530(3)
–O7	2.577(3)	–O5	2.552(3)
–O5	2.596(4)	–O2	2.723(3)
–O6	2.795(3)	–O1	2.757(3)
		–O7	2.825(3)
Sr2–O8	2.483(3)	Sr2–O8	2.409(3)
–O6	2.524(3)	–O1	2.486(3)
–O5	2.528(3)	–O2	2.589(3)
–O3	2.550(4)	–O7	2.622(3)
–O7	2.802(3)	–O5	2.752(3)
–O3	2.854(4)		
O2–Ga1–O4	117.8(2)	O4–Ga1–O3	120.0(1)
O2–Ga1–O3	114.8(2)	O4–Ga1–O8	106.2(2)
O2–Ga1–O5	109.5(2)	O4–Ga1–O5	98.2(1)
O4–Ga1–O3	101.2(2)	O3–Ga1–O8	105.9(2)
O4–Ga1–O5	107.3(2)	O3–Ga1–O5	112.2(1)
O3–Ga1–O5	105.0(2)	O8–Ga1–O5	114.5(1)
Mean	109.3	Mean	109.5
O8–Ga2–O1	108.0(2)	O3–Ga2–O1	111.6(1)
O8–Ga2–O4	122.3(2)	O3–Ga2–O7	99.6(1)
O8–Ga2–O6	107.0(2)	O3–Ga2–O6	111.2(2)
O1–Ga2–O4	100.5(2)	O1–Ga2–O7	121.7(1)
O1–Ga2–O6	111.5(2)	O1–Ga2–O6	100.6(1)
O4–Ga2–O6	107.5(2)	O7–Ga2–O6	112.6(2)
Mean	109.5	Mean	109.6
O5–Ga3–O1	100.7(2)	O4–Ga3–O8	107.3(1)
O5–Ga3–O6	117.6(2)	O4–Ga3–O2	112.8(1)
O5–Ga3–O7	109.0(2)	O4–Ga3–O1	104.6(1)
O1–Ga3–O6	104.7(2)	O8–Ga3–O2	120.4(2)
O1–Ga3–O7	116.4(2)	O8–Ga3–O1	106.9(1)
O6–Ga3–O7	108.6(2)	O2–Ga3–O1	103.5(1)
Mean	109.5	Mean	109.3
O8–Ga4–O2	117.1(2)	O6–Ga4–O2	112.4(1)
O8–Ga4–O3	107.6(2)	O6–Ga4–O7	103.8(1)
O8–Ga4–O7	106.2(2)	O6–Ga4–O5	107.8(1)
O2–Ga4–O3	116.8(2)	O2–Ga4–O7	99.6(2)

TABLE 4 Continued

β-SrGa$_2$O$_4$		γ-SrGa$_2$O$_4$	
O2–Ga4–O7	115.6(2)	O2–Ga4–O5	110.9(1)
O3–Ga4–O7	102.3(2)	O7–Ga4–O5	122.1(1)
Mean	110.9	Mean	109.4
Ga2–O1–Ga3	133.4(2)	Ga2–O1–Ga3	111.5(2)
Ga1–O2–Ga4	117.5(2)	Ga4–O2–Ga3	116.4(2)
Ga1–O3–Ga4	129.3(2)	Ga2–O3–Ga1	118.7(2)
Ga1–O4–Ga2	119.4(2)	Ga1–O4–Ga3	122.5(2)
Ga3–O5–Ga1	117.2(2)	Ga4–O5–Ga1	110.1(2)
Ga3–O6–Ga2	112.2(2)	Ga4–O6–Ga2	120.8(2)
Ga3–O7–Ga4	114.5(2)	Ga2–O7–Ga4	141.7(2)
Ga4–O8–Ga2	121.4(2)	Ga3–O8–Ga1	108.5(2)

O atoms. In both phases all neighboring tetrahedra belonging to different adjacent layers adopt an orientation close to the energetically favourable staggered conformation.
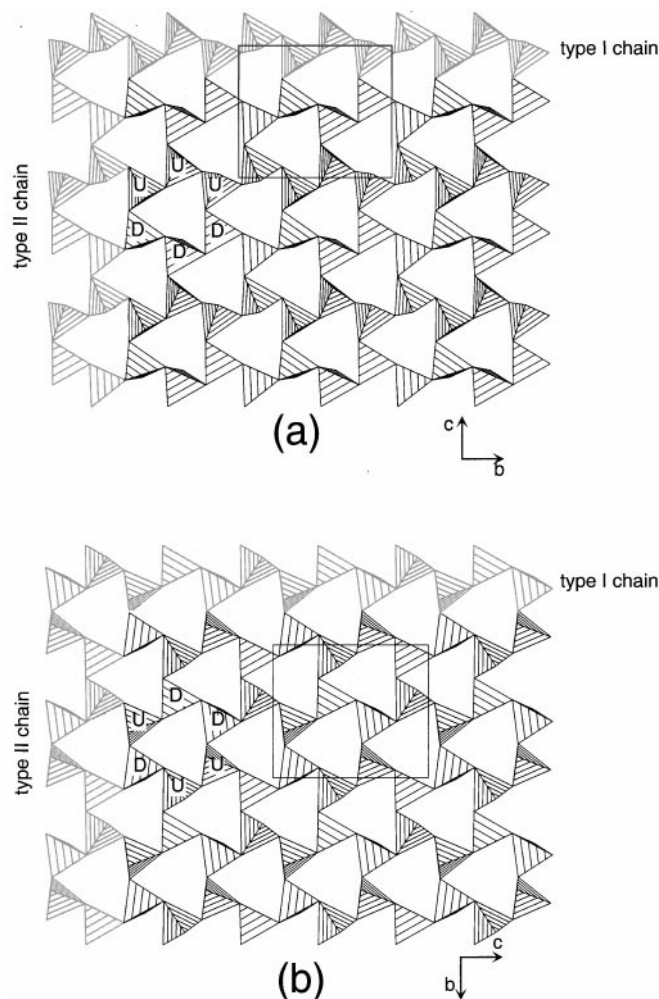
FIG. 1. Single tetrahedral layers with six-membered rings in the strontium monogallate modifications in a projection parallel [100]: (a) γ- and (b) β-SrGa$_2$O$_4$.
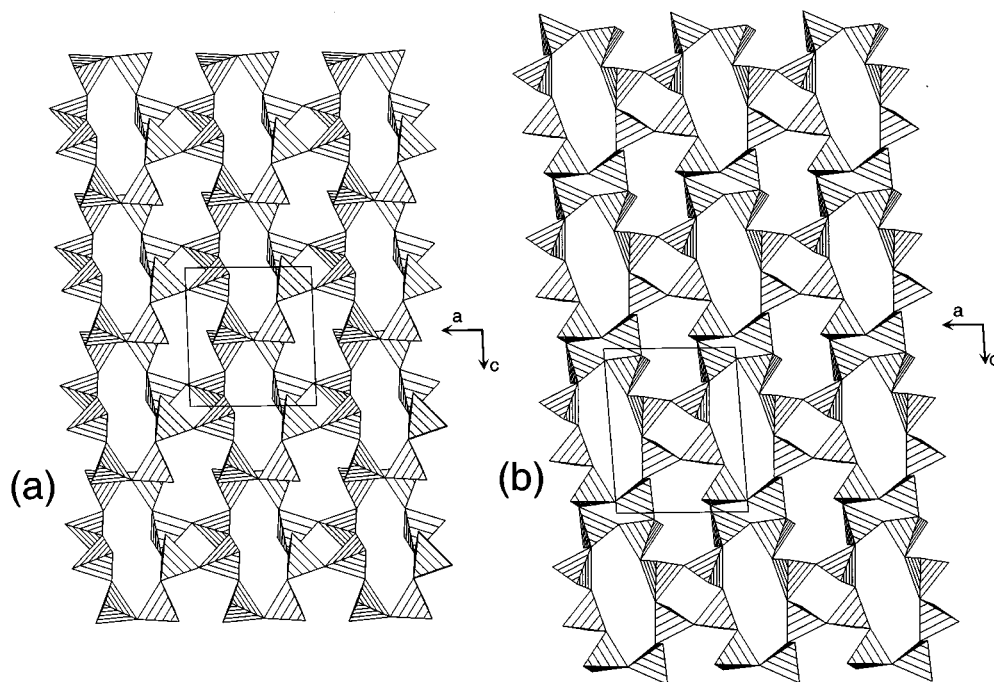
FIG. 2. Single tetrahedral layers with four- and eight-membered rings in the strontium monogallate modifications in a projection parallel [010]: (a) γ- and (b) β-SrGa$_2$O$_4$.

Both structural modifications contain layers of four- (S4R) and eight- (S8R) membered rings perpendicular to [010] (cf. Fig. 2). In γ-SrGa$_2$O$_4$ these sheets contain the vierer single chains of type II. The corresponding layers in the β-phase are built from type I chains. The stronger folding of the type II vierer single chains relative to type I is directly reflected in a significant shortening of the c axis from 10.680 Å in the β-phase to 9.057 Å in γ-SrGa$_2$O$_4$. As a compensating effect there is an increase of the translation period parallel [010] from 8.994 Å (β) to 10.761 Å (γ). In addition, there is a considerable specific volume change, ΔV, between the two modifications where $\Delta V = V_\beta - V_\gamma$ equals 12.7 Å^3 per unit cell, corresponding to 1.91 cm^3/mol or a relative change of 1.6%. This is attributed to a stronger compression of the elliptical S8R parallel to [100] in the quenched high-pressure polymorph γ-SrGa$_2$O$_4$. Nevertheless, both phases have high framework density (18) values of 19.9 tetrahedral atoms/1000 Å^3 for the β-compound and 20.3 tetrahedral atoms/1000 Å^3 for the γ-compound.

The main difference between the two crystal structures results from the different relative orientation of the apices of adjacent tetrahedra within a single S6R of the layers perpendicular to [100]. The sequence of directedness is UUUDDD (for γ-SrGa$_2$O$_4$) and UUDUDD (for β-SrGa$_2$O$_4$), respectively. This inversion of only two of the tetrahedra of a single S6R is responsible for the observed differences. An analysis of the tetrahedral topology with the program KRIBER (19) revealed that both phases also differ in the coordination sequences (CS) (20) of the tetrahedra. Within one phase the sequences of the four different crystallographic tetrahedral sites are identical. The CS values are 4-11-24-41-63-91-123-160-202-249 for β-SrGa$_2$O$_4$ and 4-10-21-36-54-78-106-136-173-214 for γ-SrGa$_2$O$_4$.

The interatomic distances and angles within the tetrahedral Ga-O frameworks are within the normal range of oxogallate structures (cf. Table 4). Especially for β-SrGa$_2$O$_4$ no extraordinarily short Ga-O distances were observed. We attribute the unusually low Ga-O distances in (7) for the β-phase to wrong atomic positions or to typographical errors of at least one of the Ga atoms in the unit cell. The spread of the individual O-Ga-O angles and the Ga-O distances suggests that the tetrahedra deviate form regularity. The quadratic elongations λ and the angle variances σ^2 (17) have values between $\lambda = 1.009$–1.012 and $\sigma^2 = 38.6$–52.3 for β-SrGa$_2$O$_4$ as well as $\lambda = 1.010$–1.017 and $\sigma^2 = 40.2$–69.0 for the γ-phase, indicating that the distortion of the tetrahedra in the high-pressure modification is more pronounced and that the structure is in general more strained. This increased strain at normal pressure can explain why γ-SrGa$_2$O$_4$ can only be synthesized at high pressure. The calculations of the bond-valence sums (BVS) for the different crystallographic tetrahedral sites using the parameters for the Ga-O bond given in (21) were very close to the expected value of 3.00 valence units (v.u.) for gallium (BVS = 2.96–2.98 v.u. for β-SrGa$_2$O$_4$ and BVS = 2.97–3.06 v.u. for γ-SrGa$_2$O$_4$).

The strontium atoms within the channels are off-center and have irregular coordinations which are 6-fold for Sr1 and Sr2 in β-SrGa$_2$O$_4$ with bonds up to 3.0 Å. The Sr^{2+} cations in the γ-phase exhibit a 7-fold (Sr1) and a 5-fold (Sr2) surrounding. Calculation of the bond valences confirms that the coordination of the Sr1 cations are essentially octahedral and monocapped trigonal prismatic, for the β- and γ-phases. However, in each case three definitely weaker bonds must be taken into account to achieve proper bond valence sums of 1.95 and 2.00 v.u., respectively. The Sr2 sites show an underbonding (BVS = 1.66 and 1.54 v.u.) which remains significant for the Sr2 in γ-SrGa$_2$O$_4$ (BVS = 1.70 v.u.) even if the coordination sphere is increased to 3.4 Å. This underbonding of the Sr2 site in the γ-phase appears to be an additional reason for the metastable character of this phase at normal pressures. Perspective views of the whole structures parallel to [100] are given in Fig. 3.

RELATIONSHIPS WITH OTHER STRUCTURES

γ-SrGa$_2$O$_4$

Analysis of the topology of this structure indicates that it belongs to the zeolite ABW-type initially assigned (22) to the compound LiAlSiO$_4$·H$_2$O (Li-A) first described by Barrer and White (23). The zeolite structure code ABW is derived from the authors' initials added to the letter "A" from the type of material. Many other compounds with the same framework topology, including anhydrous compositions, belong to the same family of structures, but they are usually designated *Jcmm*-type structures where *Jcmm* (standard setting *Jmma*) represents the space group in the highest possible topological symmetry of these framework structures. This designation is more commonly used in the mineralogically oriented literature to describe this type of stuffed framework derivatives (24), many of which are ferroelectric (25). In the following text, we refer to this structural family just as ABW-type structures, which covers all hydrous and anhydrous compounds with this framework topology. Up to date, more than 70 different crystal structure determinations of $ABCO_4$ compounds with ABW-type crystal structures are known (26,27), crystallizing in eight different space groups from the aristotypic space group *Jmma* down to $P\bar{1}$. However, the γ-phase is unique in many respects. First of all, it is the only member of this structure type with a divalent nonframework cation and only one type of cation occupying the tetrahedral positions. So far, in all reported ABW members, monovalent cations were located on the A site in the formula given above and the tetrahedral B and C positions were occupied by two different cations with charge combinations: B^{3+}/C^{4+}, B^{2+}/C^{5+}, and B^{+}/C^{6+}. The combination of a small nonframework cation like Sr^{2+} ($r = 1.21$ Å) (28) with a large tetrahedral ion like Ga^{3+} ($r = 0.47$ Å) represents a limiting case when compared with the ionic
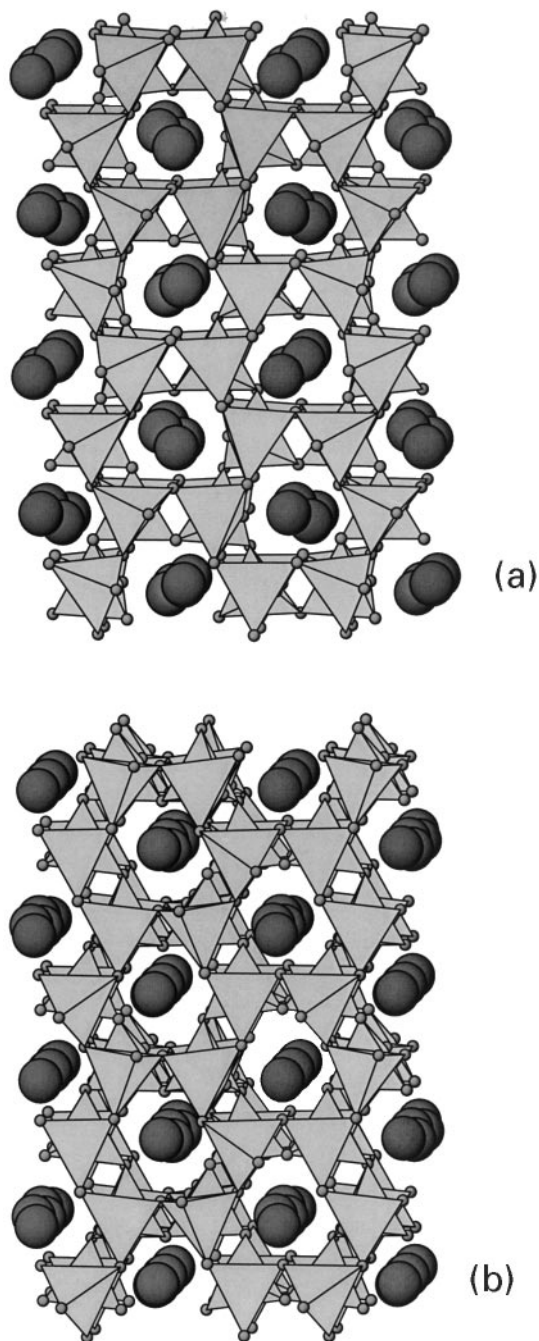

FIG. 3. Side view of the whole crystal structures 4° off [100]: (a) γ- and (b) β-SrGa$_2$O$_4$. The large spheres in the interstitial sites represent Sr cations.

radii of the cation combinations usually observed in ABW-type structures.

γ-SrGa$_2$O$_4$ is apparently the only ABW-type compound with vierer single chains running parallel to [010]. In all other known ABW-members zweier single chains are observed in the corresponding direction. The existence of vierer single chains requires a doubling of the b axis from
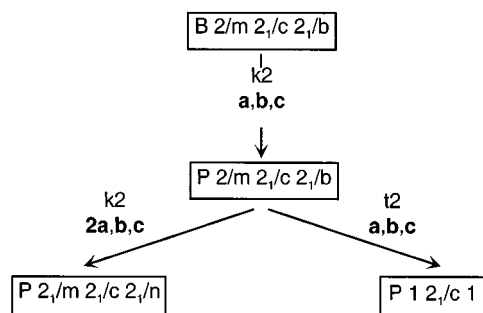
FIG. 4. Bärnighausen tree illustrating the subgroup–supergroup relationships within the framework type of β-$SrGa_2O_4$ and related compounds.

about 5.5 Å in the ABW aristotype (space group *Jmma*) to about 11 Å in γ-$SrGa_2O_4$ and is due to antirotations of GaO_4 tetrahedra about [010].

β-$SrGa_2O_4$

The β-phase is isostructural with the monoclinic modification of $CaGa_2O_4$(29). Six-membered rings with UUDUDD conformation have been also reported for the structure family named for the mineral beryllonite ($NaBePO_4$) (30). Other representatives of this group are $CaAl_2O_4$, (31), $AgBePO_4$/$AgZnPO_4$ (32), and $NaBCO_4$ with B = Al, Ga and C = Si, Ge (33). However, in all these structures there is an additional second ring type: one-third of the rings have UDUDUD topology.

Another framework structure where all 6-fold rings have UUDUDD orientation is one of the $BaFe_2O_4$ modifications (34) (space group *Pmcn*). Interestingly, all tetrahedra have the same coordination sequence as the one observed for β-$SrGa_2O_4$ or $CaGa_2O_4$, and actually the structure belongs to the same framework type. However, the *a* axis is doubled relative to the unit cell of the β-phase. The maximal topological symmetry of the framework can be described in space group *Bmcb* (different but equivalent notation of *Bmab*, standard setting *Cmca*). The symmetry relationships between the aristotype and the observed space groups *Pmcn* and $P12_1/c1$ are illustrated in a Bärnighausen tree (35) (cf. Fig. 4). The reduction in symmetry from *Pmcb* to the lower symmetrical space groups within the tree is mainly due to rotations of the tetrahedra.

ACKNOWLEDGMENT

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