

The Crystal Structures of the Strontium Gallates $\text{Sr}_{10}\text{Ga}_6\text{O}_{19}$ and $\text{Sr}_3\text{Ga}_2\text{O}_6$

V. Kahlenberg¹

Fachbereich Geowissenschaften (Kristallographie), Universität Bremen, Klagenfurter Strasse, D-28359 Bremen, Germany

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The crystal structures of $\text{Sr}_{10}\text{Ga}_6\text{O}_{19}$ and $\text{Sr}_3\text{Ga}_2\text{O}_6$ have been characterized using X-ray diffraction techniques. In the case of $\text{Sr}_{10}\text{Ga}_6\text{O}_{19}$, the structure was determined from a single crystal diffraction data set collected at room conditions and refined to a final *R* index of 0.061 for 3471 observed reflections ($I > 2\sigma(I)$). The compound is monoclinic with space group $C12/c1$ ($a = 34.973(4) \text{ \AA}$, $b = 7.934(1) \text{ \AA}$, $c = 15.943(2) \text{ \AA}$, $\beta = 103.55(1)^\circ$, $V = 4300.7(6) \text{ \AA}^3$, $Z = 8$, $D_{\text{calc}} = 4.94 \text{ g/cm}^3$, $\mu(\text{MoK}\alpha) = 32.04 \text{ mm}^{-1}$) and can be classified as an oligogallate. It is the first example of an inorganic compound where six $[\text{TO}_4]$ -tetrahedra of only one chemical species occupying the tetrahedral centres are linked via bridging oxygen atoms to form $[\text{T}_6\text{O}_{19}]$ groups. The hexamers are not linear, but highly puckered. Eleven symmetrically different Sr cations located in planes parallel (100) crosslink between the oligo-groups. They are coordinated by six to eight oxygen ligands. The structure of $\text{Sr}_3\text{Ga}_2\text{O}_6$ has been refined from powder diffraction data using the Rietveld method (space group $Pa\bar{3}$, $a = 16.1049(1)$, $V = 4177.1(1) \text{ \AA}^3$, $Z = 24$, $D_{\text{calc}} = 4.75 \text{ g/cm}^3$). The compound is isostructural with tricalcium aluminate and contains highly puckered, six-membered $[\text{Ga}_6\text{O}_{18}]^{18-}$ rings. The rings are linked by strontium cations having six to nine nearest oxygen neighbors. © 2001 Academic Press

INTRODUCTION

The preparation and the properties of various double oxides of the system $\text{SrO-Ga}_2\text{O}_3$ have been described in the literature (1–3). According to the phase equilibrium studies of Kobzareva *et al.* (4) seven different strontium gallates have to be distinguished: $\text{Sr}_4\text{Ga}_2\text{O}_7$, $\text{Sr}_7\text{Ga}_4\text{O}_{13}$, $\text{Sr}_3\text{Ga}_2\text{O}_6$, $\text{Sr}_3\text{Ga}_4\text{O}_9$, SrGa_2O_4 , SrGa_4O_7 , and $\text{SrGa}_{12}\text{O}_{19}$. Furthermore, for strontium monogallate different polymorphic forms have been reported (3–6). To date the compounds $\text{SrGa}_{12}\text{O}_{19}$ (7, 8), SrGa_2O_4 (5, 6), SrGa_4O_7 (9), and $\text{Sr}_3\text{Ga}_4\text{O}_9$ (10) have been completely characterized by structure analysis. $\text{SrGa}_{12}\text{O}_{19}$ is isotypic with magnetoplumbite. The different polymorphs of SrGa_2O_4 belong to

the group of stuffed tetrahedral frameworks. SrGa_4O_7 also belongs to the group of framework structures with sixfold tetrahedral rings, though the structure is more complex and not a simple derivative of high tridymite. The crystal structure of $\text{Sr}_3\text{Ga}_4\text{O}_9$, containing tetrahedral single layers, has been determined only recently. The space groups and crystal structures of the compounds belonging to the Sr-rich part of the phase diagram remain to be solved; for $\text{Sr}_3\text{Ga}_2\text{O}_6$, an indexed X-ray powder diffraction pattern based on a cubic unit cell with $a = 16.095 \text{ \AA}$ has been published (11). However, there may exist a second tetragonal polymorphic form for this compound (12).

As a part of an ongoing study on the crystal chemistry of alkaline earth gallates, single crystals of a novel strontium gallate with composition $\text{Sr}_{10}\text{Ga}_6\text{O}_{19}$ have been synthesized. This compound has not been observed before in the phase equilibrium studies mentioned above and represents a new type of oligogallate. Similarities and differences in comparison with other gallates are described. Furthermore, the crystal structure of $\text{Sr}_3\text{Ga}_2\text{O}_6$ has been refined from a powder diffraction data set confirming the hypothesis that this phase is isostructural with $\text{Ca}_3\text{Al}_2\text{O}_6$.

EXPERIMENTAL DETAILS

Sample Preparation

SrCO_3 (Fluka, > 98%) and Ga_2O_3 (Fluka, 99.99%) corresponding to the molar ratio 3:1 were used as starting materials. The reagents were carefully mixed in an agate mortar under acetone and pressed into discs. The pellets confined in open platinum crucibles were precalcined at 1000°C in air and subsequently sintered for another three times at 1000°C for 24 h with intermediate grindings before final quenching in air. Preliminary X-ray powder diffraction showed only one phase to be present: $\text{Sr}_3\text{Ga}_2\text{O}_6$ (PDF-2 data base entry 24-1200).

The single crystals used for the structure analysis of $\text{Sr}_{10}\text{Ga}_6\text{O}_{19}$ were grown from slow cooling of a non-stoichiometric melt. One gram of the material obtained from the solid state reactions mentioned above was placed

¹E-mail: vkahlen@min.uni-bremen.de.



in an open 50-ml platinum crucible and heated in air from 400°C in 7 h to 1550°C. The mixture was held at this temperature for 1 h then cooled to 1050°C at a rate of 5°C/h, and finally quenched to room temperature. The run product contained colorless, transparent, highly birefringent crystals, which could be separated mechanically from the solidified melt.

X-Ray Data Collection and Structure Analysis

The X-ray powder data collection for the Rietveld analysis of $\text{Sr}_3\text{Ga}_2\text{O}_6$ was performed on a Philips X'Pert diffractometer in Bragg–Brentano geometry. The diffractometer is equipped with a curved Ge(111) monochromator in the primary beam yielding a strictly monochromatic $\text{CuK}\alpha_1$ -radiation (45 kV, 40 mA). The fine-grained powder was front loaded in a round low background silicon sample holder of 13 mm in diameter. The data were collected at room temperature in consecutive steps of $0.02^\circ 2\theta$ covering a range between 10° and $130^\circ 2\theta$ with a counting time of 9.0 s/step. A first inspection of the X-ray diffraction pattern revealed that all peaks could be indexed on the basis of a cubic cell close to the cell reported in (11). There was no indication of additional reflections from the starting material. For Rietveld analysis as well as distance and angle calculations the GSAS program package (13) was employed. The data set was first fitted using LeBail's method for

intensity extraction (14) while varying lattice parameters, zero shift, and peak-profile parameters. The background was fitted using a shifted Chebyshev function with eight parameters. The pseudo-Voigt function was chosen for the simulation of the peak shape with one variable parameter defining the Lorentzian and Gaussian character of the peaks as a function of 2θ . The angular variation of the line width was accounted for using the Cagliotti function (15). After convergence of the LeBail fit, peak-profile parameters and background coefficients were fixed before switching to Rietveld refinement of the structural parameters, i.e., lattice constant, atomic coordinates (based on the model for $\text{Ca}_3\text{Al}_2\text{O}_6$) as well as isotropic displacement parameters. In addition, a soft constraint was applied on the rigid Ga–O bonds helping to avoid convergence problems during the simultaneous refinement of the positional parameters of the “light” oxygen atoms and the “heavy” atoms Sr and Ga. The final refinement calculations resulted in residuals of $R_{\text{wp}} = 0.045$, $R_{\text{p}} = 0.174$ and $R(F^2) = 0.040$. The graphical comparison between the observed and calculated powder pattern is given in Fig. 1.

Preliminary investigations of the $\text{Sr}_{10}\text{Ga}_6\text{O}_{19}$ crystals included polarized light microscopy. A small platy crystal of good optical quality (max./min. diameter: 0.06 mm/0.115 mm), was measured on a STOE imaging plate single crystal diffractometer. Parameters of the data collection and of the subsequent structure refinement are summarized in

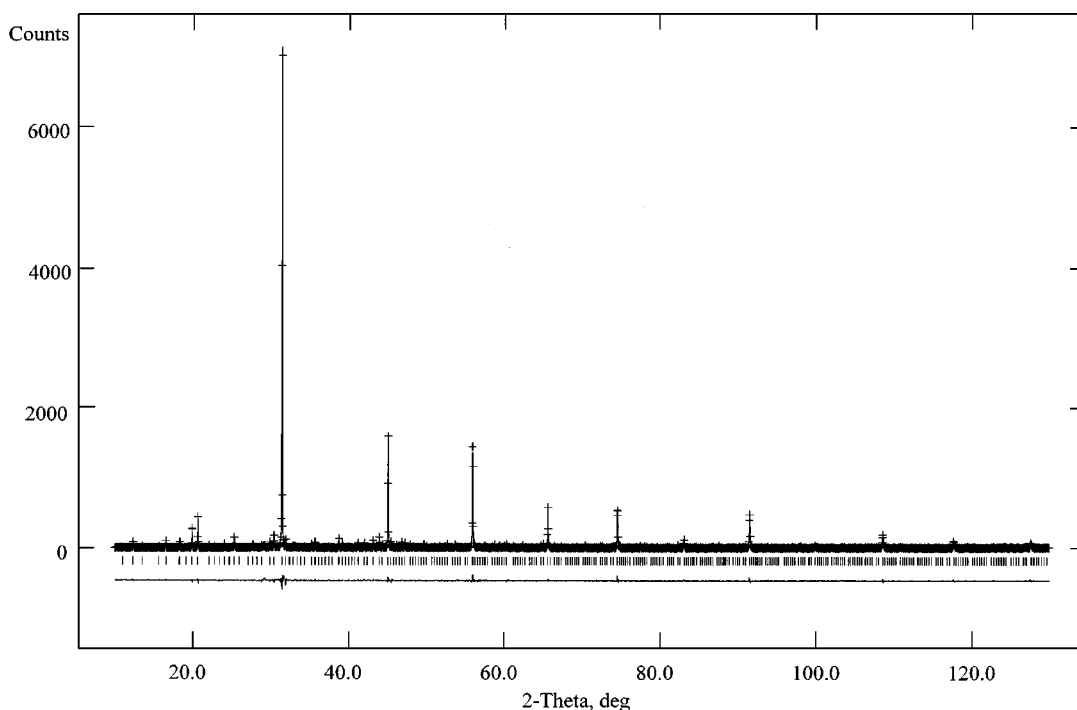


FIG. 1. Observed (crosses) and calculated (solid line) step intensities and their difference (dotted line at the bottom of the figure) of $\text{Sr}_3\text{Ga}_2\text{O}_6$. Peak positions permitted by the unit cell metric are indicated by tick marks.

TABLE 1
Data Collection and Refinement Parameters for
Sr₁₀Ga₆O₁₉

(A) Crystal data	
<i>a</i> (Å)	34.973(4)
<i>b</i> (Å)	7.934(1)
<i>c</i> (Å)	15.943(2)
β (°)	103.55(1)
<i>V</i> (Å ³)	4300.7(6)
Space group	<i>C</i> 12/ <i>c</i> 1
<i>Z</i>	8
Chemical formula	Sr ₁₀ Ga ₆ O ₁₉
<i>D</i> _{calc} (g cm ⁻³)	4.94
μ (mm ⁻¹)	32.04
(B) Intensity measurements	
Crystal shape	Fragment of a plate
Diffractometer	Stoe-IPDS
Monochromator	Graphite
Radiation	MoK α , $\lambda = 0.71073$ Å
X-ray power	50 kV, 40 mA
Detector to sample distance	70 mm
Rotation width in ϕ (°)	1.0
No. of exposures	360
Irradiation time/exposure (min.)	1.5
θ -range (°)	2.0°–28.0°
Reflection range	–45 ≤ <i>h</i> ≤ 46; <i>k</i> ≤ 10; –20 ≤ <i>l</i> ≤ 21
No. of measured reflections	20952
No. of unique reflections in 2/ <i>m</i>	5171
<i>R</i> _{int.} in 2/ <i>m</i> after absorption correction	0.116
No. of observed reflections (<i>I</i> > 2 σ (<i>I</i>))	3471
(C) Refinement of the structure	
No. of parameters used in the refinement	317
<i>R</i> 1 (<i>F</i> _o > 4 σ (<i>F</i> _o)); <i>R</i> 1 (all data)	0.061; 0.095
<i>wR</i> 2 (<i>F</i> _o > 4 σ (<i>F</i> _o))	0.164
Weighting parameter <i>a</i> , <i>b</i>	0.0782, 49.47
Goodness of fit	1.068
Final $\Delta\rho_{\min}$ (e/Å ³)	–1.69
Final $\Delta\rho_{\max}$ (e/Å ³)	1.43
$R1 = \sum F_o - F_c / \sum F_o $	$wR2 = (\sum (w(F_o^2 - F_c^2)^2) / \sum (w(F_o^2)^2))^{1/2}$
$w = 1/(\sigma^2(F_o^2) + (aP)^2 + bP)$	$P = (2F_c^2 + \max(F_o^2, 0))/3$

TABLE 2
Atomic Coordinates and Equivalent Isotropic Displacement
Factors (Å² × 10³) for Sr₁₀Ga₆O₁₉

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq)
Sr1	0.1267(1)	0.2534(2)	0.3309(1)	18(1)
Sr2	0.1200(1)	0.7057(2)	0.0762(1)	22(1)
Sr3	0.0646(1)	0.4509(1)	0.1667(1)	15(1)
Sr4	0.0031(1)	0.7553(2)	0.0272(1)	28(1)
Sr5	0.1870(1)	0.0213(2)	0.4794(1)	20(1)
Sr6	0.1241(1)	0.7511(2)	0.3177(1)	30(1)
Sr7	0.2502(1)	0.2264(2)	0.3531(1)	34(1)
Sr8	0.1302(1)	0.2413(2)	0.0600(1)	48(1)
Sr9	0	0.7069(2)	$\frac{1}{4}$	31(1)
Sr10	0	0.1555(2)	$\frac{1}{4}$	26(1)
Sr11	0.2539(1)	0.2458(2)	0.1217(1)	30(1)
Ga1	0.0564(1)	0.5366(2)	–0.0902(1)	14(1)
Ga2	0.0640(1)	0.9897(2)	–0.0682(1)	16(1)
Ga3	0.0735(1)	0.9926(2)	0.1519(1)	20(1)
Ga4	0.1798(1)	0.9728(2)	0.2149(1)	13(1)
Ga5	0.1852(1)	0.5082(2)	0.2357(1)	15(1)
Ga6	0.1948(1)	0.4916(2)	0.4644(1)	15(1)
O1	0.1838(3)	0.0548(18)	0.3229(7)	44(3)
O2	0.1675(3)	0.3180(12)	0.4931(7)	32(2)
O3	0.0225(3)	0.0753(13)	–0.1428(6)	25(2)
O4	0.0647(3)	0.7672(11)	0.1670(6)	29(2)
O5	0.2290(3)	0.4395(20)	0.2071(8)	51(3)
O6	0.0516(3)	0.0464(11)	0.0381(5)	21(2)
O7	0.1891(5)	0.4626(21)	0.3472(7)	70(5)
O8	0.1358(3)	0.4486(15)	0.1798(7)	32(2)
O9	0.0656(3)	0.1606(10)	0.2215(6)	24(2)
O10	0.0817(3)	0.4883(10)	–0.1747(5)	20(2)
O11	0.0623(6)	0.7607(14)	–0.0618(9)	74(6)
O12	0.1273(3)	0.9891(15)	0.1550(11)	69(5)
O13	0.2463(5)	0.5086(20)	0.5186(11)	44(3)
O14	0.0730(3)	0.4437(12)	0.0160(6)	28(2)
O15	0.1142(3)	0.0383(19)	–0.0720(8)	49(3)
O16	0.1867(5)	0.7421(13)	0.2310(12)	69(5)
O17	0.0040(3)	0.5039(18)	–0.1244(8)	47(3)
O18	0.1735(4)	0.7079(19)	0.4647(10)	40(3)
O19	0.2031(4)	0.0403(16)	0.1324(8)	52(3)

Note. *U*(eq) is defined as one third of the trace of the orthogonalized *U*_{*ij*} tensor. Sr9 and Sr10 reside on the Wyckoff-site 4(e). All other atoms occupy general positions.

Table 1. An analytical absorption correction based on nine indexed faces was applied which improved the internal consistency of the data set significantly (*R*_{int.} before correction: 0.197; *R*_{int.} after correction 0.116). The diffraction symmetry was consistent with the diffraction symbol 2/*mC*1*c*1. Data reduction included Lorentz and polarization corrections.

The crystal structure was solved by direct methods using the program SIR92 (16). Evaluation of the intensity statistics ($|E^2 - 1|$) did not clearly indicate the presence or absence of a center of symmetry. Both possible space groups, *C*1*c*1 and *C*12/*c*1, were tested. However, only in the

noncentrosymmetric case was a phase set found, the most intense peaks of which could be interpreted as the atomic positions of the Sr and Ga atoms. X-ray scattering factors for neutral atoms together with real and imaginary anomalous-dispersion coefficients were taken from the “International Tables for X-Ray Crystallography” (17). The oxygen atom positions were located using difference Fourier calculations (program SHELXL-93, (18)). An inspection of the atomic coordinates obtained using the program PLATON (19) revealed that, after applying an origin shift, pairs of atoms of the same kind can be found which fulfill the symmetry requirements of *C*12/*c*1 within a maximal

TABLE 3
Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for
 $\text{Sr}_{10}\text{Ga}_6\text{O}_{19}$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Sr1	17(1)	20(1)	17(1)	2(1)	2(1)	2(1)
Sr2	22(1)	28(1)	17(1)	-5(1)	10(1)	-6(1)
Sr3	12(1)	17(1)	16(1)	5(1)	3(1)	0(1)
Sr4	40(1)	29(1)	16(1)	8(1)	12(1)	23(1)
Sr5	16(1)	19(1)	24(1)	-1(1)	5(1)	4(1)
Sr6	35(1)	27(1)	27(1)	9(1)	4(1)	-11(1)
Sr7	24(1)	45(1)	38(1)	15(1)	18(1)	4(1)
Sr8	58(1)	63(1)	23(1)	-7(1)	12(1)	35(1)
Sr9	66(2)	16(1)	12(1)	0	11(1)	0
Sr10	31(1)	24(1)	26(1)	0	9(1)	0
Sr11	26(1)	48(1)	16(1)	-9(1)	9(1)	-4(1)
Ga1	14(1)	17(1)	10(1)	-2(1)	5(1)	1(1)
Ga2	16(1)	18(1)	14(1)	2(1)	6(1)	7(1)
Ga3	28(1)	13(1)	13(1)	-2(1)	-5(1)	7(1)
Ga4	13(1)	14(1)	14(1)	2(1)	7(1)	1(1)
Ga5	15(1)	19(1)	12(1)	4(1)	5(1)	3(1)
Ga6	20(1)	16(1)	10(1)	0(1)	3(1)	-4(1)
O1	31(6)	89(10)	17(5)	-16(6)	12(5)	4(7)
O2	44(7)	27(5)	32(6)	2(4)	20(5)	-8(5)
O3	25(5)	38(6)	13(5)	-4(4)	6(4)	14(4)
O4	60(8)	9(4)	20(5)	2(4)	13(5)	13(4)
O5	26(6)	87(11)	45(8)	-14(7)	16(6)	8(7)
O6	27(5)	25(5)	13(4)	-3(4)	6(4)	3(4)
O7	102(13)	101(13)	7(5)	-12(6)	15(7)	-70(11)
O8	5(4)	58(7)	31(6)	6(5)	0(4)	-5(5)
O9	48(7)	10(4)	18(5)	-5(4)	12(5)	-8(4)
O10	33(5)	20(4)	12(4)	3(3)	17(4)	0(4)
O11	168(19)	14(5)	56(9)	6(6)	57(11)	16(8)
O12	16(6)	40(7)	129(14)	-50(8)	-26(7)	9(5)
O13	29(4)	62(4)	41(4)	4(3)	8(4)	-2(3)
O14	47(7)	25(5)	11(4)	0(4)	7(4)	7(5)
O15	17(5)	98(11)	32(7)	-33(7)	8(5)	-6(6)
O16	89(12)	9(5)	97(14)	18(7)	0(10)	3(6)
O17	13(5)	88(11)	37(7)	-24(7)	0(5)	3(6)
O18	58(4)	25(4)	41(4)	1(3)	21(3)	0(3)
O19	79(10)	54(8)	37(7)	16(6)	43(7)	-9(7)

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

deviation of about five esd's. Therefore, the coordinates were transformed and the structure refinement was repeated in space group $C12/c1$. Since a refinement of the site occupancies did not reveal any indication for Sr- or Ga- vacancies, in the final least squares cycles using anisotropic displacement parameters full occupancy of the cation sites was assumed. These calculations converged to a residual of $R1 = 0.061$ for 317 parameters for all independent observed reflections (cf. Table 1). The largest shift/esd 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 for both phases are given in Tables 2 to 5. Figures showing structural details were made using the program ATOMS (20).

TABLE 4
Atomic Coordinates for $\text{Sr}_3\text{Ga}_2\text{O}_6$

Atom	x	y	z
Sr1	0	0	0
Sr2	$\frac{1}{2}$	0	0
Sr3	0.2550(9)	0.2550(9)	0.2550(9)
Sr4	0.3781(8)	0.3781(8)	0.3781(8)
Sr5	0.1353(9)	0.3743(9)	0.1308(10)
Sr6	0.3779(9)	0.3861(9)	0.1252(8)
Ga1	0.2523(7)	0.0136(9)	0.0178(9)
Ga2	0.2415(9)	0.2360(8)	0.0039(9)
O1	0.2673(15)	0.1250(15)	0.0013(12)
O2	0.4878(16)	0.1280(14)	0.2448(13)
O3	0.2680(13)	0.2790(14)	0.1030(15)
O4	0.2337(14)	0.4036(16)	0.2820(16)
O5	0.3484(15)	-0.0301(10)	-0.0210(14)
O6	0.1515(13)	-0.0167(14)	-0.0201(15)

Note. The isotropic temperature factors for the three different types of atoms were constrained to be equal and have the following values: $U_{\text{O}} = 0.029(3)$, $U_{\text{Ga}} = 0.006(1)$ and $U_{\text{Sr}} = 0.010(1)$.

DESCRIPTION OF THE STRUCTURES

$\text{Sr}_{10}\text{Ga}_6\text{O}_{19}$

The most interesting structural feature is the presence of heteropolyanions formed by the condensation of six

TABLE 5
Selected Bond Distances (\AA) up to 3.4 \AA , Angles ($^\circ$), Distortion Parameters, and Bond Valence Sums (v.u.)

(a) $\text{Sr}_{10}\text{Ga}_6\text{O}_{19}$			
Ga1-O17	1.801(8)	Ga2-O3	1.782(9)
O14	1.813(9)	O15	1.811(9)
O10	1.819(8)	O11	1.821(11)
O11	1.834(11)	O6	1.900(9)
Mean	1.817	Mean	1.829
Q.E.	1.012	Q.E.	1.019
A.V.	46.55	A.V.	80.01
BVS	3.17	BVS	3.09
Ga3-O9	1.797(9)	Ga4-O19	1.783(11)
O4	1.839(9)	O1	1.815(11)
O6	1.847(9)	O16	1.856(11)
O12	1.870(8)	O12	1.866(11)
Mean	1.838	Mean	1.830
Q.E.	1.019	Q.E.	1.027
A.V.	81.95	A.V.	120.42
BVS	2.99	BVS	3.07
Ga5-O5	1.782(10)	Ga6-O2	1.796(10)
O7	1.788(11)	O13	1.811(14)
O8	1.814(8)	O7	1.847(11)
O16	1.858(11)	O18	1.872(15)
Mean	1.810	Mean	1.832
Q.E.	1.015	Q.E.	1.015
A.V.	61.87	A.V.	57.15
BVS	3.23	BVS	3.05

TABLE 5—Continued

Sr1-O9	2.531(9)	Sr2-O2	2.364(10)
O1	2.572(11)	O12	2.560(13)
O10	2.573(8)	O8	2.602(11)
O2	2.693(10)	O11	2.649(16)
O7	2.705(15)	O14	2.682(9)
O15	2.874(13)	O4	2.716(10)
O8	2.943(11)	O16	2.986(16)
O11	3.132(17)		
BVS	1.63	BVS	1.84
Sr3-O17	2.363(8)	Sr4-O6	2.505(8)
O8	2.449(6)	O3	2.601(9)
O9	2.461(8)	O17	2.622(13)
O14	2.489(9)	O4	2.716(10)
O10	2.505(9)	O11	2.773(17)
O4	2.509(8)	O6	2.846(9)
		O14	3.032(9)
		O17	3.140(13)
BVS	2.39	BVS	1.54
Sr5-O13	2.338(13)	Sr6-O10	2.429(8)
O19	2.422(13)	O15	2.508(13)
O2	2.475(10)	O18	2.587(15)
O1	2.486(10)	O4	2.785(10)
O18	2.529(9)	O16	2.850(14)
O15	2.532(15)	O1	3.178(13)
		O7	3.182(16)
		O12	3.232(16)
BVS	2.40	BVS	1.53
Sr7-O1	2.635(11)	Sr8-O18	2.418(14)
O5	2.639(15)	O8	2.494(11)
O13	2.749(16)	O12	2.526(14)
O7	2.827(16)	O14	2.531(9)
O5	2.832(14)	O15	2.605(13)
O16	2.843(14)	O19	3.000(13)
O19	2.958(13)	O6	3.102(8)
O2	3.335(10)		
BVS	1.25	BVS	1.90
Sr9-O3	2.428(10)	Sr10-O9	2.441(9)
O3	2.428(10)	O9	2.441(9)
O17	2.587(13)	O3	2.503(10)
O17	2.587(13)	O3	2.503(10)
O4	2.917(10)	O11	3.337(15)
O4	2.917(10)	O11	3.337(15)
O10	3.224(8)	O17	3.347(14)
O10	3.224(8)	O17	3.347(14)
BVS	1.76	BVS	1.69
Sr11-O5	2.351(13)		
O19	2.448(13)		
O13	2.523(16)		
O16	2.748(17)		
O13	2.922(16)		
O7	2.968(16)		
O18	3.175(13)		
BVS	1.73		
O17-Ga1-O14	107.8(5)	O3-Ga2-O15	122.7(5)
O17-Ga1-O10	112.4(5)	O3-Ga2-O11	112.7(6)
O17-Ga1-O11	105.3(7)	O3-Ga2-O6	100.6(4)
O14-Ga1-O10	120.0(4)	O15-Ga2-O11	105.0(7)
O14-Ga1-O11	99.8(5)	O15-Ga2-O6	113.9(5)
O10-Ga1-O11	109.9(6)	O11-Ga2-O6	99.7(6)
Mean	109.2	Mean	109.1

TABLE 5—Continued

O9-Ga3-O4	125.8(4)	O19-Ga4-O1	130.2(6)
O9-Ga3-O6	110.2(4)	O19-Ga4-O16	109.4(6)
O9-Ga3-O12	107.1(5)	O19-Ga4-O12	99.6(6)
O4-Ga3-O6	108.0(4)	O1-Ga4-O16	104.1(7)
O4-Ga3-O12	100.4(5)	O1-Ga4-O12	108.0(6)
O6-Ga3-O12	102.4(6)	O16-Ga4-O12	102.6(6)
Mean	108.9	Mean	109.0
O5-Ga5-O7	108.9(6)	O2-Ga6-O13	117.7(6)
O5-Ga5-O8	124.9(5)	O2-Ga6-O7	102.9(6)
O5-Ga5-O16	105.2(6)	O2-Ga6-O18	117.7(5)
O7-Ga5-O8	106.0(6)	O13-Ga6-O7	110.7(7)
O7-Ga5-O16	104.2(8)	O13-Ga6-O18	106.5(6)
O8-Ga5-O16	105.8(6)	O7-Ga6-O18	99.6(7)
Mean	109.2	Mean	109.2
		(b) Sr ₃ Ga ₂ O ₆	
Ga1-O6	1.80(3)	Ga2-O3	1.79(3)
O5	1.81(3)	O4	1.81(3)
O2	1.83(3)	O1	1.84(3)
O1	1.83(3)	O2	1.87(3)
Mean	1.816	Mean	1.827
Q.E.	1.014	Q.E.	1.026
A.V.	58.08	A.V.	102.91
BVS	3.16	BVS	3.08
Sr1-O6	2.48(2) × 6	Sr2-O5	2.51(2) × 6
BVS	2.23	BVS	2.08
Sr3-O4	2.46(3) × 3	Sr4-O1	2.67(3) × 3
O3	2.49(3) × 3	O4	2.82(3) × 3
		O5	2.97(3) × 3
BVS	2.29	BVS	1.43
Sr5-O5	2.42(3)	Sr6-O4	2.46(3)
O2	2.54(3)	O6	2.47(3)
O3	2.67(3)	O3	2.50(3)
O1	2.76(3)	O2	2.70(3)
O5	2.90(3)	O6	2.73(3)
O4	2.94(3)	O6	2.85(3)
O3	2.98(3)	O1	2.95(3)
O2	3.00(3)		
BVS	1.58	BVS	1.78
O6-Ga1-O5	123.3(1.3)	O3-Ga2-O4	127.3(1.3)
O6-Ga1-O1	109.6(1.3)	O3-Ga2-O1	110.0(1.2)
O6-Ga1-O2	106.9(1.2)	O3-Ga2-O2	107.0(1.2)
O5-Ga1-O1	102.6(1.2)	O4-Ga2-O1	99.3(1.2)
O5-Ga1-O2	103.0(1.1)	O4-Ga2-O2	100.6(1.2)
O1-Ga1-O2	111.2(1.2)	O1-Ga2-O2	112.3(1.2)
Mean	109.4	Mean	109.4

[GaO₄]-tetrahedra. The existence of such a noncyclic anion comprising six tetrahedra has not been described before among the oxo-gallates. Adopting the nomenclature introduced by Liebau (21) for the structural chemistry of silicates, Sr₁₀Ga₆O₁₉ could be classified as an “unbranched oligogallate.” The hexagallate ion gives further practical evidence for considerably long, unbranched polynuclear ions intermediate between [Ga₂O₇]⁸⁻, which is observed in Ba₄Ga₂O₇ (22) or Na₈Ga₂O₇ (23), and infinite [GaO₃]_∞³⁻

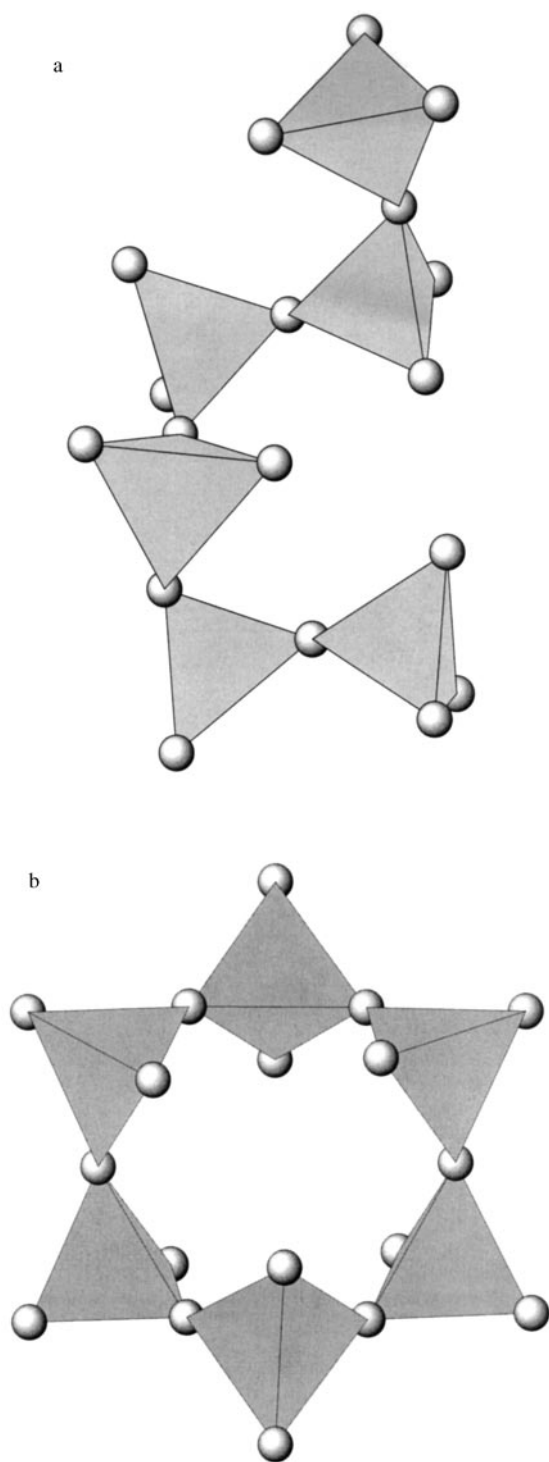


FIG. 2. Linkage between the six $[\text{GaO}_4]$ tetrahedra in (a) $\text{Sr}_{10}\text{Ga}_6\text{O}_{19}$ and (b) $\text{Sr}_3\text{Ga}_2\text{O}_6$.

chains, which can be found in $\text{Ca}_2\text{Ga}_2\text{O}_5$ (24). The only other known example of six tetrahedra linked together to form a chain fragment is the vanadatopentasilicate ion $[\text{VSi}_5\text{O}_{18}(\text{OH})]^{12-}$ occurring in the mineral medaite (25).

However, both hexamers differ considerably with regard to their conformation. Whereas the oligo-groups in medaite are almost linear, the arrangement of the six tetrahedra in $\text{Sr}_{10}\text{Ga}_6\text{O}_{19}$ is highly puckered. Actually, the geometry can be described as an open five-membered tetrahedral ring with one additionally attached sixth tetrahedron (cf. Fig. 2a). The packing of the hexamers in the crystal as observed in a projection parallel $[010]$ is given in Fig. 3.

The individual Ga–O bond distances show a considerable scatter. However, the observed values are in the normal range observed for oxo-gallate structures. The spread of the Ga–O distances as well as the deviations from ideal tetrahedral geometry are less pronounced for the two primary (Q^1) tetrahedra around Ga1 and Ga6 at the end of hexamer, compared to the inner four secondary (Q^2) tetrahedra (Ga2–Ga4). Numerically, the degree of distortion can be expressed using the quadratic elongation (Q.E.) and the angle variance (A.V.) parameters as defined by Robinson *et al.* (26). These values have been calculated and are listed in Table 5 for every individual tetrahedron. The bond-valence sums (BVS) for the crystallographically different tetrahedral sites using the parameters for the Ga–O bond given in (27) were only slightly higher compared to the expected value of 3.00 valence units (v.u.) for gallium (BVS = 2.99–3.23 v.u.).

Charge balance in the structure is achieved by incorporation of Sr^{2+} cations in voids between the oligo-groups. They are located in planes parallel (100) at about $x = \frac{1}{16}, \frac{1}{8}, \frac{3}{16}$ etc. (cf. Fig. 3). The Sr–O distances cover a wide range as can be seen from Table 5, where Sr–O distances up to 3.4 Å are listed. For Sr3 and Sr5, the oxygen ligands form distorted octahedra. The bond distances vary from 2.33 to 2.53 Å, with only minor differences between the two polyhedra. The BVS values indicate a pronounced overbonding (Sr3: 2.39 v.u.; Sr5: 2.40 v.u.). The remaining strontium cations occupy seven- and eight-coordinated oxygen polyhedra. However, the arrangement of the O atoms surrounding these cations is much more irregular compared to Sr3 and Sr5. Furthermore, the bond valence sums for all nine Sr atoms belonging to the second group are significantly lower than 2.0 v.u. In the case of Sr9 and Sr10 residing on the Wyckoff site 4(e) (point group symmetry 2.) four inner ($\langle\text{Sr}-\text{O}\rangle$: 2.49 Å) and four outer ligands ($\langle\text{Sr}-\text{O}\rangle$: 3.21 Å) must be distinguished.

$\text{Sr}_3\text{Ga}_2\text{O}_6$

The crystal structure of $\text{Sr}_3\text{Ga}_2\text{O}_6$ is isostructural with $\text{Ca}_3\text{Al}_2\text{O}_6$ (28), one of the four major phases in Portland cement clinkers. Since $\text{Sr}_3\text{Al}_2\text{O}_6$ (29) and $\text{Sr}_3(\text{Al}_{0.36}\text{Ga}_{0.64})_2\text{O}_6$ (30) adopt the same structure type, there seems to exist a homogenous solid solution series $\text{Sr}_3(\text{Al}_x\text{Ga}_{1-x})_2\text{O}_6$ with $\text{Sr}_3\text{Ga}_2\text{O}_6$ being one of the end members.

The main building unit of the structure are Ga_6O_{18} -rings centered on the $\bar{3}$ -axes (cf. Fig. 2b). The relative orientation

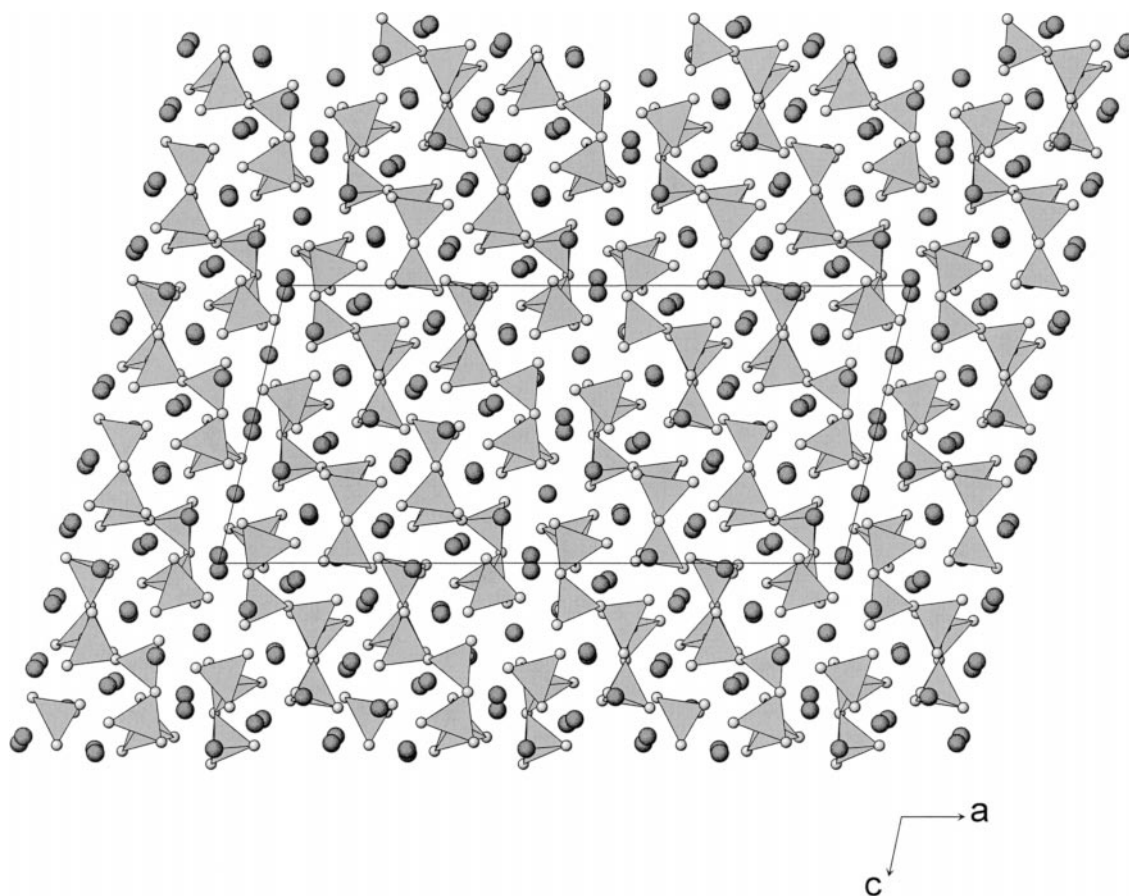


FIG. 3. Projection of the whole structure of $\text{Sr}_{10}\text{Ga}_6\text{O}_{19}$ parallel $[010]$. The dark gray spheres represent the Sr cations occupying the voids between the oligo-groups.

of up (U) and down (D) pointing apices of adjacent tetrahedra in the six-membered rings is UDUDUD. The same sequence of directedness has been observed in the tetrahedral rings of BaGa_2O_4 (31). However, the rings in $\text{Sr}_3\text{Ga}_2\text{O}_6$ are extremely puckered, such that the Ga atoms in the centers of the six tetrahedra are located near the corner of a cube with edge lengths of about $\frac{1}{4}a$. No such puckering has been observed in barium monogallate. The unit cell contains eight of these subcell cubes centered at $(\frac{1}{8}, \frac{1}{8}, \frac{1}{8})$ and the symmetrically equivalent sites. The tetrahedra comprising the rings are distorted; Ga–O distances vary between 1.80 and 1.83 Å for Ga1 and 1.79 and 1.87 Å for Ga2. The comparison of the grand mean value of the T–O distances for $\text{Sr}_3\text{Ga}_2\text{O}_6$ (1.821 Å) with those for $\text{Sr}_3\text{Al}_2\text{O}_6$ (1.758 Å) (29) shows the expected trend resulting from the substitution of the smaller Al^{3+} by the larger Ga^{3+} . For both tetrahedral sites the bond distances to the bridging oxygen atoms O1 and O2 are longer than the nonbridging bond lengths. The scatter of the O–Ga–O angles is considerable: 102° – 123° for Ga1 and 99° – 127° for Ga2, respectively. The corresponding Q.E. and A.V. values are given in Table 5.

The tetrahedral rings within the structure are connected by Sr ions. On the basis of the coordination spheres two different groups can be distinguished. Sr1, Sr2, and Sr3 have six nearest oxygen neighbors with distances between 2.458 and 2.512 Å. Sr1 and Sr2 (site symmetry $\bar{3}$) have an octahedral coordination environment compressed parallel to the $\bar{3}$ axis. The six oxygen atoms around Sr3 form a distorted trigonal prism. The coordination spheres of the remaining Sr atoms are much more irregular. To an upper limit of 3.0 Å nine, eight, and seven ligands can be found for Sr4, Sr5, and Sr6, respectively. A projection of the whole structure of $\text{Sr}_3\text{Ga}_2\text{O}_6$ is given in Fig. 4.

Comparing the two crystal structures of $\text{Sr}_{10}\text{Ga}_6\text{O}_{19}$ and $\text{Sr}_3\text{Ga}_2\text{O}_6$ it is interesting to note that both phases contain tetrahedral hexamer groups. However, the slightly higher Sr:Ga ratio of 1.667 in the first compound results in the formation of an oligogallate, whereas the tetrahedra in $\text{Sr}_3\text{Ga}_2\text{O}_6$ (Sr:Ga = 1.50) form closed six-membered rings. In general, there is a consistent inverse correlation between the degree of polymerization of the $[\text{GaO}_4]$ tetrahedra and

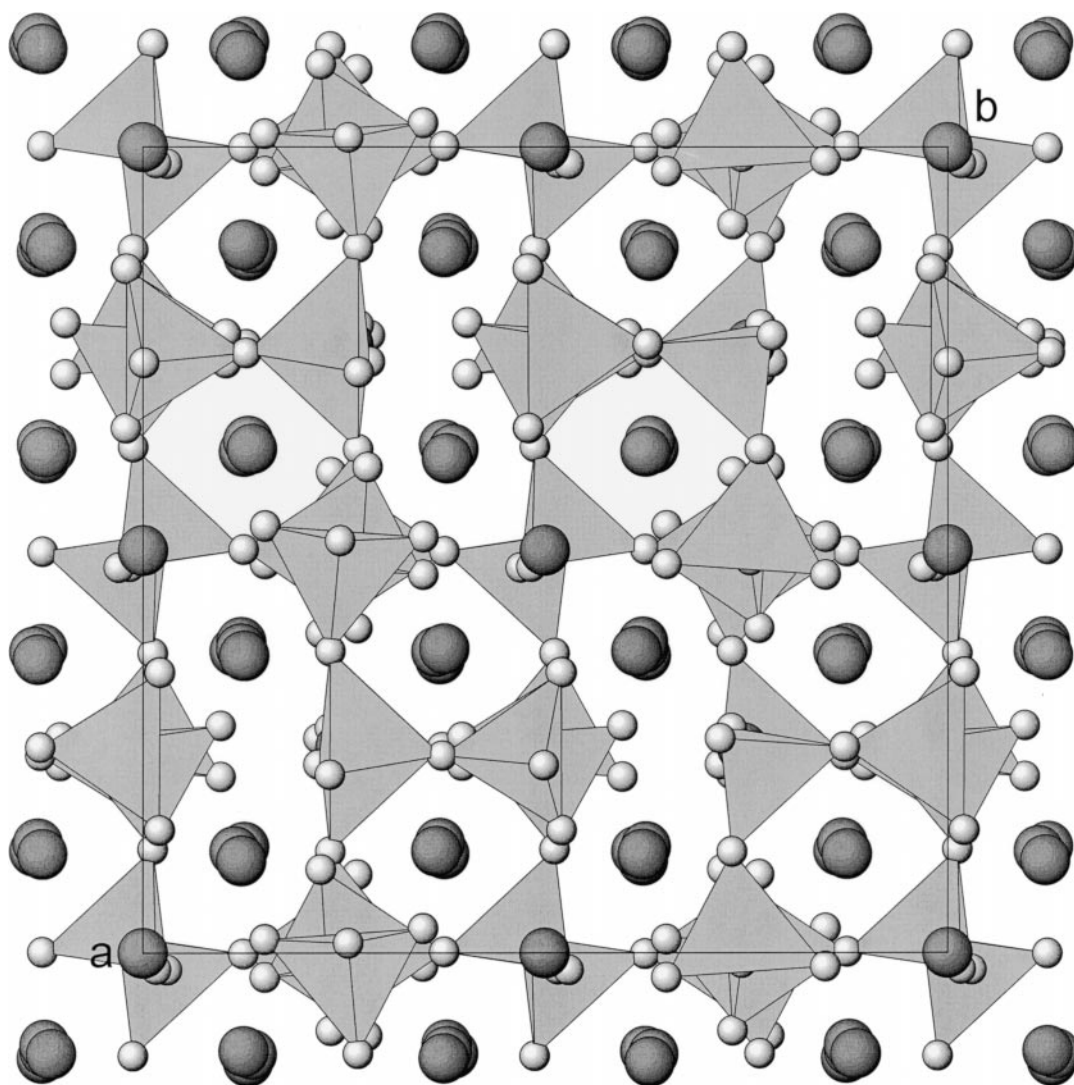


FIG. 4. Projection of the structure of $\text{Sr}_3\text{Ga}_2\text{O}_6$ parallel [001]. Dark gray spheres represent Sr atoms.

the Sr:Ga ratio within the group of the strontium gallates including the phases mentioned in the introduction and the two new Sr–Ga oxides investigated in this paper.

In the system $\text{BaO–Ga}_2\text{O}_3$, a pyrogallate phase containing isolated $[\text{Ga}_2\text{O}_7]$ -groups has been reported only recently (22). Further studies are currently in progress to find out if a similar phase with a low connectivity of the $[\text{GaO}_4]$ -tetrahedra can be prepared in the $\text{SrO–Ga}_2\text{O}_3$ system.

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