

Tetrastrontium-digalliumoxide ($\text{Sr}_4\text{Ga}_2\text{O}_7$)—synthesis and crystal structure of a mixed anion strontium gallate related to perovskite

Volker Kahlenberg^{a,*}, Biljana Lazić^a, Sergey V. Krivovichev^{a,b}

^aInstitut für Mineralogie und Petrographie, Leopold-Franzens-Universität Innsbruck, Innrain 52, A-6020 Innsbruck, Austria

^bDepartment of Crystallography, St. Petersburg State University, University Emb. 7/9, 199034, St. Petersburg, Russia

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Abstract

Crystal growth experiments yielded single crystals of $\text{Sr}_4\text{Ga}_2\text{O}_7$. The title compound is monoclinic, space group $P1c1$, $a = 13.0822(7)$ Å, $b = 15.7967(6)$ Å, $c = 15.8586(8)$ Å, $\beta = 90.643(6)^\circ$, $V = 3277.1(3)$ Å³, $Z = 16$ ($R1 = 0.041$ for 7155 observed reflections and 660 parameters). The crystals showed twinning by pseudo-merohedry. Furthermore, the diffraction data exhibited the typical features of a superstructure. $\text{Sr}_4\text{Ga}_2\text{O}_7$ can be classified as a mixed anion gallate comprising insular $[\text{GaO}_4]$ -groups and $[\text{Ga}_3\text{O}_{10}]$ -trimers. Both anion groups are located in layers perpendicular to $[100]$. 32 symmetrically independent Sr-cations crosslink between the tetrahedral anion groups. Alternatively, the compound can be described as a $3 \times 4 \times 4$ superstructure of ABO_3 perovskite, with 22.2% vacancies in the oxygen sublattice. The relationship with perovskite can be expressed in the following crystal chemical formula: $\text{Sr}(\text{Ga}_{2/3}\text{Sr}_{1/3})(\text{O}_{7/9}\square_{2/9})_3$. A discussion of the structure in the context with other similar defect perovskites is presented.

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1. Introduction

This paper represents part of a body of work undertaken to elucidate the structures of phases in the systems $AO-B_2O_3$, where $A = \text{Sr}, \text{Ba}$ and $B = \text{Ga}, \text{Al}$. Although one should expect that the double oxides of these main group elements have been studied in great detail, it is interesting to note that especially in the more alkaline earth rich parts of the corresponding phase diagrams there is a considerable lack of information concerning the number of existing phases and their crystal structures. This may be at least partially attributed to the fact that many of the relevant compounds form single crystals of poor quality and crystallize in structures of low symmetry with comparatively large unit cell volumes, impeding a structure determination from powder diffraction data. Furthermore, many of the phases are easily hydrated in air of

normal humidity. In case of the system $\text{SrO-Ga}_2\text{O}_3$, for example, the crystal structures of the $\text{Sr}_3\text{Ga}_4\text{O}_9$ [1] and $\text{Sr}_{10}\text{Ga}_6\text{O}_{19}$ (occurring in two modifications [2,3]) have been solved only recently.

A strontium gallium oxide with composition $\text{Sr}_4\text{Ga}_2\text{O}_7$ has been first mentioned by Hoffman and Brown [4]. They reported an unindexed powder diffraction pattern with a small number of diffraction lines (ICDD PDF-2 database entry 21-1181). First crystallographic information on $\text{Sr}_4\text{Ga}_2\text{O}_7$ was given by Plakhtii et al. [5] who indexed the powder pattern using a tetragonal unit cell with $a = 3.99$ Å and $c = 4.295$ Å. In the course of their subsequent phase equilibrium studies Kobzareva et al. [6] pointed out that the crystal structure of $\text{Sr}_4\text{Ga}_2\text{O}_7$ has to be much more complex having a symmetry which is not higher than monoclinic. Analyzing the powder pattern the authors proposed a monoclinic “sub-cell” with $a = 4.251$ Å, $b = 3.949$ Å, $c = 3.959$, $\beta = 90.58^\circ$. From a comparison of the unit cell parameters Kovba et al. [7] suggested that $\text{Sr}_4\text{Ga}_2\text{O}_7$ could be structurally related to perovskite.

*Corresponding author. Fax.: +43 512 507 2926.

E-mail address: volker.kahlenberg@uibk.ac.at (V. Kahlenberg).

In summary, one can say that previous structural characterizations of $\text{Sr}_4\text{Ga}_2\text{O}_7$ were hindered from the complexity of the powder diffraction pattern. An obvious solution is a structure analysis based on single crystal diffraction data. The object of the present paper was to grow single crystal material, to provide a structure model for $\text{Sr}_4\text{Ga}_2\text{O}_7$ and to clarify the relationships between this phase and other compounds.

2. Experimental details

2.1. Preparation of $\text{Sr}_4\text{Ga}_2\text{O}_7$ and chemical analysis

Mixtures of SrCO_3 (Fluka, >98%) and Ga_2O_3 (Fluka, 99.99%) in the molar ratio 4:1 were used as reactants for the synthesis experiment. The starting material was mixed in an agate mortar under acetone. A sample of 1 g of the mixture was placed in an open 50 mL platinum crucible. The starting material was heated in air from 100 °C in 14 h to 1600 °C in a resistance heated furnace and subsequently held at this temperature for 2 h to homogenize the melt. Crystallization was performed in two steps: from 1600 °C down to 1490 °C with a rate of 5 °C/h and finally with 100 °C/h down to 500 °C where the sample was quenched to room temperature. The yield contained two different types of crystalline material which could be easily distinguished using polarized light microscopy: (1) prismatic colorless crystals of $\beta\text{-Sr}_{10}\text{Ga}_6\text{O}_{19}$ and (2) platy slightly violet specimen showing polysynthetic twinning. Since exclusively all crystals of phase 2 were subject to twinning, several twinned specimen were selected for chemical and structural investigations.

The composition of one of the twinned crystals was determined with a Cameca SX50 beam microprobe operated at 15 kV (accelerating voltage) and a beam current of 15 nA. The following standards and X-ray lines were used for the WDX-analysis: $\text{SrCuSi}_4\text{O}_{10}$ (Sr-L_α) and Ga_2O_3 (Ga-L_α). The counting time was set at 15 s. The intensities obtained were corrected for electron scattering, absorption and fluorescence radiation (so-called ZAF correction). The average composition of the analyzed crystal was 30.54 (± 0.42) wt% Ga_2O_3 and 69.46 (± 0.38) wt% SrO almost identical to a molar $\text{SrO}:\text{Ga}_2\text{O}_3$ ratio of 4:1 (numbers in brackets are standard deviations for 10 spot analyses).

2.2. X-ray diffraction data collection and structure determination

Single crystal diffraction experiments were performed on a STOE imaging plate diffractometer. Parameters pertaining to the data collection are summarized in Table 1. The diffraction pattern showed an unusual complexity which could be explained by the super-

position of four different reciprocal lattices. Therefore, a comparatively large sample–detector distance of 80 mm was selected to increase the resolution between neighboring diffraction spots. Furthermore, a pronounced pseudo-translational symmetry causing a large number of weak superlattice reflections was obvious. Reflections (hkl) with very high intensities exclusively belonged to the following class: $h = 3n, k = 4n, l = 4n$. The program RECIPE of the STOE software package was employed to isolate the diffraction spots coming from the different orientations of the domains. The diffraction peaks were indexed independently and the superimposed diffraction patterns were integrated simultaneously. The integration was repeated twice (with and without overlap check) for each twin domain. From the combination of the resulting two data sets, the non-overlapping as well as the almost completely overlapping reflections were extracted for the structure solution. The final choice of the domain used for the structure determination was based on the mean intensity of the data set containing the non-overlapping reflections. Further data reduction including Lorentz and polarization corrections was performed with the STOE program package X-RED. Due to the high linear absorption coefficient of $\mu = 32.34 \text{ mm}^{-1}$ for $\text{MoK}\alpha$ —radiation an analytical absorption correction based on eight indexed faces was applied. 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* [8].

Laue symmetry $2/m$ in combination with the observed systematic absences ($h0l$): $l = 2n + 1$ resulted in two possible space groups $P12/c1$ and $P1c1$, respectively. Evaluation of the intensity statistics ($\langle |E^2 - 1| \rangle$) indicated the absence of a center of symmetry. The choice of the non-centrosymmetric space group Pc was confirmed by the structure solution which was performed by direct methods using the program SHELXS97 [9]. Attempts to solve the structure in $P2/c$ were not successful. The most prominent peaks of one of the phase sets could be interpreted as a partial model containing the Sr-, Ga- and some of the O-positions. The remaining oxygen atoms were located using difference Fourier calculations (program SHELXL97 [10]). This model was the starting point for the subsequent refinement calculations. Floating origin restraints, to prevent the structure drifting along the ($x0z$)-plane, were automatically generated by SHELXL97 (which does not require fixing the x - and z -coordinate of a single atom). Iterative full matrix least squares calculations based on F^2 using isotropic displacement factors converged to an unweighted $R1$ index of 0.05. The introduction of anisotropic displacement parameters for all atoms improved the residual index $R1$ only slightly ($R1 = 0.04$) but resulted in non-positive definite temperature factors for some of the oxygen atoms. A re-examination of the diffraction data,

Table 1
Crystal data and structure refinement parameters for Sr₄Ga₂O₇

<i>(A) Crystal—cell data</i>		
Unit cell dimensions	$a = 13.0822(7) \text{ \AA}$ $b = 15.7967(6) \text{ \AA}$ $c = 15.8586(8) \text{ \AA}$	$\alpha = 90^\circ$ $\beta = 90.643(6)^\circ$ $\gamma = 90^\circ$
Volume	3277.1(3) Å ³	
Space group	<i>P1c1</i>	
Z	16	
Density (calculated)	4.88 g cm ⁻³	
Absorption coefficient	32.335 mm ⁻¹	
<i>(B) Intensity measurement</i>		
Crystal shape	Fragment of a plate	
Crystal size	0.04 × 0.09 × 0.14 mm ³	
Diffractometer	Stoe-IPDS	
Monochromator	Graphite	
Radiation	Mo-K α , $\lambda = 0.71073 \text{ \AA}$	
X-ray power	50 kV, 40 mA	
Detector to sample distance	80 mm	
Rotation width in ϕ	1.0°	
Number of exposures	360	
Irradiation time per exposure	5 min	
θ -range for data collection	1.82–24.04°	
Index ranges	$-14 < = h < = 14, -18 < = k < = 18, -18 < = l < = 18$	
No. of reflections collected	38128	
No. of independent reflections	10656	
Absorption correction	Analytical, based on crystal shape	
Min., max. Transmission	0.058, 0.299	
R_{int} before absorption correction	0.1513	
R_{int} after absorption correction	0.0890	
No. of observed reflections [$I > 2\sigma(I)$]	7155	
<i>(C) Refinement of the structure</i>		
No. of parameters used in the refinement	660	
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0406, wR_2 = 0.0632$	
R indices (all data)	$R_1 = 0.0733, wR_2 = 0.0693$	
Absolute structure parameter	-0.022(10)	
Largest diff. peak and hole	1.160 and -1.020 e Å ⁻³	

the resulting bond distances and angles as well as a critical check of the structure and its space group including the MISSYM algorithm implemented in the program PLATON [11] did not reveal any indication that a wrong or unnecessarily low space group symmetry had been chosen. Furthermore, the introduction of a Larson-type extinction correction did not improve the results. We attribute the problems with the thermal motion of the oxygen atoms primarily to an unfavorable ratio of parameters to observed reflections. As mentioned earlier, the compound showed pronounced superstructure effects resulting in large number of weak reflections. To model the anisotropic motion of each atom, the total number of parameters is increased to 937 and the over-determination for the least-squares refinement is reduced to $10656/937 \approx 11$, or to factor of 7, if the reflections with $I > 2\sigma(I)$ are considered. Furthermore, with highly absorbing materials like strontium gallium oxides absorption effects are the crucial point for data accuracy. Due to shading effects of the different domains no really satisfactory absorp-

tion corrections are known for twinned and intergrown crystals [12]. Therefore, the problems encountered during the refinement of the anisotropic temperature factors of the oxygens may be also at least partially due to shortcomings in the absorption correction. The atomic coordinates of the calculations based on anisotropic temperature factors for the cations and isotropic temperature factors for the oxygens as well as selected bond distances and angles are given in Tables 2 and 3, respectively. The largest shift in the last cycle for these refinements was < 0.001 . Anisotropic temperature coefficients for the cations are summarized in Table 4. Drawings of structural details were prepared using the program ATOMS5.1 [13].

3. Description of the structure

The structure of Sr₄Ga₂O₇ belongs to the group of mixed anion gallates with tetrahedral insular [GaO₄]- and [Ga₃O₁₀]-groups. In detail, four crystallographically

Table 2

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{Sr}_4\text{Ga}_2\text{O}_7$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq)
Sr(1)	4310(2)	8710(2)	8292(1)	17(1)
Sr(2)	4460(2)	8730(2)	5839(2)	23(1)
Sr(3)	5992(2)	121(2)	7186(1)	15(1)
Sr(4)	7481(2)	8847(2)	5828(1)	15(1)
Sr(5)	7572(2)	6403(2)	5560(1)	21(1)
Sr(6)	1420(2)	8902(2)	5811(1)	14(1)
Sr(7)	4433(2)	6294(2)	8343(2)	21(1)
Sr(8)	1031(2)	8773(2)	8320(1)	17(1)
Sr(9)	4325(2)	6169(2)	3198(1)	18(1)
Sr(10)	5918(2)	5207(2)	7028(1)	15(1)
Sr(11)	860(2)	6513(2)	8245(1)	17(1)
Sr(12)	7704(2)	3786(2)	5847(1)	16(1)
Sr(13)	−2217(2)	6596(2)	8336(1)	16(1)
Sr(14)	9382(2)	5028(2)	4569(2)	14(1)
Sr(15)	7559(2)	5972(2)	3214(1)	23(1)
Sr(16)	2582(2)	7476(2)	4434(1)	14(1)
Sr(17)	7515(2)	8274(2)	3575(1)	22(1)
Sr(18)	1311(2)	6279(2)	5955(1)	18(1)
Sr(19)	−566(2)	7667(1)	6536(1)	16(1)
Sr(20)	9472(2)	7418(2)	2256(1)	14(1)
Sr(21)	4540(2)	1311(2)	5743(1)	17(1)
Sr(22)	4584(2)	3753(2)	5761(1)	23(1)
Sr(23)	894(2)	6339(2)	692(1)	19(1)
Sr(24)	2873(2)	7475(2)	−376(1)	15(1)
Sr(25)	7748(2)	1199(2)	5613(1)	18(1)
Sr(26)	1129(2)	8961(1)	2857(1)	17(1)
Sr(27)	978(2)	5688(2)	3087(1)	22(1)
Sr(28)	898(2)	1203(2)	5635(1)	15(1)
Sr(29)	4295(2)	8741(2)	3365(1)	14(1)
Sr(30)	8065(2)	1112(2)	3270(1)	18(1)
Sr(31)	4195(2)	6163(2)	5597(1)	20(1)
Sr(32)	9433(2)	9625(2)	4438(1)	16(1)
Ga(1)	6208(2)	7544(2)	6939(2)	14(1)
Ga(2)	6174(2)	9812(2)	4520(1)	12(1)
Ga(3)	5761(2)	7468(2)	4679(1)	15(1)
Ga(4)	2526(2)	7345(2)	1991(1)	13(1)
Ga(5)	2609(2)	4(2)	−593(2)	13(1)
Ga(6)	9635(2)	7453(2)	4404(1)	16(1)
Ga(7)	2505(2)	4878(2)	4642(1)	15(1)
Ga(8)	2744(2)	4931(2)	6920(2)	16(1)
Ga(9)	−885(2)	5206(2)	6940(1)	15(1)
Ga(10)	9191(2)	48(2)	6890(2)	14(1)
Ga(11)	−3887(2)	7472(2)	9676(1)	15(1)
Ga(12)	2616(2)	7652(2)	7047(2)	14(1)
Ga(13)	6287(2)	2567(2)	6986(1)	15(1)
Ga(14)	2917(2)	9933(2)	7087(2)	14(1)
Ga(15)	9524(2)	2360(2)	4408(1)	14(1)
Ga(16)	6216(2)	4850(2)	4555(1)	14(1)
O(1)	7615(11)	7665(10)	6883(7)	29(3)
O(2)	5991(10)	6640(9)	7639(7)	21(3)
O(3)	5611(10)	8577(8)	7082(6)	17(3)
O(4)	5795(9)	7183(9)	5825(6)	16(3)
O(5)	7608(12)	5101(10)	4602(8)	28(4)
O(6)	1195(10)	7700(9)	7077(6)	19(3)
O(7)	1208(11)	9975(9)	4561(7)	24(3)
O(8)	5964(10)	8635(8)	4711(7)	16(3)
O(9)	5991(10)	215(8)	5596(7)	18(3)
O(10)	2737(10)	7947(8)	2988(6)	16(3)
O(11)	5326(10)	77(8)	3648(7)	17(3)
O(12)	1007(8)	2428(8)	4507(6)	9(3)
O(13)	827(10)	7533(10)	5034(7)	28(3)

Table 2 (continued)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq)
O(14)	4460(10)	7297(9)	4324(6)	18(3)
O(15)	1700(11)	5578(9)	7366(7)	23(3)
O(16)	9513(10)	9265(8)	6062(6)	16(3)
O(17)	9755(9)	9753(7)	7933(6)	9(3)
O(18)	2676(12)	9985(8)	−1753(8)	23(3)
O(19)	3032(10)	8767(9)	6856(6)	18(3)
O(20)	9451(10)	6416(8)	3830(6)	19(3)
O(21)	4170(11)	348(10)	6886(7)	25(3)
O(22)	9610(10)	8272(8)	3564(6)	17(3)
O(23)	1222(8)	7545(8)	1634(6)	13(3)
O(24)	3097(9)	7412(8)	8100(6)	15(3)
O(25)	7655(10)	2776(9)	7180(6)	18(3)
O(26)	9341(9)	2414(8)	3235(6)	16(3)
O(27)	7790(11)	9922(9)	6963(7)	21(3)
O(28)	−321(10)	4119(9)	6720(7)	19(3)
O(29)	1166(10)	4618(9)	4383(7)	21(3)
O(30)	9275(10)	1260(9)	4677(6)	18(3)
O(31)	4070(13)	5210(11)	7079(8)	38(4)
O(32)	8514(9)	7745(8)	5073(6)	16(3)
O(33)	−2769(12)	7933(10)	9205(7)	33(4)
O(34)	6829(10)	6952(9)	4147(7)	22(3)
O(35)	−623(9)	5499(8)	8060(6)	14(3)
O(36)	−2265(10)	5059(8)	6844(7)	16(3)
O(37)	5673(10)	3594(9)	7057(7)	20(3)
O(38)	−5248(10)	7661(9)	9406(7)	23(3)
O(39)	3468(8)	7468(8)	1129(6)	15(3)
O(40)	−544(10)	6016(9)	6114(7)	24(3)
O(41)	9424(10)	1140(8)	6618(7)	17(3)
O(42)	3131(10)	1023(9)	−231(7)	22(3)
O(43)	2953(10)	7167(9)	6016(7)	20(3)
O(44)	6218(10)	2256(9)	5829(6)	23(3)
O(45)	2558(11)	6179(10)	2270(7)	28(3)
O(46)	5658(11)	5094(9)	3525(7)	22(3)
O(47)	5903(10)	1626(8)	7595(6)	14(3)
O(48)	3393(11)	4028(9)	4537(7)	26(3)
O(49)	2797(11)	5967(10)	4280(7)	29(4)
O(50)	5590(11)	5151(9)	5545(7)	24(3)
O(51)	2393(14)	4999(11)	5818(9)	36(4)
O(52)	1693(10)	240(8)	6598(6)	15(3)
O(53)	6298(11)	3652(9)	4726(7)	24(3)
O(54)	7592(11)	9795(10)	4325(7)	25(3)
O(55)	9107(12)	3335(10)	4930(7)	30(3)
O(56)	3106(11)	8961(9)	−288(7)	27(3)

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

independent trimers around the following Ga-atoms can be distinguished: Ga(1)–Ga(3)–Ga(2); Ga(13)–Ga(11)–Ga(16); Ga(4)–Ga(8)–Ga(7) and Ga(5)–Ga(14)–Ga(12). The arrangement of the three tetrahedra in a single trimer is not linear, but “horseshoe-like” with a distance between the terminal oxygen atoms of about 3.5 Å (cf. Fig. 1). Although the maximum possible point symmetry of such a T_3O_{10} -group is $mm2$, the trimers in $\text{Sr}_4\text{Ga}_2\text{O}_7$ possess only point symmetry 1. They are located in slabs perpendicular to [100] at about $x \approx 0.44$ (see Fig. 2). The slab in turn contains two layers of trimers at about $x \approx 0.27$ (layer A) and $x \approx 0.61$ (layer B), respectively. The $[\text{Ga}_3\text{O}_{10}]$ -groups are connected by

Table 3
Selected bond lengths [Å] and bond angles [deg] for Sr₄Ga₂O₇

Sr(1)–O(11)	2.396(13)	Sr(1)–O(38)	2.486(13)
Sr(1)–O(3)	2.588(13)	Sr(1)–O(24)	2.609(13)
Sr(1)–O(56)	2.791(13)	Sr(1)–O(19)	2.812(11)
Sr(1)–O(18)	2.937(15)		
Sr(2)–O(42)	2.447(12)	Sr(2)–O(3)	2.480(11)
Sr(2)–O(19)	2.482(13)	Sr(2)–O(8)	2.679(13)
Sr(2)–O(4)	3.005(13)	Sr(2)–O(21)	3.073(14)
Sr(2)–O(9)	3.111(14)	Sr(2)–O(43)	3.174(14)
Sr(3)–O(27)	2.403(15)	Sr(3)–O(21)	2.452(15)
Sr(3)–O(47)	2.468(13)	Sr(3)–O(3)	2.495(13)
Sr(3)–O(11)	2.506(11)	Sr(3)–O(9)	2.526(11)
Sr(4)–O(27)	2.505(13)	Sr(4)–O(1)	2.513(14)
Sr(4)–O(32)	2.516(12)	Sr(4)–O(8)	2.666(11)
Sr(4)–O(16)	2.761(13)	Sr(4)–O(54)	2.819(13)
Sr(4)–O(9)	2.930(13)		
Sr(5)–O(5)	2.557(15)	Sr(5)–O(32)	2.576(13)
Sr(5)–O(34)	2.582(11)	Sr(5)–O(4)	2.669(13)
Sr(5)–O(40)	2.679(13)	Sr(5)–O(1)	2.894(14)
Sr(5)–O(36)	2.947(12)		
Sr(6)–O(52)	2.479(12)	Sr(6)–O(16)	2.594(13)
Sr(6)–O(13)	2.603(14)	Sr(6)–O(7)	2.621(13)
Sr(6)–O(19)	2.676(12)	Sr(6)–O(6)	2.781(13)
Sr(6)–O(42)	2.799(13)		
Sr(7)–O(2)	2.397(14)	Sr(7)–O(48)	2.399(13)
Sr(7)–O(24)	2.513(13)	Sr(7)–O(31)	2.675(15)
Sr(7)–O(46)	2.729(15)	Sr(7)–O(38)	2.768(13)
Sr(7)–O(53)	3.263(13)		
Sr(8)–O(17)	2.353(12)	Sr(8)–O(6)	2.612(12)
Sr(8)–O(12)	2.673(12)	Sr(8)–O(7)	2.797(13)
Sr(8)–O(18)	2.882(15)	Sr(8)–O(26)	2.902(12)
Sr(8)–O(30)	3.166(12)		
Sr(9)–O(46)	2.485(14)	Sr(9)–O(14)	2.528(12)
Sr(9)–O(37)	2.568(13)	Sr(9)–O(49)	2.668(15)
Sr(9)–O(45)	2.726(13)	Sr(9)–O(31)	2.827(16)
Sr(10)–O(50)	2.387(12)	Sr(10)–O(36)	2.409(14)
Sr(10)–O(31)	2.420(18)	Sr(10)–O(46)	2.449(12)
Sr(10)–O(2)	2.465(14)	Sr(10)–O(37)	2.569(14)
Sr(11)–O(15)	2.317(14)	Sr(11)–O(35)	2.532(13)
Sr(11)–O(29)	2.568(13)	Sr(11)–O(26)	2.612(12)
Sr(11)–O(12)	2.613(11)	Sr(11)–O(6)	2.674(13)
Sr(12)–O(55)	2.459(15)	Sr(12)–O(53)	2.552(13)
Sr(12)–O(36)	2.559(12)	Sr(12)–O(25)	2.649(12)
Sr(12)–O(5)	2.868(15)	Sr(12)–O(28)	2.964(13)
Sr(12)–O(44)	3.101(14)		
Sr(13)–O(26)	2.576(12)	Sr(13)–O(2)	2.581(13)
Sr(13)–O(33)	2.628(15)	Sr(13)–O(35)	2.750(13)
Sr(13)–O(1)	2.863(13)	Sr(13)–O(53)	2.981(13)
Sr(13)–O(55)	3.050(13)		
Sr(14)–O(5)	2.324(15)	Sr(14)–O(29)	2.444(14)
Sr(14)–O(20)	2.489(13)	Sr(14)–O(35)	2.533(10)
Sr(14)–O(55)	2.759(16)	Sr(14)–O(40)	2.906(12)
Sr(15)–O(34)	2.352(13)	Sr(15)–O(25)	2.573(13)
Sr(15)–O(5)	2.596(14)	Sr(15)–O(36)	2.727(12)
Sr(15)–O(20)	2.742(13)	Sr(15)–O(46)	2.894(14)
Sr(15)–O(37)	3.134(12)		
Sr(16)–O(49)	2.413(15)	Sr(16)–O(10)	2.423(10)
Sr(16)–O(14)	2.481(13)	Sr(16)–O(13)	2.496(13)
Sr(16)–O(42)	2.533(14)	Sr(16)–O(43)	2.595(11)
Sr(17)–O(34)	2.450(14)	Sr(17)–O(47)	2.611(12)
Sr(17)–O(54)	2.684(15)	Sr(17)–O(22)	2.741(13)
Sr(17)–O(25)	2.772(12)	Sr(17)–O(8)	2.786(13)
Sr(17)–O(32)	2.825(10)		
Sr(18)–O(40)	2.477(14)	Sr(18)–O(51)	2.478(18)
Sr(18)–O(13)	2.538(14)	Sr(18)–O(15)	2.543(12)

Table 3 (continued)

Sr(18)–O(43)	2.567(14)	Sr(18)–O(6)	2.869(13)
Sr(19)–O(1)	2.448(14)	Sr(19)–O(6)	2.449(13)
Sr(19)–O(32)	2.605(10)	Sr(19)–O(16)	2.636(13)
Sr(19)–O(40)	2.693(14)	Sr(19)–O(26)	2.701(10)
Sr(19)–O(13)	3.023(12)		
Sr(20)–O(25)	2.399(13)	Sr(20)–O(22)	2.479(11)
Sr(20)–O(41)	2.492(13)	Sr(20)–O(23)	2.510(11)
Sr(20)–O(28)	2.588(14)	Sr(20)–O(20)	2.955(11)
Sr(21)–O(21)	2.421(13)	Sr(21)–O(39)	2.466(13)
Sr(21)–O(56)	2.511(12)	Sr(21)–O(9)	2.581(13)
Sr(21)–O(44)	2.657(14)	Sr(21)–O(38)	2.687(13)
Sr(22)–O(39)	2.491(13)	Sr(22)–O(37)	2.501(11)
Sr(22)–O(48)	2.513(12)	Sr(22)–O(50)	2.596(14)
Sr(22)–O(53)	2.798(14)	Sr(22)–O(38)	3.108(13)
Sr(22)–O(31)	3.186(16)	Sr(22)–O(44)	3.189(14)
Sr(23)–O(28)	2.401(13)	Sr(23)–O(23)	2.455(12)
Sr(23)–O(29)	2.596(13)	Sr(23)–O(55)	2.670(14)
Sr(23)–O(12)	2.712(12)	Sr(23)–O(51)	2.890(18)
Sr(23)–O(45)	3.308(12)		
Sr(24)–O(56)	2.371(14)	Sr(24)–O(24)	2.439(10)
Sr(24)–O(12)	2.450(11)	Sr(24)–O(48)	2.474(14)
Sr(24)–O(39)	2.503(9)	Sr(24)–O(38)	2.503(13)
Sr(25)–O(30)	2.504(12)	Sr(25)–O(44)	2.632(14)
Sr(25)–O(41)	2.698(12)	Sr(25)–O(33)	2.701(13)
Sr(25)–O(9)	2.776(14)	Sr(25)–O(27)	2.941(13)
Sr(25)–O(54)	3.020(14)		
Sr(26)–O(52)	2.481(12)	Sr(26)–O(22)	2.538(13)
Sr(26)–O(10)	2.649(13)	Sr(26)–O(18)	2.687(14)
Sr(26)–O(17)	2.717(12)	Sr(26)–O(41)	2.960(12)
Sr(26)–O(23)	2.964(12)	Sr(26)–O(7)	3.143(13)
Sr(27)–O(15)	2.494(14)	Sr(27)–O(45)	2.571(14)
Sr(27)–O(20)	2.599(13)	Sr(27)–O(29)	2.669(13)
Sr(27)–O(28)	2.757(11)	Sr(27)–O(35)	2.810(13)
Sr(27)–O(49)	3.055(13)		
Sr(28)–O(52)	2.385(12)	Sr(28)–O(41)	2.495(13)
Sr(28)–O(23)	2.566(12)	Sr(28)–O(30)	2.599(12)
Sr(28)–O(7)	2.616(14)	Sr(28)–O(12)	2.641(12)
Sr(29)–O(10)	2.461(13)	Sr(29)–O(47)	2.511(13)
Sr(29)–O(11)	2.542(13)	Sr(29)–O(42)	2.738(12)
Sr(29)–O(14)	2.749(13)	Sr(29)–O(21)	2.755(12)
Sr(29)–O(18)	2.927(15)	Sr(29)–O(8)	3.041(11)
Sr(30)–O(33)	2.388(15)	Sr(30)–O(26)	2.649(12)
Sr(30)–O(17)	2.658(12)	Sr(30)–O(27)	2.660(13)
Sr(30)–O(30)	2.731(11)	Sr(30)–O(54)	2.745(15)
Sr(30)–O(1)	2.982(14)		
Sr(31)–O(43)	2.372(14)	Sr(31)–O(50)	2.428(14)
Sr(31)–O(4)	2.663(13)	Sr(31)–O(14)	2.724(12)
Sr(31)–O(49)	2.779(13)	Sr(31)–O(31)	2.797(15)
Sr(31)–O(51)	3.012(18)		
Sr(32)–O(7)	2.393(15)	Sr(32)–O(54)	2.428(14)
Sr(32)–O(22)	2.559(13)	Sr(32)–O(30)	2.619(14)
Sr(32)–O(17)	2.620(10)	Sr(32)–O(16)	2.639(10)
Ga(1)–O(3)	1.824(13)	Ga(1)–O(2)	1.833(13)
Ga(1)–O(1)	1.854(15)	Ga(1)–O(4)	1.927(10)
Ga(2)–O(11)	1.811(12)	Ga(2)–O(9)	1.840(12)
Ga(2)–O(54)	1.884(15)	Ga(2)–O(8)	1.905(14)
Ga(3)–O(14)	1.807(13)	Ga(3)–O(34)	1.832(14)
Ga(3)–O(8)	1.863(14)	Ga(3)–O(4)	1.873(10)
Ga(4)–O(23)	1.819(11)	Ga(4)–O(39)	1.862(11)
Ga(4)–O(10)	1.863(11)	Ga(4)–O(45)	1.895(15)
Ga(5)–O(56)	1.835(14)	Ga(5)–O(42)	1.838(14)
Ga(5)–O(18)	1.843(13)	Ga(5)–O(7)	1.852(15)
Ga(6)–O(13)	1.847(12)	Ga(6)–O(22)	1.857(12)
Ga(6)–O(32)	1.877(12)	Ga(6)–O(20)	1.887(13)
Ga(7)–O(48)	1.784(14)	Ga(7)–O(29)	1.841(14)

Table 3 (continued)

Ga(7)–O(49)	1.854(15)	Ga(7)–O(51)	1.882(14)
Ga(8)–O(31)	1.804(17)	Ga(8)–O(51)	1.804(15)
Ga(8)–O(15)	1.853(14)	Ga(8)–O(45)	1.856(15)
Ga(9)–O(36)	1.825(14)	Ga(9)–O(35)	1.863(10)
Ga(9)–O(40)	1.887(13)	Ga(9)–O(28)	1.903(14)
Ga(10)–O(41)	1.806(14)	Ga(10)–O(27)	1.849(15)
Ga(10)–O(16)	1.856(12)	Ga(10)–O(17)	1.861(10)
Ga(11)–O(53)	1.794(15)	Ga(11)–O(33)	1.803(16)
Ga(11)–O(38)	1.851(13)	Ga(11)–O(44)	1.883(11)
Ga(12)–O(24)	1.819(10)	Ga(12)–O(6)	1.862(13)
Ga(12)–O(43)	1.863(12)	Ga(12)–O(19)	1.869(14)
Ga(13)–O(37)	1.814(14)	Ga(13)–O(25)	1.842(13)
Ga(13)–O(47)	1.844(13)	Ga(13)–O(44)	1.901(11)
Ga(14)–O(21)	1.797(15)	Ga(14)–O(52)	1.837(12)
Ga(14)–O(18)	1.872(13)	Ga(14)–O(19)	1.884(14)
Ga(15)–O(30)	1.819(14)	Ga(15)–O(55)	1.835(16)
Ga(15)–O(26)	1.875(9)	Ga(15)–O(12)	1.948(11)
Ga(16)–O(46)	1.823(12)	Ga(16)–O(50)	1.842(13)
Ga(16)–O(5)	1.865(15)	Ga(16)–O(53)	1.914(15)
O–Ga–O angles			
O(3)–Ga(1)–O(2)	123.4(6)	O(3)–Ga(1)–O(1)	109.9(7)
O(2)–Ga(1)–O(1)	105.7(6)	O(3)–Ga(1)–O(4)	105.2(5)
O(2)–Ga(1)–O(4)	106.3(6)	O(1)–Ga(1)–O(4)	104.8(5)
Mean	109.2		
O(11)–Ga(2)–O(9)	122.9(6)	O(11)–Ga(2)–O(54)	118.3(6)
O(9)–Ga(2)–O(54)	107.2(6)	O(11)–Ga(2)–O(8)	105.0(5)
O(9)–Ga(2)–O(8)	99.8(5)	O(54)–Ga(2)–O(8)	99.0(6)
Mean	108.7		
O(14)–Ga(3)–O(34)	120.7(5)	O(14)–Ga(3)–O(8)	106.9(6)
O(34)–Ga(3)–O(8)	110.1(6)	O(14)–Ga(3)–O(4)	106.2(5)
O(34)–Ga(3)–O(4)	109.3(5)	O(8)–Ga(3)–O(4)	102.1(5)
Mean	109.2		
O(23)–Ga(4)–O(39)	112.3(4)	O(23)–Ga(4)–O(10)	107.8(5)
O(39)–Ga(4)–O(10)	118.4(5)	O(23)–Ga(4)–O(45)	105.1(6)
O(39)–Ga(4)–O(45)	105.1(6)	O(10)–Ga(4)–O(45)	107.2(5)
Mean	109.3		
O(56)–Ga(5)–O(42)	125.1(6)	O(56)–Ga(5)–O(18)	103.2(6)
O(42)–Ga(5)–O(18)	107.7(6)	O(56)–Ga(5)–O(7)	109.2(6)
O(42)–Ga(5)–O(7)	108.0(6)	O(18)–Ga(5)–O(7)	100.9(6)
Mean	109.1		
O(13)–Ga(6)–O(22)	110.4(6)	O(13)–Ga(6)–O(32)	109.7(5)
O(22)–Ga(6)–O(32)	103.1(5)	O(13)–Ga(6)–O(20)	115.0(6)
O(22)–Ga(6)–O(20)	104.9(5)	O(32)–Ga(6)–O(20)	112.9(6)
Mean	109.3		
O(48)–Ga(7)–O(29)	115.4(6)	O(48)–Ga(7)–O(49)	122.2(6)
O(29)–Ga(7)–O(49)	109.7(6)	O(48)–Ga(7)–O(51)	103.1(6)
O(29)–Ga(7)–O(51)	99.2(7)	O(49)–Ga(7)–O(51)	103.4(7)
Mean	108.8		
O(31)–Ga(8)–O(51)	110.7(7)	O(31)–Ga(8)–O(15)	121.6(7)
O(51)–Ga(8)–O(15)	99.0(7)	O(31)–Ga(8)–O(45)	108.6(7)
O(51)–Ga(8)–O(45)	108.3(7)	O(15)–Ga(8)–O(45)	107.8(6)
Mean	109.3		
O(36)–Ga(9)–O(35)	106.4(5)	O(36)–Ga(9)–O(40)	105.6(6)
O(35)–Ga(9)–O(40)	116.8(5)	O(36)–Ga(9)–O(28)	104.8(6)
O(35)–Ga(9)–O(28)	109.3(5)	O(40)–Ga(9)–O(28)	112.9(6)
Mean	109.3		
O(41)–Ga(10)–O(27)	106.7(6)	O(41)–Ga(10)–O(16)	115.3(5)
O(27)–Ga(10)–O(16)	101.9(6)	O(41)–Ga(10)–O(17)	112.7(5)
O(27)–Ga(10)–O(17)	107.5(5)	O(16)–Ga(10)–O(17)	111.8(5)
Mean	109.3		
O(53)–Ga(11)–O(33)	108.0(7)	O(53)–Ga(11)–O(38)	107.4(6)
O(33)–Ga(11)–O(38)	128.5(6)	O(53)–Ga(11)–O(44)	100.0(6)
O(33)–Ga(11)–O(44)	105.0(6)	O(38)–Ga(11)–O(44)	104.3(5)
Mean	108.8		
O(24)–Ga(12)–O(6)	108.7(5)	O(24)–Ga(12)–O(43)	129.7(6)

Table 3 (continued)

O(6)–Ga(12)–O(43)	106.6(5)	O(24)–Ga(12)–O(19)	104.3(5)
O(6)–Ga(12)–O(19)	105.0(6)	O(43)–Ga(12)–O(19)	100.0(5)
Mean	109.0		
O(37)–Ga(13)–O(25)	105.0(6)	O(37)–Ga(13)–O(47)	124.3(6)
O(25)–Ga(13)–O(47)	109.1(6)	O(37)–Ga(13)–O(44)	106.0(6)
O(25)–Ga(13)–O(44)	104.1(5)	O(47)–Ga(13)–O(44)	106.6(6)
Mean	109.2		
O(21)–Ga(14)–O(52)	128.5(6)	O(21)–Ga(14)–O(18)	108.8(6)
O(52)–Ga(14)–O(18)	104.3(6)	O(21)–Ga(14)–O(19)	104.3(6)
O(52)–Ga(14)–O(19)	104.3(6)	O(18)–Ga(14)–O(19)	104.4(5)
Mean	109.1		
O(30)–Ga(15)–O(55)	129.9(6)	O(30)–Ga(15)–O(26)	104.8(5)
O(55)–Ga(15)–O(26)	111.9(6)	O(30)–Ga(15)–O(12)	102.4(6)
O(55)–Ga(15)–O(12)	102.6(6)	O(26)–Ga(15)–O(12)	101.1(5)
Mean	108.8		
O(46)–Ga(16)–O(50)	122.1(6)	O(46)–Ga(16)–O(5)	111.8(6)
O(50)–Ga(16)–O(5)	110.7(6)	O(46)–Ga(16)–O(53)	111.0(6)
O(50)–Ga(16)–O(53)	99.1(6)	O(5)–Ga(16)–O(53)	98.7(6)
Mean	108.9		
Ga–O–Ga angles			
Ga(4)–O(45)–Ga(8)	148.3(7)	Ga(8)–O(51)–Ga(7)	158.7(9)
Ga(12)–O(19)–Ga(14)	150.0(7)	Ga(14)–O(18)–Ga(5)	172.8(9)
Ga(16)–O(53)–Ga(11)	164.8(8)	Ga(11)–O(44)–Ga(13)	151.8(8)
Ga(2)–O(8)–Ga(3)	169.3(6)	Ga(3)–O(4)–Ga(1)	145.3(8)

SrO₆-octahedra providing linkage between (1) the trimers of a single layer by corner sharing with the equatorial oxygen atoms of the terminal tetrahedra and (2) the trimers belonging to the neighboring layer of a slab by corner sharing with the apical oxygen atom of the central tetrahedron. The Ga-atoms in the tetrahedral centers of adjacent trimers from different layers are located near the corners of an imaginary distorted cube with a mean edge length of about 4 Å. The remaining two vertices of the cube are occupied by Sr-cations (Fig. 3a). Concerning the arrangement of the trimers and the octahedra both sub-layers differ considerably. Whereas in the layer *A* the octahedra are connected to either two or four different [Ga₃O₁₀]-groups, each octahedron in the layer *B* shares its four equatorial corners with three neighboring trimers (Fig. 4a and b).

The sixth oxygen ligand of the above-mentioned SrO₆-groups links the trimers with the insular tetrahedra around Ga(6), Ga(9), Ga(10) and Ga(15) which are also located in layers parallel to (100) at about $x \approx -0.05$. The insular tetrahedra in turn are connected by SrO₆-octahedra about Sr(14), Sr(19), Sr(20) and Sr(32), sharing common corners or edges (in case of Sr(20)) (Fig. 4c).

Individual Ga–O bonds scatter considerably. However, the observed values are in the normal range for oxo-gallate compounds. Within the trimers the most pronounced spread of the Ga–O bond lengths occurs at the two terminal tetrahedra. For example, the Ga(4)–Ga(8)–Ga(7) trimer: for both outer tetrahedra the Ga–O bond distances to the bridging oxygen atoms (Ga(4)–O(45):1.895 Å; Ga(7)–O(51):1.882 Å) are

Table 4
Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for the cations in $\text{Sr}_4\text{Ga}_2\text{O}_7$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Sr(1)	20(2)	15(1)	17(1)	0(1)	2(1)	-4(1)
Sr(2)	14(2)	51(2)	5(1)	3(1)	-1(1)	13(2)
Sr(3)	14(1)	16(2)	15(1)	1(1)	3(1)	2(1)
Sr(4)	16(1)	13(1)	16(1)	-2(1)	-1(1)	2(1)
Sr(5)	19(1)	20(2)	25(1)	-5(1)	-3(1)	2(1)
Sr(6)	15(1)	13(1)	13(1)	0(1)	0(1)	-1(1)
Sr(7)	29(2)	16(2)	19(1)	1(1)	9(1)	3(1)
Sr(8)	23(1)	9(1)	19(1)	3(1)	-1(1)	-1(1)
Sr(9)	16(1)	19(2)	18(1)	-3(1)	1(1)	0(1)
Sr(10)	14(1)	16(2)	15(1)	-3(1)	1(1)	0(1)
Sr(11)	18(2)	17(1)	17(1)	-2(1)	2(1)	1(1)
Sr(12)	18(1)	16(1)	15(1)	0(1)	3(1)	-1(1)
Sr(13)	15(1)	16(1)	16(1)	-1(1)	-1(1)	1(1)
Sr(14)	10(2)	13(2)	20(2)	1(1)	5(1)	1(1)
Sr(15)	36(2)	17(2)	17(1)	-2(1)	4(1)	-1(1)
Sr(16)	12(1)	16(2)	15(1)	0(1)	1(1)	1(1)
Sr(17)	18(1)	21(1)	27(1)	-11(1)	-2(1)	1(1)
Sr(18)	14(1)	16(1)	22(1)	6(1)	1(1)	-2(1)
Sr(19)	14(1)	18(1)	16(1)	1(1)	2(1)	0(1)
Sr(20)	17(1)	12(1)	14(1)	-1(1)	2(1)	1(1)
Sr(21)	16(1)	15(2)	20(1)	3(1)	0(1)	2(1)
Sr(22)	30(2)	19(2)	19(1)	3(1)	-4(1)	-8(2)
Sr(23)	25(2)	18(2)	15(1)	-2(1)	7(1)	0(1)
Sr(24)	13(1)	13(1)	18(1)	2(1)	0(1)	1(1)
Sr(25)	13(1)	19(2)	23(1)	5(1)	2(1)	2(1)
Sr(26)	16(1)	14(1)	21(1)	3(1)	4(1)	-2(1)
Sr(27)	24(1)	19(1)	23(1)	0(1)	6(1)	8(1)
Sr(28)	20(1)	9(1)	15(1)	2(1)	-1(1)	1(1)
Sr(29)	15(1)	11(1)	17(1)	2(1)	2(1)	-2(1)
Sr(30)	20(2)	16(2)	17(1)	-3(1)	2(1)	0(1)
Sr(31)	18(1)	18(2)	23(1)	6(1)	1(1)	3(1)
Sr(32)	15(1)	17(1)	15(1)	1(1)	1(1)	-1(1)
Ga(1)	14(2)	11(2)	17(1)	1(1)	0(1)	-1(1)
Ga(2)	13(2)	10(2)	12(1)	0(1)	-1(1)	2(1)
Ga(3)	15(1)	14(2)	16(1)	0(1)	-1(1)	2(1)
Ga(4)	13(1)	12(2)	14(1)	0(1)	4(1)	1(1)
Ga(5)	13(2)	12(2)	14(1)	-3(1)	-1(1)	-1(1)
Ga(6)	13(2)	16(2)	18(1)	-1(1)	-2(1)	2(1)
Ga(7)	18(2)	14(2)	14(1)	-2(1)	3(1)	1(1)
Ga(8)	14(2)	21(2)	15(1)	2(1)	1(1)	0(1)
Ga(9)	11(2)	16(2)	17(1)	-1(1)	5(1)	-2(1)
Ga(10)	14(2)	12(2)	17(1)	-1(1)	1(1)	0(1)
Ga(11)	16(2)	14(2)	15(1)	1(1)	2(1)	0(1)
Ga(12)	15(2)	14(2)	13(1)	-1(1)	3(1)	1(1)
Ga(13)	14(2)	15(2)	15(1)	-1(1)	-1(1)	-1(1)
Ga(14)	19(2)	11(2)	13(1)	-2(1)	2(1)	1(1)
Ga(15)	21(2)	10(2)	12(1)	3(1)	-4(1)	-3(1)
Ga(16)	12(2)	16(2)	15(1)	2(1)	1(1)	-1(1)

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

significantly longer than the non-bridging Ga–O bonds, which average at about 1.848 and 1.826 Å, respectively. The central Ga(8)-tetrahedron has more uniform Ga–O distances. The average values of the O–Ga–O bond angles of the tetrahedral comprising the trimers are very close to the ideal value of 109.47°. However, the individual O–Ga–O angles show a pronounced varia-

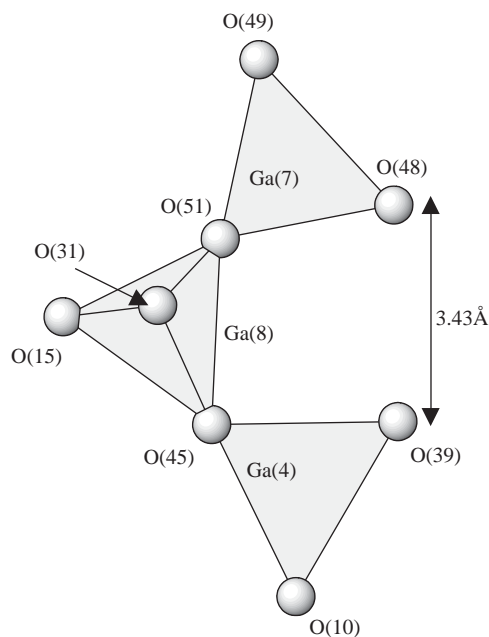


Fig. 1. A single “horseshoe-like” $[\text{Ga}_3\text{O}_{10}]$ -group in $\text{Sr}_4\text{Ga}_2\text{O}_7$ formed by the Ga(7), Ga(8) and Ga(9) atoms.

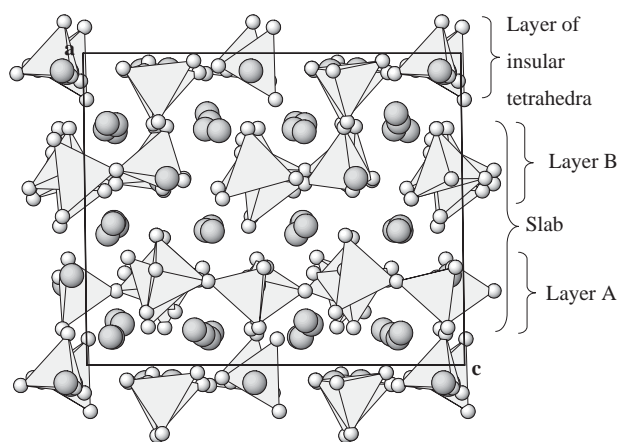


Fig. 2. Projection of the whole structure parallel to $[010]$. The dark gray spheres represent the Sr atoms.

tion: in case of the Ga(4)–Ga(8)–Ga(7) group, for example, they range from 99 to 122°. A more detailed inspection reveals, that long Ga–O bonds are involved in small O–Ga–O angles and vice versa.

Bond valence sums (BVS) were calculated using the parameters for the Ga–O and Sr–O bonds given in [14]. For the 16 crystallographically independent gallium sites the results were close to the expected value of 3.00 valence units (v.u.) for Ga (BVS: 2.75–3.07 v.u.).

Concerning the coordination environments and the bond valence sums at least two groups of Sr-cations have to be distinguished. The coordination polyhedra around eight crystallographically independent strontium atoms (Sr(3), Sr(10), Sr(14), Sr(19), Sr(16), Sr(20),

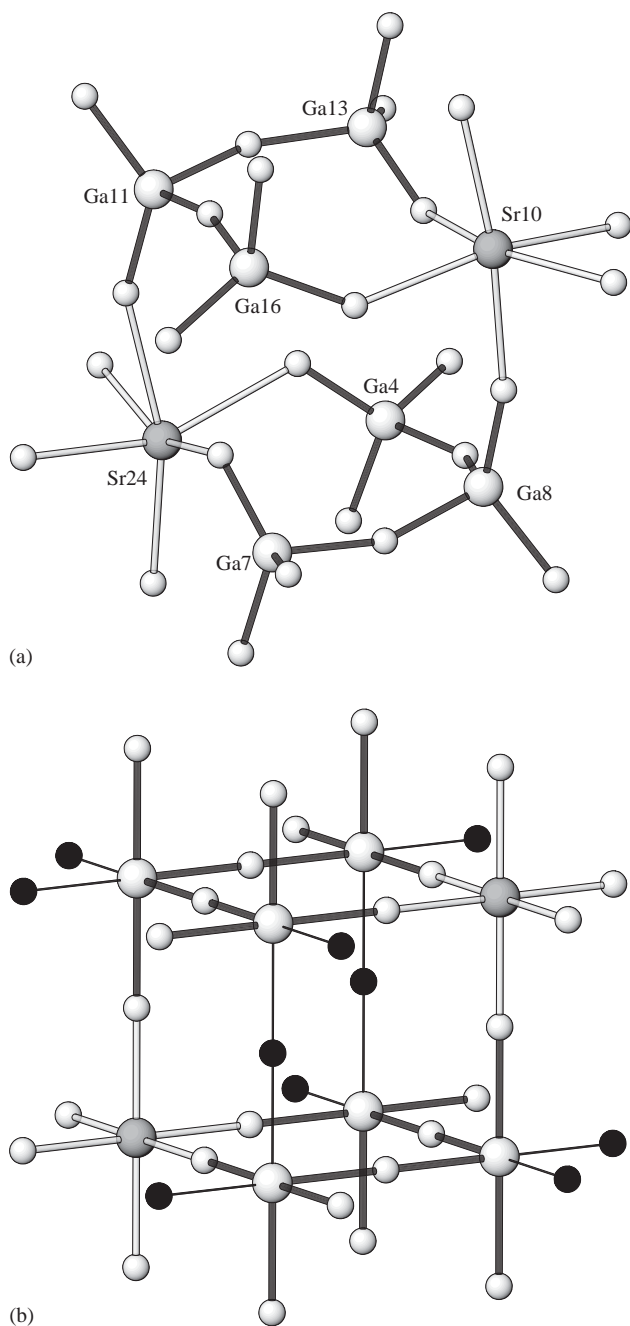


Fig. 3. (a) Real and (b) idealized arrangement of the cations and anions belonging to a single sub-cube. The big spheres correspond to the Sr-cations (medium gray) and the Ga-atoms (light gray). Oxygen ligands (light gray) and oxygen vacancies (dark) are represented by small spheres. The dark gray rods illustrate Ga–O bonds within two adjacent triple tetrahedra. Thin lines joining the Ga atoms and the vacancies have been added as a guide for the eyes. In order to obtain concise drawings the Sr-cation occupying the center of the sub-cube has been omitted.

Sr(24), Sr(32)) can be described as distorted octahedra (type I). The BVS-values of these Sr(I)-atoms are close to or higher than 2 v.u. (1.84 v.u. for Sr19–2.48 for Sr10, respectively). The coordination spheres of the remaining Sr atoms (type II) are much more irregular. To an upper

limit of about 3.3 Å six to eight oxygen ligands can be found. Focussing on the inner oxygen ligands some of the polyhedra can be regarded as strongly distorted octahedra (e.g., Sr(1), Sr(7), Sr(9), Sr(18), Sr(21)) or trigonal prisms (Sr(11), Sr(28)). Several of the strontium atoms of type II are significantly underbonded with valences as low as 1.32 v.u. (for Sr(13)). The pronounced positive and negative deviations from 2 v.u. in the BVS-values for many Sr-cations may explain why Sr₄Ga₂O₇ shows a high reactivity in air of normal humidity. The deviations indicate that the structure contains a considerable amount of internal strain and that this stored potential energy makes it easier to break up bonds during the hydration process.

A different understanding of the crystal structure can be obtained by comparing it with the *ABO*₃-perovskite structure type: Sr₄Ga₂O₇ can be considered as a defect perovskite. The unit cell can be sub-divided into 48 distorted perovskite type sub-cells with an average edge length *a'* of about 4.09 Å. This formal decomposition is also reflected in the lattice constants: *a* ≈ 3*a'*, *b* ≈ 4*a'* and *c* ≈ 4*a'*. A side view of the cationic sub-structure containing the distorted sub-cubes is given in Fig. 5. As far as the metal atoms are concerned, the Sr cations of type II correspond to the *A*-sites, whereas the Ga atoms and the Sr cations of type I are equivalent to the *B*-sites in perovskite, i.e., within a single sub-cell, the Sr(II) atoms occupy the center of the cube and the Ga atoms and the Sr(I) atoms are located at the corners. In detail, two different classes of sub-cells can be distinguished with (a) six Ga- and two Sr(I)-atoms and (b) five Ga- and three Sr(I)-atoms at the corners.

From the 144 oxygen positions within a hypothetical perovskite structure of the same unit cell volume as Sr₄Ga₂O₇ only 112 are actually occupied in the structure, corresponding to 22.2% vacancies in the oxygen sub-lattice. The oxygen vacancies (32 per unit cell) are ordered in such a way that all Sr(I) atoms are coordinated to 6 oxygens, keeping the octahedral coordination characteristic of the perovskite structure, whereas all the Ga atoms are coordinated to 4 oxygens. The principal arrangement of the vacancies and the oxygen atoms belonging to a single sub-cell is shown in Fig. 3b. In the real structure of Sr₄Ga₂O₇ the oxygens are shifted from their ideal positions in perovskite in order to provide an approximate tetrahedral coordination environment around the gallium atoms. In order to express the structural relationship of Sr₄Ga₂O₇ with perovskite the crystal chemical formula could be rewritten as Sr(Ga_{2/3}Sr_{1/3})(O_{7/9}□_{2/9})₃.

4. Discussion and comparison with related structures

The pronounced superstructure effects in the diffraction pattern can be directly linked to the result of the

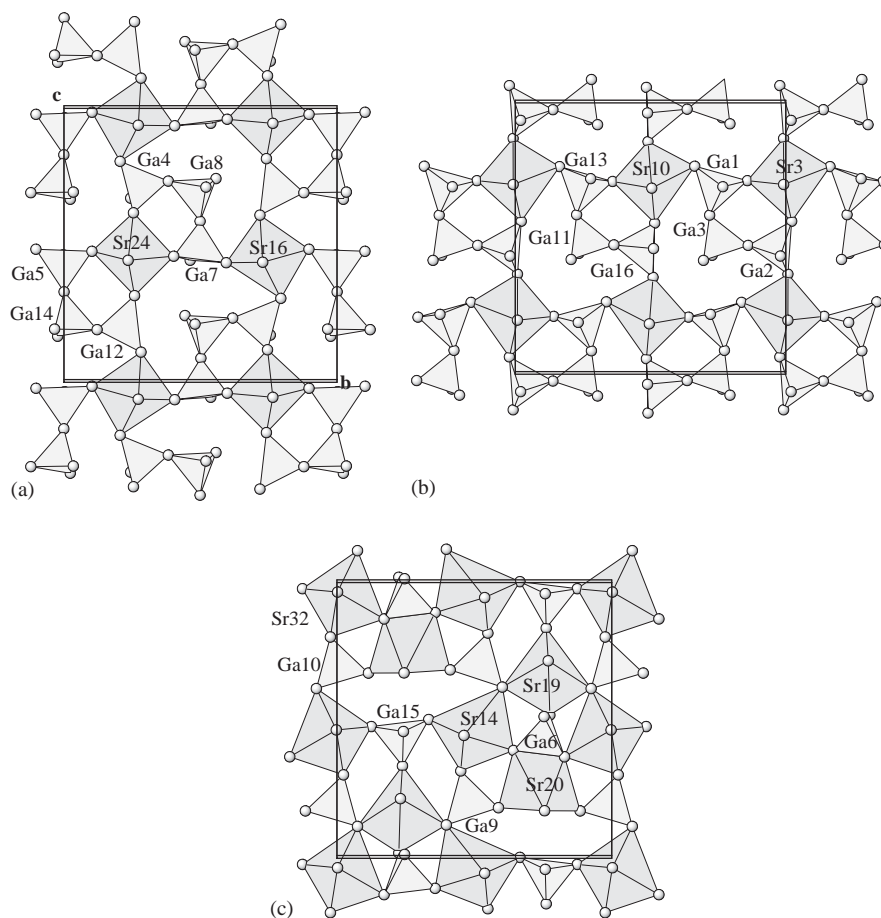


Fig. 4. Projections on to (100) of the single layers in: (a) $x \approx 0.27$ (type A) and (b) $x \approx 0.61$ (type B) containing triple tetrahedra as well as (c) insular tetrahedra in $x \approx -0.05$. The linking SrO_6 octahedra located in the same planes are also shown.

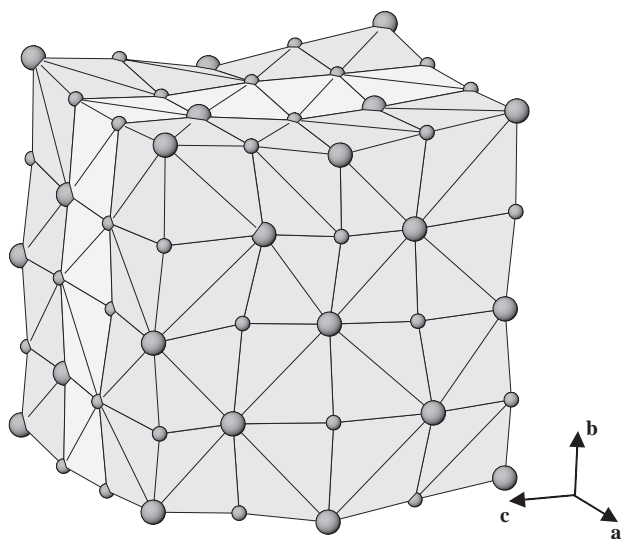


Fig. 5. Side view of the cation sub-structure of $\text{Sr}_4\text{Ga}_2\text{O}_7$ within one unit cell divided into perovskite-type cubes. Big and small dark gray spheres represent Sr- and Ga-atoms, respectively. Medium and light gray colored cubes correspond to the type (a) and (b) sub-cells mentioned in the text.

structure determination: the substructure of the cations has a pseudo-translational symmetry. The very strong reflections ($h = 3n$, $k = 4n$, $l = 4n$) correspond to the small perovskite-type cell that can be approximately used for the description of the heavily scattering Sr- and Ga-ions. This small sub-cell corresponds to the one that has been reported for $\text{Sr}_4\text{Ga}_2\text{O}_7$ in earlier studies, indicating that many weak intensity lines in the powder patterns have been overlooked. Furthermore, the relationship with perovskite is also reflected in the pseudo-tetragonal metric of $\text{Sr}_4\text{Ga}_2\text{O}_7$ which is responsible for the formation of the multiple twins encountered in the crystals. The diffraction pattern can be explained by the superposition of four domains. This could be attributed to the simultaneous occurrence of two different twin laws in the same crystal resulting either from two successive phase transitions (each with its own twinning scheme) or by one phase transition with loss of two kinds of symmetry elements. For example, in the present case a tetragonal-monoclinic ($4mm \leftrightarrow m$) phase transition could explain the observed effects in reciprocal space. A similar tetragonal-monoclinic case of such

Table 5
Comparison between different perovskite related compounds in the alkaline earth rich regions of the systems (Sr,Ba)O–(Al,Ga)₂O₃

Phase, reference (Crystal system)	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	β (deg)	Volume (Å ³) in terms of perovskite sub-cells	Formula in terms of perovskite (<i>ABO</i> ₃)
Sr ₃ Al ₂ O ₆ , [18] (cubic)	15.8556				3986.0 = 64 (= 4 × 4 × 4)	(Sr _{7/8} □ _{1/8})(Al _{3/4} Sr _{1/4})(O _{3/4} □ _{1/4}) ₃
Sr ₃ Ga ₂ O ₆ , [2] (cubic)	16.1049				4177.1 = 64 (= 4 × 4 × 4)	(Sr _{7/8} □ _{1/8})(Ga _{3/4} Sr _{1/4})(O _{3/4} □ _{1/4}) ₃
Ba ₃ Al ₂ O ₆ , [19] (cubic)	16.494				4487.2 = 64 (= 4 × 4 × 4)	Ba(Al _{3/4} Ba _{1/8} □ _{1/8})(O _{3/4} □ _{1/4}) ₃
Ba ₃ Ga ₂ O ₆ , [20] (cubic)	16.746				4696.0 = 64 (= 4 × 4 × 4)	Ba(Ga _{3/4} Ba _{1/8} □ _{1/8})(O _{3/4} □ _{1/4}) ₃
α -Sr ₁₀ Ga ₆ O ₁₉ , [2] (monoclinic)	34.973	7.934	15.943	103.55	4300.7 = 64 (= 8 × 2 × 4)	Sr(Ga _{3/4} Sr _{1/4})(O _{19/24} □ _{5/24}) ₃
Sr ₁₀ Al ₆ O ₁₉ , [21] (monoclinic)	34.582	7.846	15.749	103.68	4151.9 = 64 (= 8 × 2 × 4)	Sr(Al _{3/4} Sr _{1/4})(O _{19/24} □ _{5/24}) ₃
β -Sr ₁₀ Al ₆ O ₁₉ , [21] (orthorhombic)	34.316	7.8918	15.9558		4321.1 = 64 (= 8 × 2 × 4)	Sr(Ga _{3/4} Sr _{1/4})(O _{19/24} □ _{5/24}) ₃
Ba ₄ Al ₂ O ₇ , [16] (orthorhombic)	11.3126	11.7045	27.1850		3599.4 = 48 (= 2√2 × 2√2 × 6)	Ba(Al _{2/3} Sr _{1/3})(O _{7/9} □ _{2/9}) ₃
Sr ₄ Ga ₂ O ₇ (monoclinic)	13.0822	15.7967	15.8586	90.64	3277.1 = 48 (= 3 × 4 × 4)	Sr(Ga _{2/3} Sr _{1/3})(O _{7/9} □ _{2/9}) ₃

“twins of twins” has been recently described in detail by Henke [15]. Experiments to study the high-temperature behavior of Sr₄Ga₂O₇ and the existence of possible phase transformations are planned for the next future.

First alkaline earth oxo-gallates and oxo-aluminates with general composition *A*₄*B*₂O₇ have been structurally characterized only recently. Ba₄Ga₂O₇, for example, adopts a crystal structure containing [Ga₂O₇]-dimers exclusively [16]. On the other hand, a mixed anion structure very similar to Sr₄Ga₂O₇ is realized in Ba₄Al₂O₇ [17]: this compound is built up from the same single and triple tetrahedra in the same ratio 1:1. However, both structures differ in the arrangement of the trimers and the octahedra in the corresponding slabs. Whereas in the oxo-aluminate a single slab consists of two identical layers (type *B*), two different layer types (*A*, *B*) have to be distinguished in Sr₄Ga₂O₇. The structure of Ba₄Al₂O₇ can be also described as a defect perovskite with the same number of oxygen vacancies but with different numbers of perovskite-type sub-cells in different directions of the unit cell (see Table 5).

Compounds with general composition *A*₄*B*₂O₇ are not the only representatives in the systems *AO*–*B*₂O₃ (*A* = Sr, Ba; *B* = Ga, Al) that can be derived from perovskite by the introduction of oxygen vacancies. Sr₃Al₂O₆, Sr₃Ga₂O₆, Ba₃Al₂O₆, Ba₃Ga₂O₆, α -Sr₁₀Ga₆O₁₉, β -Sr₁₀Ga₆O₁₉ and Sr₁₀Al₆O₁₉ are further examples. Different *A*:*B* ratios imply different degrees of condensation of the tetrahedral anion groups. In Sr₃Al₂O₆ and Sr₃Ga₂O₆ cyclic [B₆O₁₈]-groups can be

identified. Ba₃Al₂O₆ and Ba₃Ga₂O₆ are based on highly puckered 12-membered tetrahedral rings, whereas both modifications of Sr₁₀Ga₆O₁₉ are based on non-cyclic [Ga₆O₁₉]-hexamers. The approach to classify these compounds as defect perovskite offers an elegant way to rationalize the similarities and the structural relationships (see Table 4) which can be easily overlooked by focusing on a traditional classification based the geometries and the degree of condensation of the tetrahedral polyanions.

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