

The Crystal Structures of the Calcium Aluminogallates CaAlGaO_4 and $\text{Ca}_2\text{AlGaO}_5$

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The crystal structures of two calcium aluminogallates have been investigated by single-crystal X-ray diffraction methods. $\text{Ca}_2\text{AlGaO}_5$ is a quenched high-pressure phase prepared at 1250°C and 2.5 GPa. The compound belongs to the brownmillerite structure type (space group $I2mb$, $a = 5.2823(6)$ Å, $b = 14.613(2)$ Å, $c = 5.4739(8)$ Å, $V = 422.5(9)$ Å³, $Z = 4$, $D_{\text{calc}} = 4.04$ g cm⁻³, $wR2 = 0.072$ for 586 reflections with $I > 2\sigma(I)$). Main building units are (1) layers of perovskite-type corner-connected MeO_6 -octahedra perpendicular to [010] and (2) zweier single chains of MeO_4 -tetrahedra running parallel to [100] ($\text{Me} = \text{Al}, \text{Ga}$). The stacking of the layers and sheets of single chains results in a three-dimensional network with Ca ions in the interstitial voids. Single crystals of CaAlGaO_4 (space group $P12_1/c1$, $a = 7.9817(1)$ Å, $b = 8.7415(1)$ Å, $c = 10.4430(2)$ Å, $\beta = 94.84(2)^\circ$, $V = 726.0(3)$ Å³, $Z = 8$, $D_{\text{calc}} = 3.67$ g cm⁻³, $wR2 = 0.079$ for 971 reflections with $I > 2\sigma(I)$) were synthesized at ambient pressure and a temperature of 1500°C. The structure consists of layers of S6R of MeO_4 -tetrahedra perpendicular to [100]. The stacking of the layers parallel to the a -axis results in a framework with channels occupied by the Ca cations. The sequence of up (U) and down (D) pointing apices of adjacent tetrahedra within a single ring is UUDUDD. CaAlGaO_4 is isotypic with the monoclinic modification of CaGa_2O_4 . © 2001 Academic Press

scientific properties; SrAl_2O_4 and CaAl_2O_4 doped with Eu, Dy, and Nd have been discussed recently as long persistent phosphor crystals (9, 10). However, most structural investigations have been focussed on the pure end members, neglecting the influence of $\text{Al}^{3+} \leftrightarrow \text{Ga}^{3+}$ cation substitution on the B site. Until now, crystal structure analyses on members of a solid solution series have been reported only for two compounds in the system CaAl_2O_4 – CaGa_2O_4 : CaAlGaO_4 and $\text{CaAl}_{1.5}\text{Ga}_{0.5}\text{O}_4$ (11). No structure refinement to determine the site occupancies of the different tetrahedral sites was performed. Furthermore, the structure analysis for CaAlGaO_4 yielded extremely short Me-O ($\text{Me} = \text{Ga}, \text{Al}$) bond distances of 1.40 Å. This value is much lower than the distances usually observed in oxogallates and oxoaluminates and suggests an error either in the structure model or the reported crystallographic data.

As a part of an ongoing study on the crystal chemistry of brownmillerite-type compounds we recently reported the existence of two new members of this structure family: $\text{Ca}_2\text{Al}_2\text{O}_5$ (12) and $\text{Ca}_2\text{Ga}_2\text{O}_5$ (13). Both phases can only be prepared at high pressures (2.5 GPa, 1250°C) but their crystal structures can be preserved upon quenching. They are isotypic and, therefore, the existence of a solid solution series between these two end-members is likely.

The objectives of this study on calcium aluminogallates were twofold: first, synthesis and structural characterization of an intermediate compound in the system $\text{Ca}_2(\text{Al}_{1-x}\text{Ga}_x)_2\text{O}_5$ and second, reinvestigation of the crystal structure of CaAlGaO_4 . We describe the similarities and differences of the structures with regard to the end members.

INTRODUCTION

Alkaline earth aluminates and gallates have been the subject of many structural and phase analytical studies. The compounds belonging to the family of stuffed framework structures with composition AB_2O_4 ($A = \text{Ca}, \text{Sr}, \text{Ba}$; $B = \text{Al}, \text{Ga}$) have been investigated for a better understanding of the relationship between the chemical composition and framework topology (1–6) and for their interesting ferroic properties and phase transitions (7, 8), as well as for the material

EXPERIMENTAL DETAILS

Sample Preparation

The starting material for the high-pressure phase $\text{Ca}_2\text{AlGaO}_5$ was prepared by solid-state reactions, using CaCO_3 (Fluka, > 98%), Ga_2O_3 (Fluka, 99.99%), and Al_2O_3 (Aldrich, 99.8%) as reagents. The mixed powders

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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 Pt₉₀Rh₁₀–Pt thermocouple and controlled with a Eurotherm 818 controller. Temperatures are considered accurate to within $\pm 10^\circ\text{C}$ 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 CaAlGaO₄ were grown from a melt of stoichiometric composition. One gram of mixed calcium carbonate, gallium oxide, and aluminum oxide powder was placed in a covered 50-ml platinum crucible and heated in air from 100°C in 14 h to 1500°C. The mixture was held at this temperature for 24 h and then cooled to 800°C at a rate of $10^\circ\text{C}/\text{h}$, and finally quenched to room temperature.

X-Ray Single-Crystal Data Collection

Preliminary investigations included polarization microscopy and X-ray diffraction camera techniques. Precession photographs indicated Laue symmetry $2/m$ for CaAlGaO₄ and mmm for Ca₂AlGaO₅. The single-crystal diffraction data were collected from platy transparent optical quality crystals using a Stoe-IPDS diffractometer. Experimental details pertaining to data collection are given in Table 1. The morphology of the crystals of both compounds was described by six external faces and an analytical absorption correction based on the indexed faces was applied in each case. Data reduction included Lorentz and polarization corrections.

Structure Solution and Refinement

The analysis of the systematic absences resulted in the assignment of the space groups $P12_1/c1$ (for CaAlGaO₄) and $I2mb$ or $Immb$ for Ca₂AlGaO₅. Intensity statistics yielded $|E^2 - 1| = 0.745$ for Ca₂AlGaO₅, close to the expected 0.736 for noncentrosymmetric structures. Therefore, the structure solution was started in space group $I2mb$. The

TABLE 1
Experimental Details for the X-Ray Data Collection and the Refinement of CaAlGaO₄ and Ca₂AlGaO₅

	CaAlGaO ₄	Ca ₂ AlGaO ₅
(A) Crystal-Cell Data		
<i>a</i> (Å)	7.9817(1)	5.2823(6)
<i>b</i> (Å)	8.7415(1)	14.613(2)
<i>c</i> (Å)	10.4430(2)	5.4739(8)
β (°)	94.84(2)	
<i>V</i> (Å ³)	726.0(3)	422.5(9)
Space group	$P12_1/c1$	$I2mb$
<i>Z</i>	8	4
Formula	CaAlGaO ₄	Ca ₂ AlGaO ₅
<i>D</i> _{calc} (g cm ⁻³)	3.67	4.04
μ (cm ⁻¹)	90.9	90.6
(B) Intensity Measurements		
Crystal size	80 × 40 × 10 μm ³	90 × 70 × 20 μm ³
Diffractometer	Stoe IPDS	Stoe IPDS
Monochromator	Graphite	Graphite
θ range	2.6°–30.4°	2.8°–30.3°
Reflection range	– 11 ≤ <i>h</i> ≤ 9, – 11 ≤ <i>k</i> ≤ 12, <i>l</i> ≤ 14	<i>h</i> ≤ 6, <i>k</i> ≤ 20, <i>l</i> ≤ 7
Measured reflections	7421	4483
Unique reflections	2215	606
Unique reflections (<i>I</i> > 2σ(<i>I</i>))	2155	586
<i>R</i> _{int}	0.070	0.045
(C) Refinement of the Structure		
Parameters used in the refinement	132	46
<i>R</i> 1 (<i>I</i> > 2 σ(<i>I</i>)) ^a	0.044	0.023
w <i>R</i> 2 (<i>I</i> > 2 σ(<i>I</i>)) ^a	0.063	0.072
Weighting parameter <i>a</i> , <i>b</i>	0.015, 0.00	0.048, 0.61
Goodness of fit	0.88	1.26
Final Δρ _{min} (e/Å ³)	– 1.07	– 0.80
Final Δρ _{max} (e/Å ³)	1.05	0.78

$$^a R1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|} \quad wR2 = \frac{(\sum (w(F_o^2 - F_c^2)^2))^{1/2}}{(\sum (w(F_o^2)))^{1/2}} \\ w = 1/(\sigma^2(F_o^2) + (aP)^2 + bP) \quad P = (2F_c^2 + \max(F_o^2, 0))/3.$$

space group symmetry for CaAlGaO₄ agrees with that proposed in (11). However, the *a*- and *c*-axes are exchanged with respect to our study. Hence, the orientation of the translation vector of the glide plane perpendicular to [010] is different (parallel to the long 10.44 Å axis in the present study versus the short 7.98 Å axis in the paper of Müller-Buschbaum and Schmachtel).

Initial structural models which conform to the space group symmetries were found by direct methods, using the program SIR92 (14). 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 partial structures containing calcium, aluminum/gallium, and some of the oxygen atoms. The structures were completed by difference Fourier calculations providing the starting parameters for the subsequent refinements performed

TABLE 2
Atomic Coordinates and Equivalent Isotropic Displacement Factors for (a) CaAlGaO₄ and (b) Ca₂AlGaO₅

Atom	No. of Al/Ga atoms in cell	x	y	z	$U(\text{eq})^a$
(a) CaAlGaO ₄					
Ca1		-0.0356(2)	0.2400(2)	0.6461(2)	0.0111(4)
Ca2		0.5009(2)	0.2145(2)	0.6281(2)	0.0123(4)
Me1	2.08(2)/1.92(2)	0.2705(2)	0.5594(1)	0.6310(1)	0.0075(4)
Me2	2.10(2)/1.90(2)	0.2100(2)	0.3907(1)	0.8827(1)	0.0076(4)
Me3	1.70(2)/2.30(2)	-0.1972(2)	0.4040(1)	0.8899(1)	0.0073(4)
Me4	2.12(2)/1.88(2)	0.3226(2)	0.0555(1)	0.8615(1)	0.0078(5)
O1		0.0127(7)	0.3390(6)	0.9425(5)	0.0119(11)
O2		0.2294(7)	0.5801(6)	0.4605(5)	0.0154(11)
O3		0.5231(6)	-0.0182(6)	0.8281(5)	0.0144(12)
O4		0.1449(6)	0.4345(6)	0.7174(4)	0.0117(11)
O5		-0.2675(6)	0.2452(5)	0.7893(5)	0.0095(10)
O6		0.2873(6)	0.5670(6)	0.9586(4)	0.0112(11)
O7		0.2184(6)	0.0802(6)	0.7010(4)	0.0130(11)
O8		0.3539(6)	0.2435(5)	0.9293(5)	0.0111(11)
(b) Ca ₂ AlGaO ₅					
Me1	2.26(2)/1.74(2)	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	0.0088(3)
Me2	1.74(2)/2.26(2)	0.4503(4)	$\frac{1}{4}$	0.5715(1)	0.0078(3)
Ca		0.4922(3)	0.6074(1)	0.9751(1)	0.0060(2)
O1		0.5191(7)	0.3588(2)	0.4400(4)	0.0085(6)
O2		0.6063(7)	$\frac{1}{4}$	0.8707(6)	0.0065(7)
O3		0.2502(6)	0.5109(1)	0.2515(6)	0.0055(4)

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

with the SHELXL-93 program (15). Neutral-atom X-ray scattering factors and anomalous-dispersion coefficients were taken from the *International Tables for X-ray Crystallography* (16). Initially, the positional parameters, the isotropic temperature factors, and the site occupancy parameters of the tetrahedrally and octahedrally coordinated *Me* sites were refined. For both structures a soft constraint based on the bulk chemical composition was applied, restricting the number of Al and Ga atoms per formula unit to be equal. The final least-squares calculations using anisotropic displacement parameters converged to $R1 = 0.044$ for 132 parameters for CaAlGaO₄ (cf. Table 1). For Ca₂AlGaO₅ the absolute structure parameter defined by Flack (17) had a value of 0.67(3), suggesting that the crystal is actually an inversion twin. Taking this kind of twinning into account (twin matrix $-1 \ 0 \ 0, 0 \ -1 \ 0, 0 \ 0 \ -1$), the final calculations for Ca₂AlGaO₅ using anisotropic temperature factors converged at $R1 = 0.023$ for 46 parameters. In each case the largest parameter shift in the final cycle was < 0.001 . The refined atomic coordinates and equivalent isotropic and anisotropic displacement factors as well as selected interatomic distances and angles are given in Tables 2 to 4. For drawing of structural details the program ATOMS (18) was used.

RESULTS AND DISCUSSION

Ca₂AlGaO₅

Ca₂AlGaO₅ belongs to the brownmillerite structure type. The two main building units of this compound are (1) layers of perovskite-type corner-connected *Me*O₆-octahedra perpendicular to [010] and (2) zweier single chains of *Me*O₄-tetrahedra running parallel to [100]. The alternate stacking of the octahedral layers and sheets of single chains results in a three-dimensional network. Charge balance is achieved by calcium ions located in voids of the framework and coordinated by eight oxygen atoms in the form of distorted bicapped trigonal prisms. A picture of the whole structure is given in Fig. 1.

Two groups of bond distances in the tetrahedra with values of about 1.78 Å and 1.84 Å can be distinguished. While the longer distances correspond to *Me*^[4]-O2 bonds within the zweier single chains parallel to [100], the shorter distances refer to the oxygen atoms O1 connecting the tetrahedral chains with the octahedral layers. The intrachain *Me*^[4]-O-*Me*^[4] angles are 126.6°. The average values of the O-*Me*^[4]-O angles are very close to the ideal value of 109.4°, whereas the individual O-*Me*^[4]-O angles range from 106° to 126°, respectively. This spread in both distances and angles indicates a significant distortion of the

TABLE 3
Anisotropic Displacement Parameters (Å² × 10³) for (a) CaAlGaO₄ and (b) Ca₂AlGaO₅^a

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
(a) CaAlGaO ₄						
Ca1	9(1)	12(1)	11(1)	-3(1)	-1(1)	0(1)
Ca2	12(1)	12(1)	12(1)	-2(1)	-4(1)	4(1)
Me1	8(1)	7(1)	7(1)	-1(1)	-1(1)	0(1)
Me2	6(1)	8(1)	9(1)	0(1)	-1(1)	0(1)
Me3	8(1)	7(1)	7(1)	-1(1)	0(1)	1(1)
Me4	8(1)	7(1)	8(1)	1(1)	0(1)	-1(1)
O1	8(3)	12(3)	16(3)	1(2)	1(2)	1(2)
O2	16(3)	18(3)	12(2)	1(2)	-3(2)	6(2)
O3	4(3)	18(3)	20(3)	-1(2)	-1(2)	-1(2)
O4	7(3)	17(3)	11(2)	8(2)	-3(2)	-2(2)
O5	9(3)	4(2)	15(2)	3(2)	-1(2)	-2(2)
O6	11(3)	14(3)	9(2)	-5(2)	1(2)	-4(2)
O7	18(3)	11(3)	9(2)	-5(2)	-2(2)	-3(2)
O8	13(3)	13(3)	7(3)	-4(2)	-3(2)	4(2)
(b) Ca ₂ AlGaO ₅						
Me1	6(1)	16(1)	6(1)	0(1)	0	0
Me2	8(1)	9(1)	7(1)	0	0(1)	0
Ca	7(1)	6(1)	6(1)	0(1)	0(1)	-1(1)
O1	10(2)	7(1)	9(1)	2(1)	0(1)	-1(1)
O2	6(2)	10(2)	4(2)	0	-2(1)	0
O3	3(1)	9(1)	5(1)	1(1)	-1(1)	-2(1)

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

TABLE 4
Selected Bond Distances (Å) and Angles (°) for
(a) CaAlGaO_4 and (b) $\text{Ca}_2\text{AlGaO}_5$

(a) CaAlGaO_4			
Me1-O4	1.778(5)	Me2-O8	1.766(5)
-O2	1.792(5)	-O1	1.800(5)
-O3	1.799(5)	-O4	1.802(5)
-O5	1.826(5)	-O6	1.817(5)
Mean	1.799	Mean	1.796
Me3-O5	1.801(5)	Me4-O2	1.776(5)
-O6	1.810(5)	-O3	1.787(5)
-O1	1.810(5)	-O8	1.798(5)
-O7	1.811(5)	-O7	1.820(5)
Mean	1.808	Mean	1.795
Ca1-O1	2.299(5)	Ca2-O8	2.326(5)
-O4	2.311(5)	-O6	2.367(5)
-O2	2.412(5)	-O3	2.391(5)
-O5	2.477(5)	-O5	2.408(5)
-O7	2.488(5)	-O7	2.708(5)
-O6	2.674(5)	-O3	2.910(5)
		-O2	3.009(6)
O4-Me1-O2	120.1(2)	O8-Me2-O1	106.8(2)
O4-Me1-O3	101.1(2)	O8-Me2-O4	123.2(3)
O4-Me1-O5	106.6(2)	O8-Me2-O6	108.0(2)
O2-Me1-O3	111.2(2)	O1-Me2-O4	101.3(2)
O2-Me1-O5	110.7(2)	O1-Me2-O6	109.7(2)
O3-Me1-O5	105.9(2)	O4-Me2-O6	107.3(2)
Mean	109.3	Mean	109.4
O5-Me3-O6	119.4(2)	O2-Me4-O3	107.4(3)
O5-Me3-O1	99.8(2)	O2-Me4-O8	115.6(3)
O5-Me3-O7	109.8(2)	O2-Me4-O7	115.7(2)
O6-Me3-O1	101.8(2)	O3-Me4-O8	108.0(2)
O6-Me3-O7	108.2(2)	O3-Me4-O7	102.1(2)
O1-Me3-O7	118.0(2)	O8-Me4-O7	107.0(2)
Mean	109.5	Mean	109.3
(b) $\text{Ca}_2\text{AlGaO}_5$			
<i>Me1</i> -octahedron			
$2 \times \text{Me1-O3}$	1.902(3)	O3-Me1-O3	92.7(2)
$2 \times \text{Me1-O3}$	1.915(3)	$2 \times \text{O3-Me1-O3}$	87.6(2)
$2 \times \text{Me1-O1}$	2.091(3)	O3-Me1-O3	92.1(2)
Mean	1.969	$2 \times \text{O3-Me1-O3}$	180.0
		$2 \times \text{O1-Me1-O3}$	93.6(2)
		$2 \times \text{O1-Me1-O3}$	90.2(2)
		$2 \times \text{O1-Me1-O3}$	89.9(2)
		$2 \times \text{O1-Me1-O3}$	86.3(2)
		O1-Me1-O1	174.5(2)
<i>Me2</i> -tetrahedron			
$2 \times \text{Me2-O1}$	1.783(3)	O1-Me2-O1	126.2(2)
Me2-O2	1.833(3)	$2 \times \text{O2-Me2-O1}$	105.6(1)
Me2-O2	1.844(4)	$2 \times \text{O2-Me2-O1}$	105.7(1)
Mean	1.811	O2-Me2-O2	106.8(1)
		Mean	109.3
Ca-O2	2.328(2)	Ca-O1	2.330(2)
Ca-O3	2.431(3)	Ca-O3	2.467(3)
Ca-O3	2.482(3)	Ca-O1	2.519(3)
Ca-O1	2.555(3)	Ca-O1	2.833(3)

tetrahedra and can be expressed numerically with the quadratic elongation $l = 1.010$ and the angle variance $\sigma^2 = 69.210$ as defined in Ref. (19). The individual octahedra

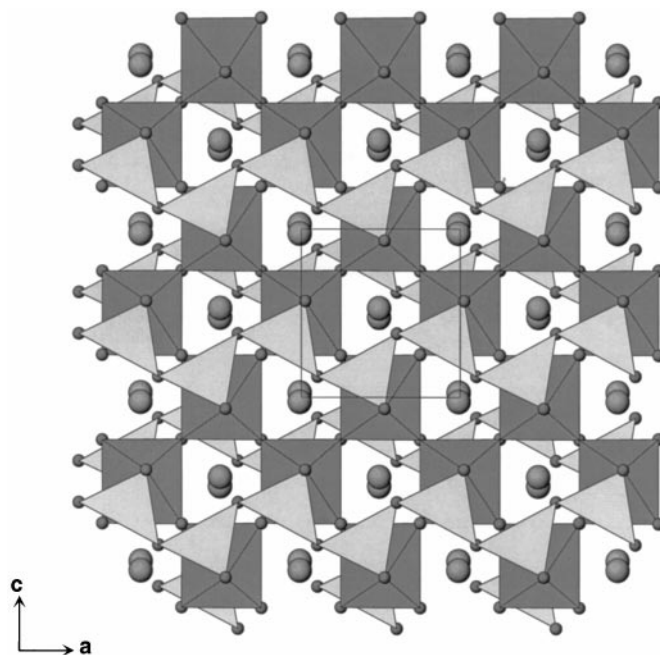


FIG. 1. Projection of the whole structure of $\text{Ca}_2\text{AlGaO}_5$ parallel to [010]. The large spheres in the interstitial sites represent Ca atoms; smaller spheres correspond to oxygen atoms.

within the perovskite-type sheets are significantly less distorted ($l = 1.006$; $\sigma^2 = 6.939$). The distribution of Al and Ga among the tetrahedral and octahedral sites shows a slight preference of aluminum for the sixfold coordinated position.

Unlike the solid solution series in the system $\text{Ca}_2\text{Fe}_2\text{O}_5\text{-Ca}_2\text{Al}_2\text{O}_5$ (20) where two different space groups $Pnma$ and $I2mb$ have to be distinguished, the end members in the system $\text{Ca}_2(\text{Al}_{1-x}\text{Ga}_x)_2\text{O}_5$ as well as the intermediate compound with $x = 0.5$ adopt the same space group $I2mb$. A comparison of some basic crystallographic data of the structurally characterized phases in this system is given in Table 5. The trend in the evolution of the lattice constants is as expected from the substitution of Al^{3+} with ionic radii (21) 0.39 Å and 0.535 Å for four- and sixfold coordination, respectively, for Ga^{3+} (0.47 Å/0.620 Å). Concerning the unit cell volumes, the compositions in the solid solution series $\text{Ca}_2(\text{Al}_{1-x}\text{Ga}_x)_2\text{O}_5$ seem to obey Vegard's law, indicating

TABLE 5
Comparison of the Basic Crystallographic Data of Brownmillerite-Type Structures in the Solid Solution Series $\text{Ca}_2(\text{Al}_{1-x}\text{Ga}_x)_2\text{O}_5$

x -parameter	a (Å)	b (Å)	c (Å)	V (Å ³)
0.0	5.2281(1)	14.4686(2)	5.4004(1)	408.5(1)
0.5	5.2823(6)	14.613(2)	5.4739(8)	422.5(9)
1.0	5.3525(1)	14.6666(1)	5.5651(1)	436.9(1)

a linear variation as a function of the chemical composition. However, for the individual lattice constants there are significant deviations between the observed values listed in Table 5 and the values expected for a linear trend. This is especially the case for the b -axis perpendicular to the octahedral layers ($b_{\text{exp}} = 14.568 \text{ \AA}$ versus $b_{\text{obs}} = 14.613 \text{ \AA}$).

CaAlGaO₄

CaAlGaO_4 belongs 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 MeO_4 tetrahedra ($\text{Me} = \text{Al}, \text{Ga}$) forming honeycomb-like nets. Figure 2a

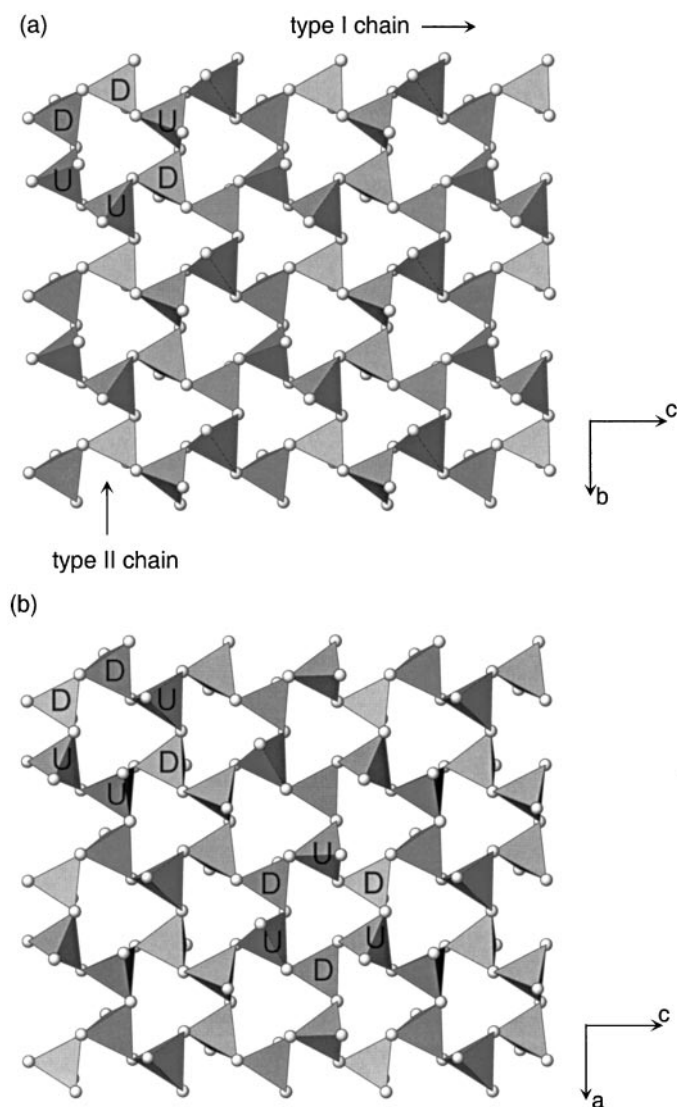


FIG. 2. Single tetrahedral layers with six-membered rings in (a) CaAlGaO_4 and (b) CaAl_2O_4 .

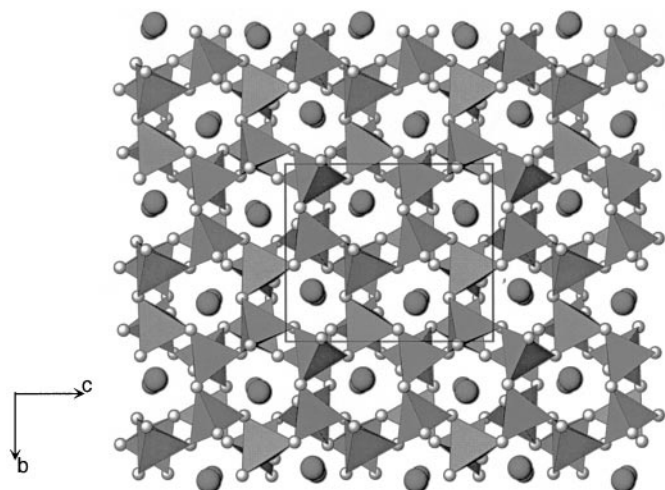


FIG. 3. Projection of the whole structure of CaAlGaO_4 parallel to $[100]$. The large spheres in the interstitial sites represent Ca cations; smaller spheres correspond to oxygen atoms.

shows a projection parallel to $[100]$ of one of the tetrahedral sheets in CaAlGaO_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 sequence of directedness of adjacent tetrahedra within a single S6R is UUDUDD (U = up, D = down). The equatorial oxygen atoms of the layers containing the S6R are not strictly coplanar. Subsequent layers are connected by bridging apical O atoms. All neighboring tetrahedra belonging to different adjacent layers adopt an orientation close to the energetically favorable staggered conformation (see Fig. 3). Perpendicular to $[010]$ CaAlGaO_4 contains layers of four- (S4R) and eight- (S8R) membered rings. The framework density (22) has a value of 22.0 tetrahedral atoms/1000 \AA^3 .

Inspection of the Al/Ga occupancies (Table 2a) of the tetrahedral sites reveals two distinguishable groups. Al and Ga are almost equally distributed among the Me_1 , Me_2 , and Me_4 sites, with only a small observed enrichment of Al. On the other hand, the Me_3 site is clearly depleted of Al and enriched in Ga. This trend is also reflected in the mean bond distances of the tetrahedra around Me_1 – Me_4 . Whereas the $\langle \text{Me}-\text{O} \rangle$ distances for the Me_1 -, Me_2 -, and Me_4 -tetrahedra are almost equal (1.795–1.799 \AA), the average value $\langle \text{Me}_3-\text{O} \rangle$ is slightly larger (1.808 \AA). Using the structural data given for CaAl_2O_4 (1) and the monoclinic modification of CaGa_2O_4 (2) we calculated the mean $\langle \text{Al}-\text{O} \rangle$ and $\langle \text{Ga}-\text{O} \rangle$ values for the pure end members: $\langle \text{Al}-\text{O} \rangle =$

1.753 Å and $\langle \text{Ga-O} \rangle = 1.846$ Å. The expected $\langle \text{Me-O} \rangle$ values for the tetrahedra in CaAlGaO_4 based on the sum of these $\langle \text{Al-O} \rangle$ and $\langle \text{Ga-O} \rangle$ data, weighted by the site occupancies, are 1.798 Å for *Me1*, *Me2*, and *Me4* as well as 1.806 Å for *Me4*. The predicted values are in very good agreement with the actually observed mean bond lengths. The crystal chemically unrealistically short *Me-O* bond distances resulting from the atomic coordinates reported in (11) for CaAlGaO_4 can be likely attributed to a mismatch between the setting of the monoclinic space group and the order of the lattice constants.

A comparison of crystal structures in the system $\text{Ca}(\text{Al}_{1-x}\text{Ga}_x)_2\text{O}_4$ reveals that the solid solution series is not isostructural. The interstitial compound with $x = 0.50$ investigated in this paper is isotypic with the monoclinic modification of the end member with $x = 1.0$ (CaGa_2O_4). A change in space group symmetry occurs between $x = 0.50$ and $x = 0.25$: the composition with $x = 0.25$ (11) adopts the same crystal structure as CaAl_2O_4 ($x = 0.0$). The main difference between the two observed structure types in the system CaAl_2O_4 – CaGa_2O_4 can be attributed to different sequences of up- and down-pointing tetrahedra in the S6R. As mentioned above the gallium-rich compounds exhibit only one sequence of directedness within a single ring: UUDUDD. For the more aluminum-rich compositions an additional second ring sequence has to be distinguished: UDUDUD. For a better comparison, the single tetrahedral layers of both structure types containing the S6R are shown in Figs. 2a and 2b.

CaGa_2O_4 exists in two polymorphic forms. A monoclinic phase (2) and an orthorhombic modification (3) crystallize simultaneously from reactions between oxidic starting materials. Using the tetrahedral sequences it is also possible to find an explanation why the crystal structures of the gallium-rich solid solutions are based on the monoclinic structure type. In the orthorhombic form of the pure gallium end member the S6R exclusively have an UUUUDD tetrahedral sequence, which does not occur in CaAl_2O_4 .

The monoclinic forms of CaGa_2O_4 and CaAl_2O_4 share at least one common ring type.

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