

The Stuffed Framework Structure of BaGa₂O₄

V. Kahlenberg,*† R. X. Fischer,* and J. B. Parise†

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

†*CHIPR, Department of Geosciences, State University of New York at Stony Brook, Stony Brook, New York 11794*

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Crystals of barium monogallate were obtained by growth from a stoichiometric melt at 1350°C. The hexagonal crystals belong to space group $P6_3$, $a = 18.6403(7)$ Å and $c = 8.6801(2)$ Å, $V = 2611.9(2)$ Å³, $Z = 24$, $D_{\text{calc.}} = 5.20$ g cm⁻³. The structure was solved by Patterson techniques using a single crystal diffraction data set. Merohedral twinning of the crystal (twin element $2_{[110]}$) was accounted for in the refinement calculations ($wR2 = 0.056$ for 4183 reflections). The main structural features of BaGa₂O₄ are layers of six-membered rings of GaO₄ tetrahedra perpendicular to the c -axis. The stacking of the layers parallel to c results in a three-dimensional framework containing tunnels, where the barium cations are located. Within a single layer two different types of ditrigonal-shaped six-membered rings are distinguished on the basis of relative orientation of up (U) and down (D) pointing apices of adjacent tetrahedra: one-fourth of the rings have an UDUDUD topology, whereas the sequences of directedness of the remaining rings is UUUDDD. The structure is isotypic with KAlGeO₄. It is the first member of this structure family containing exclusively trivalent tetrahedral ions of only one chemical species and divalent nonframework cations within the channels. © 2000 Academic Press

bond angles equal 180°, a feature which is frequently observed in stuffed derivatives (e.g., in nephelines (10) or in BaAl₂O₄ (11)), but it requires a complete reorientation of the tetrahedra, including a change in the sequence of directedness within the single S6R. Moreover, the refinement calculations converged at a relatively high residual of 0.13. We decided, therefore, to reinvestigate the crystal structure of BaGa₂O₄ as a part of our ongoing studies on alkaline earth aluminates and gallates. Our first synthesis experiments resulted in hexagonal crystals of barium monogallate having a definite unit cell volume larger than the previously reported ($a = \sqrt{3} \cdot a'$, $c = c'$). One explanation for the lack of agreement is to assume that Deiseroth and Müller-Buschbaum obtained a different polymorph of this compound. Therefore, an attempt was made to duplicate the preparation given in (8, 9) as closely as possible, as well as to prepare BaGa₂O₄ over a wide range of temperatures. However, the crystalline products always gave unit cells with an a -lattice constant of about 18.64 Å. The present paper presents the crystal structure of this phase and a comparison with other related structures.

INTRODUCTION

Double oxides of composition AB_2O_4 , where A represents a divalent cation (Ca, Sr, Ba) and B a trivalent cation (Al, Ga), are known to show interesting ferroic properties and a great variety of different polymorphic forms (1–7). All these compounds belong to the group of stuffed tetrahedral framework structures. The main differences between the various structures can be attributed to different framework topologies. The existence of barium monogallate was first mentioned by Hoppe and Schepers (8). An initial structure analysis of this phase was reported by Deiseroth and Müller-Buschbaum (9). According to their results the structure adopts space group $P6_3$ with $a' = 10.74$ Å and $c' = 8.675$ Å. Their model, however, shows some peculiarities, the most striking being a disorder of some of the tetrahedra belonging to the three-dimensional network. It is not concerned with only a slight tilting of some tetrahedra to avoid T–O–T

EXPERIMENTAL DETAILS

The single crystals used for the structure analysis were grown from a stoichiometric melt of composition BaO · Ga₂O₃. One gram of mixed barium carbonate (Fluka, >99%) and gallium oxide (Fluka, 99.99%) powder was placed in a covered 50-ml platinum crucible and heated in air from 100°C in 10 h to 1350°C. The mixture was held at this temperature for 4 days and then cooled down to 600°C at a rate of 5°C/h, and finally quenched to room temperature. Colorless, transparent, highly birefringent crystals of up to $0.3 \times 0.3 \times 0.1$ mm³ could be separated mechanically from the solidified melt.

Preliminary investigations included polarization microscopy and X-ray diffraction camera techniques. Precession photographs of single crystal were consistent with a hexagonal, $6/m$ Laue symmetry. Systematic absences either suggested space group $P6_3$ or $P6_3/m$. Subsequent structure

TABLE 1
Experimental Details of the Structure Analysis of BaGa₂O₄

| (A) Crystal data | |
|--|---|
| <i>a</i> (Å) | 18.6403(7) |
| <i>c</i> (Å) | 8.6801(2) |
| <i>V</i> (Å ³) | 2,611.9(2) |
| Space group | <i>P</i> 6 ₃ |
| <i>Z</i> | 24 |
| Chemical formula | BaGa ₂ O ₄ |
| <i>D</i> _{calc} (g cm ⁻³) | 5.20 |
| <i>μ</i> (cm ⁻¹) | 211.15 |
| (B) Intensity measurements | |
| Crystal shape | Plate (80 × 80 × 40 μm ³) |
| Diffractometer | Bruker CCD |
| Monochromator | Graphite |
| Radiation | MoKα, λ = 0.71073 Å |
| X-ray powder | 50 kV, 30 mA |
| Detector to sample distance | 50 mm |
| Rotation width in φ(°) | 0.3 |
| Irradiation time/exposure (s) | 60 |
| θ-range (°) | 2.3°–28.0° |
| Reflection range | <i>h</i> ≤ 24; <i>k</i> ≤ 24; <i>l</i> ≤ 11 |
| No. of measured reflections | 22,771 |
| No. of unique reflections | 4,183 |
| <i>R</i> _{int} after absorption correction | 0.050 |
| No. of observed reflections (<i>I</i> > 2σ(<i>I</i>)) | 3,776 |
| (C) Refinement of the structure | |
| No. of parameters used in the refinement | 254 |
| <i>R</i> 1 (<i>F</i> _o > 4σ(<i>F</i> _o)); <i>R</i> 1 (all data) | 0.028; 0.033 |
| w <i>R</i> 2 (<i>F</i> _o > 4σ(<i>F</i> _o)); w <i>R</i> 2 (all data) | 0.055; 0.056 |
| Weighting parameter <i>a</i> | 0.022 |
| Goodness of Fit | 1.016 |
| Final Δρ _{min} (e/Å ³) | – 0.955 |
| Final Δρ _{max} (e/Å ³) | 1.045 |
| <i>R</i> 1 = Σ <i>F</i> _o – <i>F</i> _c /Σ <i>F</i> _o | w <i>R</i> 2 = (Σ(w(<i>F</i> _o ² – <i>F</i> _c ²)/Σ(w(<i>F</i> _o ²)) ²) ^{1/2} |
| <i>w</i> = 1/(σ ² (<i>F</i> _o ²) + (<i>aP</i>) ²) | <i>P</i> = (2 <i>F</i> _c ² + max(<i>F</i> _o ² , 0))/3 |

refinement confirmed the adequacy of the choice of the noncentrosymmetric space group. The single crystal diffraction data were collected from platy transparent optical quality crystals using a Bruker CCD diffractometer. Experimental details pertaining to data collection are given in Table 1. An empirical absorption correction based on the symmetry equivalent reflections was applied. Data reduction included Lorentz and polarization corrections.

STRUCTURE SOLUTION AND TWINNING

Structure determination was initiated using a Patterson-function peak-search/solution algorithm implemented in the program SHELXS-86 (12). A trial structure based on the positions of the Ba and Ga atoms was refined, and the oxygen atom positions were found using difference Fourier calculations (program SHELXL-93 (13)). 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* (14). Although the structure model seemed to be reasonable with regard to bond distances and bond angles, iterative full-matrix least-squares refinements based on *F*² using isotropic displacement factors converged at an unconvincingly high w*R*2 index of 0.165. The situation was not significantly improved after introduction of anisotropic displacement parameters.

Finally, possible twinning of the crystal was considered to be the reason for the problems during the refinement calculations. Twinning and especially twinning by merohedry are features often encountered in stuffed derivatives (15). For twinning by merohedry, the twin element belongs to the point group of the translation lattice of the crystal (holohedry), but it is not an element of the Laue group of the crystal. It cannot be detected by optical methods, because the optical indicatrix is unaffected. For the specific case all elements of the hexagonal holohedry 6/*m* 2/*m* 2/*m* not contained in the Laue group 6/*m* are possible twin elements. Actually, the differences in the *R*_{int} values for merging the data set in the two hexagonal Laue groups were not very pronounced: 0.088 for 6/*m* 2/*m* 2/*m* and 0.055 for 6/*m*, respectively. Provided that the hypothesis of twinning is true, the slightly higher value for 6/*m* 2/*m* 2/*m* indicates that the volume fraction α of the two twin individuals in the crystal is not very different from 0.5.

The existence of twinning by merohedry can be verified by a statistical test proposed by Britton (16), assuming α ≠ 0.5. For every pair of twin related reflections (*h*₁*k*₁*l*₁) and (*h*₂*k*₂*l*₂) in the data set, the ratio *k* = *J*₁/(*J*₁ + *J*₂) is calculated. According to Britton, the relative frequency distribution of *k*, *W*(*k*), can be evaluated to detect the presence of twinning.

In contrast with an untwinned crystal, where all possible values of *k* in the interval 0 ≤ *k* ≤ 1 can occur with a certain probability, the values of *W*(*k*) ≠ 0 for a twinned crystal are restricted to a region with *k*₁ ≤ *k* ≤ *k*₂ symmetrical to *k* = 0.5. The values *k*₁ and *k*₂ of the discontinuities of *W*(*k*) correspond to the volume fractions α and 1 – α of the two twin individuals. The function *W*(*k*) for the present data set was calculated using the program TWIN2.0 (17) and the result is shown in Fig. 1, assuming the twofold axis 2₁₁₀ as the element of twinning. The form of the distribution confirms the hypothesis of twinning by merohedry. The volume fractions of the two twin individuals are estimated to be 0.44 and 0.56, respectively.

The fraction of the twin components with the total fraction constrained to 1.0 and the twin model described above was introduced into the calculations. It substantially improved the refinement after a few cycles (w*R*2 = 0.086). The refinement of the value α for the twin component 1 converged to 0.437(2), which is in very good agreement with the estimated value from the Britton test. The Flack

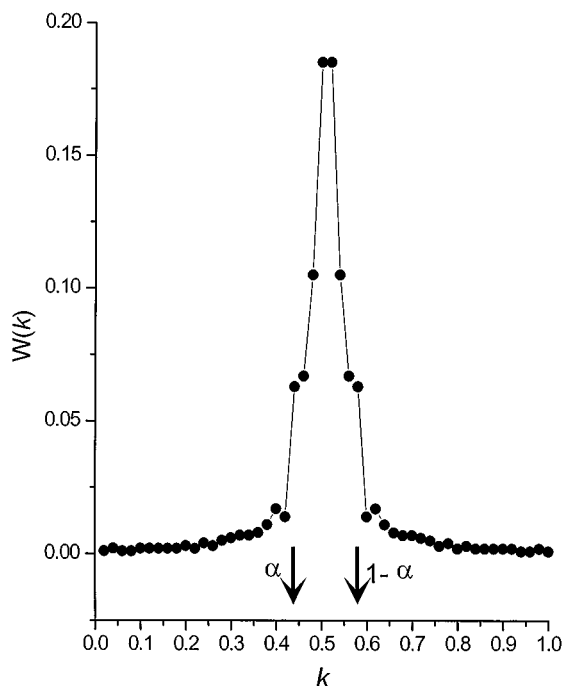


FIG. 1. Relative frequency distribution $W(k)$ for the twinned crystal. The arrows indicate the volume ratios of the two twin individuals.

parameter had a value of 0.06(5), indicating that no additional inversion twinning is present. The final least squares calculations using anisotropic displacement parameters converged to $wR2 = 0.056$ for 254 parameters for all independent reflections (cf. Table 1). The largest shift/esd in the final cycle was < 0.01 . The refined atomic coordinates, equivalent isotropic and anisotropic displacement factors as well as selected interatomic distances and angles are given in Tables 2 to 4. Figures showing structural details were made using the program Atoms (18) and Ortep3 (19).

DESCRIPTION OF THE STRUCTURE

BaGa_2O_4 is isotypic with the structure of KAlGeO_4 (20, 21) and belongs to the group of stuffed framework structures consisting of sequences of tetrahedral layers. Each layer perpendicular to $[001]$ is composed of trigonally shaped 6-membered rings (S6R) of GaO_4 tetrahedra forming honeycomb-like nets. Figure 2 shows a projection parallel to $[001]$ of one of the tetrahedral sheets in barium monogallate. The equatorial oxygen atoms of the layers are not strictly coplanar, but the layers are corrugated normal to the $[001]$ direction. Within a single layer perpendicular to $[001]$ two different types of six-membered ditrigonal-shaped rings have to be distinguished with respect to the relative orientation of up (U) and down (D) pointing apices of adjacent tetrahedra: one-fourth of the rings have an UDUDUD topology and are located about the 6_3 - and

the 3-axis running parallel to $[001]$. The remaining rings adopt an UUDDDD conformation. Subsequent tetrahedral sheets are connected by bridging apical O atoms. Neighboring tetrahedra belonging to different adjacent layers adopt an orientation close to the energetically favorable staggered conformation. In the direction perpendicular to $[210]$ and $[120]$ the framework contains layers of 10-membered rings (cf. Fig. 3). The framework density (22) of the compound has a value of 18.4 tetrahedral atoms/1000 \AA^3 .

The interatomic distances and angles within the tetrahedral Ga–O framework are within the normal range of oxogallate structures (cf. Table 4). The spread of the individual O–Ga–O angles and the Ga–O distances, however, suggests that the tetrahedra deviate significantly from regularity. The quadratic elongations, λ , and the angle variances, σ^2 (23), have values of $\lambda = 1.002$ – 1.015 and $\sigma^2 = 8.65$ – 53.35 for tetrahedra in BaGa_2O_4 . The Ga–O–Ga angles show a considerable variation between 114.2° and 168.2° with an average of 125.6° . The calculation of the bond–valence sums

TABLE 2
Atomic Coordinates and Equivalent Isotropic Displacement Factors for BaGa_2O_4

| | x | y | z | U (eq) |
|-----|---------------|---------------|--------------|----------|
| Ba1 | 0 | 0 | 0.1986(2) | 0.014(1) |
| Ba2 | 0.16172(6) | – 0.17011(5) | 0.1688(2) | 0.014(1) |
| Ba3 | 0.3340(1) | – 0.80823(6) | 0.1676(2) | 0.018(1) |
| Ba4 | $\frac{1}{3}$ | $\frac{2}{3}$ | 0.1470(2) | 0.015(1) |
| Ba5 | $\frac{1}{3}$ | $\frac{2}{3}$ | – 0.3543(2) | 0.013(1) |
| Ba6 | 0.48513(8) | – 0.99976(6) | – 0.3224(1) | 0.016(1) |
| Ga1 | 0.1540(1) | – 0.8347(1) | 0.4759(3) | 0.012(1) |
| Ga2 | 0.1735(1) | – 0.9884(1) | 0.3701(3) | 0.010(1) |
| Ga3 | 0.3381(1) | 0.0000(1) | 0.3668(2) | 0.009(1) |
| Ga4 | 0.3281(2) | – 0.0005(1) | – 0.0423(2) | 0.012(1) |
| Ga5 | 0.3387(2) | – 0.1654(1) | – 0.0298(3) | 0.012(1) |
| Ga6 | 0.3451(1) | – 0.1660(1) | 0.3666(3) | 0.010(1) |
| Ga7 | 0.4932(1) | – 0.8280(1) | – 0.0264(3) | 0.012(1) |
| Ga8 | 0.5006(2) | – 0.8272(1) | 0.3664(3) | 0.009(1) |
| O1 | 0.3858(6) | – 0.2182(6) | – 0.1265(13) | 0.013(2) |
| O2 | 0.1063(8) | – 0.1021(7) | 0.3701(14) | 0.037(3) |
| O3 | 0.1131(7) | – 0.9460(8) | 0.4650(19) | 0.020(2) |
| O4 | 0.2171(8) | – 0.0453(9) | – 0.0907(14) | 0.025(3) |
| O5 | 0.2753(9) | – 0.9599(9) | 0.4569(19) | 0.022(3) |
| O6 | 0.2744(7) | – 0.2783(7) | 0.3844(13) | 0.016(2) |
| O7 | 0.1863(8) | – 0.9477(7) | 0.1708(12) | 0.022(2) |
| O8 | 0.2921(10) | – 0.1083(8) | 0.4293(14) | 0.019(3) |
| O9 | 0.4469(9) | – 0.9418(10) | 0.4201(13) | 0.021(2) |
| O10 | 0.3589(8) | – 0.0699(7) | – 0.1341(15) | 0.020(2) |
| O11 | 0.3825(8) | – 0.1484(6) | 0.1650(11) | 0.016(2) |
| O12 | 0.3935(8) | – 0.8935(8) | – 0.1184(17) | 0.018(3) |
| O13 | 0.4352(6) | – 0.4453(6) | 0.4765(12) | 0.018(2) |
| O14 | 0.4760(7) | – 0.8066(6) | 0.1696(11) | 0.021(2) |
| O15 | 0.3343(10) | – 0.0095(7) | 0.1632(16) | 0.035(2) |
| O16 | 0.4610(6) | – 0.7736(6) | 0.4924(10) | 0.016(2) |

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

TABLE 3
Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for BaGa₂O₄

| | U_{11} | U_{22} | U_{33} | U_{23} | U_{13} | U_{12} |
|-----|----------|----------|----------|----------|----------|----------|
| Ba1 | 17(1) | 17(1) | 10(1) | 0 | 0 | 9(1) |
| Ba2 | 19(1) | 15(1) | 10(1) | 2(1) | 4(1) | 9(1) |
| Ba3 | 18(1) | 19(1) | 17(1) | 1(1) | 7(1) | 8(1) |
| Ba4 | 14(1) | 14(1) | 15(1) | 0 | 0 | 7(1) |
| Ba5 | 14(1) | 14(1) | 11(1) | 0 | 0 | 7(1) |
| Ba6 | 17(1) | 14(1) | 12(1) | 2(1) | 2(1) | 5(1) |
| Ga1 | 12(1) | 13(1) | 11(1) | 0(1) | 0(1) | 5(1) |
| Ga2 | 8(1) | 9(1) | 13(1) | -1(1) | -1(1) | 6(1) |
| Ga3 | 9(1) | 10(1) | 8(1) | -1(1) | 1(1) | 4(1) |
| Ga4 | 13(1) | 11(1) | 13(1) | 0(1) | -2(1) | 7(1) |
| Ga5 | 11(1) | 12(1) | 12(1) | -2(1) | -2(1) | 4(1) |
| Ga6 | 10(1) | 7(1) | 12(1) | -1(1) | 0(1) | 4(1) |
| Ga7 | 12(1) | 12(1) | 13(1) | 1(1) | -2(1) | 6(1) |
| Ga8 | 9(1) | 9(1) | 10(1) | -2(1) | 0(1) | 5(1) |
| O1 | 24(4) | 16(4) | 15(4) | -8(4) | 2(4) | 3(4) |
| O2 | 30(6) | 10(5) | 68(7) | -20(6) | 2(6) | 8(5) |
| O3 | 12(5) | 15(6) | 37(6) | 5(6) | 18(6) | 10(5) |
| O4 | 19(5) | 21(6) | 45(8) | -11(4) | -1(4) | 18(5) |
| O5 | 22(6) | 28(7) | 24(6) | -12(6) | -9(6) | 20(5) |
| O6 | 20(5) | 15(5) | 10(3) | 8(5) | 3(5) | 7(4) |
| O7 | 28(6) | 20(5) | 18(6) | 4(4) | 3(5) | 12(5) |
| O8 | 27(7) | 10(5) | 27(7) | 3(4) | 9(4) | 15(5) |
| O9 | 20(6) | 19(6) | 24(6) | -7(4) | -6(4) | 9(5) |
| O10 | 28(5) | 16(5) | 22(6) | 7(4) | 9(4) | 15(4) |
| O11 | 17(4) | 23(5) | 7(4) | 0(4) | 0(4) | 8(4) |
| O12 | 7(5) | 13(5) | 26(6) | 15(5) | -2(5) | -2(4) |
| O13 | 11(4) | 18(5) | 19(4) | 3(4) | -1(4) | 3(4) |
| O14 | 27(5) | 24(5) | 17(5) | 1(5) | -7(5) | 18(4) |
| O15 | 72(7) | 45(9) | 14(3) | 8(7) | 4(5) | 42(8) |
| O16 | 30(5) | 12(4) | 12(3) | 1(3) | 11(3) | 14(4) |

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

(BVS) for the different crystallographic tetrahedral sites using the parameters for the Ga–O bond given in (24) were close to the expected value of 3.00 valence units (v.u.) for gallium (BVS = 2.75–3.16 v.u.).

Among the group of the oxygen atoms, O2 and O15 show the highest values for the anisotropic displacement parameters. Similar results have been observed for the corresponding oxygen atoms in KAlGeO₄ (20). The large magnitude for the thermal motion may indicate that O2 and O15 are disordered. Therefore, the refined coordinates for the two anions define an average position, the averaging being either in time (thermal motion interpretation) or in space (static disorder interpretation). To test the static interpretation, the final refinement cycle was repeated using two split positions for each oxygen site with isotropic temperature factors. However, the least squares refinements became unstable. Therefore, at this stage no final decision on the existence and the nature of the disorder can be made.

Charge balance is achieved by Ba ions occupying the channels of the tetrahedral network running parallel [001]

(cf. Fig. 4). Ba–O distances cover a wide range, as can be seen in Table 4. However, the values are consistent with Ba–O distances reported in the literature. The following two groups of distances can be distinguished: barium ions

TABLE 4
Selected Bond Distances (\AA) up to 3.5 \AA and Bond Angles ($^\circ$) for BaGa₂O₄

| | | | |
|------------|---------------|-------------|---------------|
| Ga1–O2 | 1.789(14) | Ga5–O1 | 1.819(10) |
| –O7 | 1.817(11) | –O11 | 1.832(9) |
| –O3 | 1.820(13) | –O16 | 1.839(10) |
| –O4 | 1.843(12) | –O10 | 1.861(11) |
| Mean | 1.817 | Mean | 1.838 |
| Ga2–O2 | 1.845(12) | Ga6–O6 | 1.840(11) |
| –O7 | 1.857(11) | –O11 | 1.854(9) |
| –O5 | 1.856(14) | –O8 | 1.867(14) |
| –O3 | 1.860(12) | –O13 | 1.879(10) |
| Mean | 1.855 | Mean | 1.860 |
| Ga3–O15 | 1.773(15) | Ga7–O14 | 1.812(10) |
| –O9 | 1.817(14) | –O12 | 1.821(13) |
| –O8 | 1.837(13) | –O6 | 1.831(11) |
| –O5 | 1.849(13) | –O13 | 1.842(10) |
| Mean | 1.819 | Mean | 1.827 |
| Ga4–O15 | 1.802(15) | Ga8–O1 | 1.847(9) |
| –O10 | 1.838(11) | –O16 | 1.865(9) |
| –O4 | 1.851(14) | –O14 | 1.858(10) |
| –O12 | 1.862(12) | –O9 | 1.909(16) |
| Mean | 1.838 | Mean | 1.870 |
| Ba1–O3 | 2.729(13) × 3 | Ba4–O6 | 2.762(12) × 3 |
| –O3 | 2.947(17) × 3 | –O1 | 3.017(11) × 3 |
| –O7 | 3.111(13) × 3 | –O11 | 3.098(10) × 3 |
| Ba2–O16 | 2.587(10) | Ba5–O1 | 2.715(10) × 3 |
| –O12 | 2.641(13) | –O6 | 2.921(11) × 3 |
| –O2 | 2.652(14) | –O14 | 3.195(11) × 3 |
| –O5 | 2.691(14) | | |
| –O4 | 3.025(13) | | |
| –O8 | 3.090(14) | | |
| –O15 | 3.113(19) | | |
| Ba3–O14 | 2.631(10) | Ba6–O10 | 2.616(12) |
| –O8 | 2.645(13) | –O11 | 2.628(9) |
| –O4 | 2.653(13) | –O13 | 2.632(10) |
| –O7 | 2.680(12) | –O9 | 2.728(14) |
| –O10 | 3.207(13) | –O9 | 2.933(13) |
| –O2 | 3.311(15) | –O13 | 3.237(11) |
| –O12 | 3.418(13) | –O15 | 3.285(23) |
| –O5 | 3.469(12) | | |
| O2–Ga1–O7 | 99.6(7) | O2–Ga2–O7 | 110.1(7) |
| O2–Ga1–O3 | 118.3(7) | O2–Ga2–O5 | 109.8(8) |
| O2–Ga1–O4 | 107.5(6) | O2–Ga2–O3 | 106.3(6) |
| O7–Ga1–O3 | 106.2(6) | O7–Ga2–O5 | 110.9(7) |
| O7–Ga1–O4 | 118.0(6) | O7–Ga2–O3 | 102.7(6) |
| O3–Ga1–O4 | 107.7(6) | O5–Ga2–O3 | 116.6(7) |
| Mean | 109.6 | Mean | 109.4 |
| O15–Ga3–O9 | 106.9(9) | O15–Ga4–O10 | 107.9(6) |
| O15–Ga3–O8 | 102.2(5) | O15–Ga4–O4 | 107.0(9) |
| O15–Ga3–O5 | 117.4(8) | O15–Ga4–O12 | 114.3(6) |
| O9–Ga3–O8 | 110.4(7) | O10–Ga4–O4 | 104.9(6) |
| O9–Ga3–O5 | 113.2(6) | O10–Ga4–O12 | 109.4(7) |
| O8–Ga3–O5 | 106.1(7) | O4–Ga4–O12 | 112.8(6) |

TABLE 4—Continued

| | | | |
|-------------|----------|-------------|----------|
| Mean | 109.4 | Mean | 109.4 |
| O1–Ga5–O11 | 103.1(5) | O6–Ga6–O11 | 105.9(5) |
| O1–Ga5–O16 | 110.9(4) | O6–Ga6–O8 | 110.3(6) |
| O1–Ga5–O10 | 111.9(5) | O6–Ga6–O13 | 117.5(5) |
| O11–Ga5–O16 | 106.1(4) | O11–Ga6–O8 | 115.7(5) |
| O11–Ga5–O10 | 115.0(5) | O11–Ga6–O13 | 101.5(4) |
| O16–Ga5–O10 | 109.7(5) | O8–Ga6–O13 | 106.1(6) |
| Mean | 109.5 | Mean | 109.5 |
| O14–Ga7–O12 | 109.0(6) | O1–Ga8–O16 | 113.9(5) |
| O14–Ga7–O6 | 104.4(5) | O1–Ga8–O14 | 106.3(5) |
| O14–Ga7–O13 | 109.2(5) | O1–Ga8–O9 | 110.1(5) |
| O12–Ga7–O6 | 113.4(5) | O16–Ga8–O14 | 103.0(4) |
| O12–Ga7–O13 | 110.4(6) | O16–Ga8–O9 | 109.3(5) |
| O6–Ga7–O13 | 110.2(5) | O14–Ga8–O9 | 114.2(5) |
| Mean | 109.4 | Mean | 109.5 |
| Ga5–O1–Ga8 | 121.4(5) | Ga8–O9–Ga3 | 114.2(8) |
| Ga1–O2–Ga2 | 122.7(7) | Ga4–O10–Ga5 | 118.6(7) |
| Ga1–O3–Ga2 | 120.7(6) | Ga5–O11–Ga6 | 138.1(5) |
| Ga1–O4–Ga4 | 117.3(7) | Ga7–O12–Ga4 | 117.7(7) |
| Ga3–O5–Ga2 | 118.5(8) | Ga7–O13–Ga6 | 119.2(5) |
| Ga7–O6–Ga6 | 122.0(6) | Ga7–O14–Ga8 | 136.8(5) |
| Ga1–O7–Ga2 | 137.7(7) | Ga3–O15–Ga4 | 168.2(8) |
| Ga3–O8–Ga6 | 117.1(8) | Ga5–O16–Ga8 | 118.9(5) |

Ba1, Ba4, and Ba5, located in the more symmetrical tunnels consisting of the UDUDUD rings, are coordinated by nine oxygen neighbors at 2.72 to 3.20 Å in form of distorted tricapped trigonal antiprisms. The Ba2, Ba3, and Ba6 sites located in the less symmetrical UUUDDD rings, are more irregularly coordinated with seven and eight oxygen ligands, respectively.

Interestingly, the crystal structure shows a distinct pseudo-symmetry. It closely resembles $P6_322$ symmetry which is already evident from the comparison of the R_{int} values for the two hexagonal Laue symmetries (see structure solution). The mean deviations from the symmetrically higher geo-

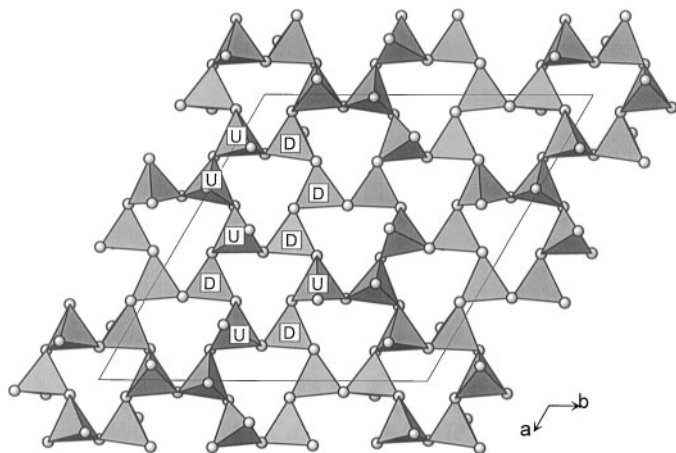


FIG. 2. Single tetrahedral layer with six-membered rings in barium monogallate in a projection parallel to [001].

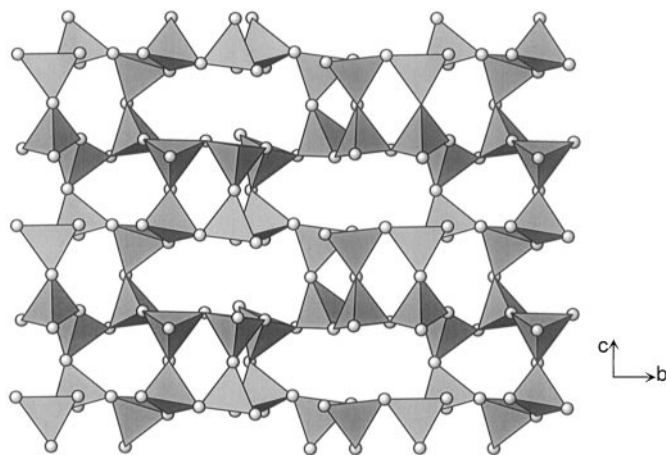


FIG. 3. Single tetrahedral layer with 10-membered rings in barium monogallate in a projection normal to the b - c plane.

metry are 0.15, 0.43, and 0.18 Å for Ga, O, and Ba atoms, respectively. This shows that the symmetry reduction is mainly due to the O atoms in the GaO_4 framework with a maximum deviation of 0.85 Å for O7 from $P6_322$ symmetry. Furthermore, the existence of pseudo-twofold axis along $2_{[100]}$ and $2_{[210]}$ explains why the crystals are subject to twinning by merohedry.

Concerning the tetrahedral framework, the same topology can be preserved in space group $P6_3/mcm$ which then represents the triple hexagonal cell ($H6_3/mcm$) of its subcell in $P6_3/mmc$ with lattice constants derived from the vector relations $\mathbf{a}' = 2/3\mathbf{a} + 1/3\mathbf{b}$, $\mathbf{b}' = -1/3\mathbf{a} + 1/3\mathbf{b}$, $\mathbf{c}' = \mathbf{c}$. This subcell represents the highest possible topological symmetry of this framework structure type; its metrical parameters ($a' = 10.76$ Å, $c' = 8.68$ Å) correspond to the unit cell parameters given in (9) for BaGa_2O_4 .

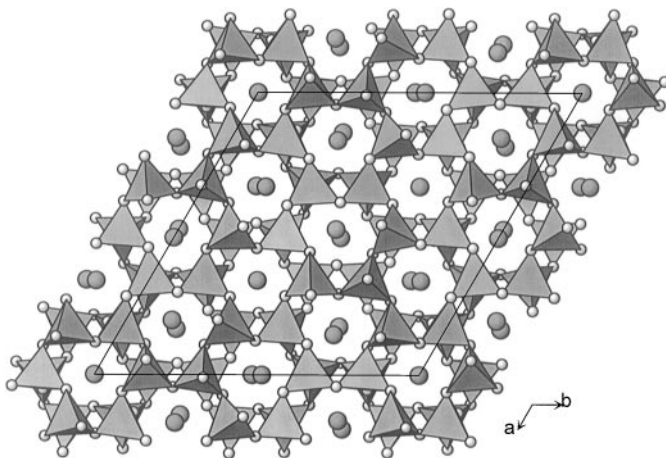


FIG. 4. View of the whole crystal structure parallel to [001]. The large spheres in the interstitial sites represent Ba cations.

However, the real structure clearly deviates from any symmetry having a mirror plane (*m*..) perpendicular to [001] which would imply that all corresponding tetrahedra in adjacent layers have an unfavorable eclipsed conformation.

COMPARISON WITH RELATED STRUCTURES AND DISCUSSION

As mentioned above, BaGa₂O₄ is isotypic with KAlGeO₄ (20). Other compounds belonging to this structure type are α -KZnPO₄ (25) and α -KCoPO₄ (26). The close relationship to KGeAlO₄ is expressed by the small deviations between their atom positions calculated from an interpenetrating model of the structures based on the lattice constants of KGeAlO₄. The mean separation between the T atoms of the two structures is 0.11 Å, between the O atoms it is 0.28 Å, and between the nonframework cations it is 0.16 Å. The similarities to KCoPO₄ and KZnPO₄ are less pronounced since each of them consists of two clearly distinct groups of T atoms, whereas the aluminogermanate has crystal chemically very similar Ge and Al atoms which conform more closely to the gallate structure. The structures of KAlGeO₄ (20) and KCoPO₄ (26) are related to that of BaGa₂O₄ by an origin shift on the polar 6₃ axis (shift in *z*: -0.32 for KAlGeO₄, +0.15 for KCoPO₄). KZnPO₄, as described in (25), is inverse to the BaGa₂O₄ structure related by mirror

planes *m*_[010] or *m*_[100], thus representing the counterpart in a twin domain.

In terms of stability of this structure type the lower cation radius for divalent barium (1.47 Å for ninefold coordination (27)) relative to the value for monovalent potassium (1.55 Å) seems to be compensated by an increase in size of the tetrahedral cations: Ga³⁺ (0.47 Å) vs 0.38 Å for the average Zn²⁺/P⁵⁺ radius and 0.375 Å for Co²⁺/P⁵⁺, respectively.

A comparison of some structural data for Ba-containing stuffed framework structures is given in Table 5. The setting of the space groups was chosen so that the *c*-axis corresponds to the direction normal to the tetrahedral layers. A feature common to almost all compounds is a *c*-lattice constant of about 8.7 Å, corresponding to a stacking of the layers in an ABAB... sequence, analogous to hexagonal close packing in metals. For BaFe₂O₄-II, the translational period normal to the sheets contains four tetrahedral layers. The lattice parameters in the plane perpendicular to the stacking sequence can all be related to the small hexagonal unit cell of BaAl₂O₄ with *A* ≈ 5.22 Å. The reflections corresponding to this subcell are the most intense ones for all compounds listed in Table 5, whereas the remaining reflections can be considered as superstructure reflections. This explains why some of these phases have been erroneously described in smaller unit cells (35).

The topology of the six-membered rings in most of the structures (Table 5) consist of only one ring type with the

TABLE 5
Comparison of Selected Structural Data of Different AB₂O₄-Type Stuffed Framework Structures Containing Ba

| | Space group | <i>a</i> (Å) | <i>b</i> (Å) | <i>c</i> (Å) | Sequence in 6R | Ref. |
|--|-----------------------------------|---|---------------------------------------|--------------|------------------|-----------|
| BaAl ₂ O ₄ -I | <i>P</i> 6 ₃ 22 | 5.218 | | 8.781 | UDUDUD | 11 |
| BaAl ₂ O ₄ -II | <i>P</i> 6 ₃ | 10.449 (<i>a</i> ≈ 2 × <i>A</i>) | | 8.793 | UDUDUD | 30 |
| BaZnGeO ₄ | <i>P</i> 6 ₃ | 9.2905 (<i>a</i> ≈ √3 × <i>A</i>) | | 8.728 | UDUDUD | 31 |
| BaCoSiO ₄ | <i>P</i> 6 ₃ | 9.1231 (<i>a</i> ≈ √3 × <i>A</i>) | | 8.6818 | UDUDUD | 32 |
| BaZnSiO ₄ | <i>P</i> 6 ₃ | 9.0955 (<i>a</i> ≈ √3 × <i>A</i>) | | 8.7251 | UDUDUD | 32 |
| BaMgSiO ₄ | <i>P</i> 6 ₃ | 9.1226 (<i>a</i> ≈ √3 × <i>A</i>) | | 8.7496 | UDUDUD | 32 |
| BaAl _{2/3} Ga _{2/3} Fe _{2/3} O ₄ | <i>P</i> 112 ₁ | 9.213 (<i>a</i> ≈ √3 × <i>A</i>) | 9.213 | 8.821 | UDUDUD | 34 |
| BaFe _{1.5} Al _{0.5} O ₄ | <i>P</i> 6 ₃ | 10.81 (<i>a</i> ≈ 2 × <i>A</i>) | | 8.707 | UDUDUD UUUUDD | 33 |
| BaGa ₂ O ₄ | <i>P</i> 6 ₃ | 18.640 (<i>a</i> ≈ 2√3 × <i>A</i>) | | 8.680 | UDUDUD UUUUDD | This work |
| BaFe ₂ O ₄ -I | <i>Bb</i> 2 ₁ <i>m</i> | 19.050 (<i>a</i> ≈ 2√3 × <i>A</i>) | 5.390 (<i>a</i> ≈ <i>A</i>) | 8.448 | UUUUUD | 28 |
| BaFe ₂ O ₄ -II | <i>Pm</i> <i>cn</i> | 9.336 (<i>a</i> ≈ √3 × <i>A</i>) | 10.882 (<i>a</i> ≈ 2 × <i>A</i>) | 17.347 | UUDUDD | 29 |

Note. The symbol *A* corresponds to the lattice parameter *a* of BaAl₂O₄. The monoclinic phase BaAl_{2/3}Ga_{2/3}Fe_{2/3}O₄ has a hexagonal metric.

UDUDUD tridymite sequence. Deviations from this simple principle (more than one sequence and/or different sequences) seem to be restricted to the structures containing larger tetrahedral cations, like Fe^{3+} and Ga^{3+} .

The question of the existence of more than one polymorphic form of barium monogallate cannot be settled with absolute certainty. However, there are some indications, that suspicion has to be attached to the structure model for BaGa_2O_4 presented in (9): First, the intensity ratio between the reflections defining the smaller cell reported in (9) and the reflections causing the larger a -lattice parameter of our model is about 15:1. Therefore, there is a possibility that this weak superlattice reflections may have been overlooked. Second, structure refinement of an artificial data set using only a subset of our reflections corresponding to the unit cell given by Deiseroth and Müller-Buschbaum resulted in the same difficulties concerning the disordering of some of the tetrahedra. This indicates that their structural model may actually correspond to an average structure defined from only the stronger sublattice reflections.

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