The Crystal Structure of a New High-Temperature Modification of YGaO₃*

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Yttrium gallium oxide, YGaO₃, quenched from a temperature of 1950°C, is hexagonal, belongs to space group P6₃mc with a = 6.065 (2) Å, c = 11.615 (4) Å and has six YGaO₃ per unit cell. It is isostructural with LuMnO₃. Convergence of all parameters could not be attained in the least-squares calculations even though the discrepancy index, \( \sum ||F_o|| - |F_c|| / \sum |F_o|| \), was reduced to 0.040, until ten thermal of a total of 29 positional and thermal parameters were held constant; thus the final interatomic distances are considered conditional. The interatomic distances are nevertheless plausible. The YGaO₃ crystal used for intensity-data collection (with a Buerger–Supper goniometer automated by a Nova 1200 computer) was very likely single domain as shown by improved agreement upon correct application of the imaginary parts of the atomic form factors of yttrium and gallium. Lattice constants of the isostructural high-temperature hexagonal HoGaO₃ and ErGaO₃ are reported.

Introduction

In a recent paper (Geller, Curlander & Ruse, 1974), it was shown that many of the perovskite-like rare-earth gallium oxides could be prepared at temperatures exceeding 1650°C. Previously all but those of La, Pr and Nd† (Geller, 1957a) did not crystallize from PbO fluxes (Remeika, 1956), probably because of the relatively low temperatures to which these were heated. It has been shown that the gallium oxide perovskites of yttrium and of Sm through Lu could be heated. It has been shown that the structure reported for LuMnO₃ is very similar to that of LuMnO₃, the work from that point on should have been straightforward. However, great difficulty because of parameter correlation (Geller, 1961; Evans, 1961; Geller & Katz, 1962) attended the refinement attempts. Even with a discrepancy index \( \sum ||F_o|| - |F_c|| / \sum |F_o|| \) of 0.04 (\( \sum |F_o|| - |F_c|| / \sum |F_o||^2 \) = 0.07), convergence could not be attained when all 29 positional and thermal parameters were allowed to vary. The crystal on which the data were measured, the discrepancy index \( \sum ||F_o|| - |F_c|| / \sum |F_o||^2 \) was 0.13. Yakel et al. (1963) also speculated that the ability of Mn³⁺ to adopt the trigonal bipyramidal coordination must be the prime reason for the stability of the structure.

The results of the work on hexagonal YGaO₃ indicate that the structure reported for LuMnO₃ is very likely correct. The outer electronic configuration, 3d⁴, of Mn³⁺ is considerably different from that, 3d¹⁰, of Ga³⁺. Thus, the formation of the structure must have little dependence on electronic configuration and a substantial dependence on relative ionic size, which seems to dominate crystal chemistry. The Mn³⁺ is one of the ions that does have unusual behavior with respect to coordination, usually preferring tetragonally distorted octahedral surroundings because of its electronic configuration. Its sesquioxide has a unique crystal structure (Geller, Cape, Grant & Espinosa, 1967; Geller, 1971; Norrestam, 1967) that does not indicate tetragonally distorted octahedra [but see Geller (1971)]. In any case, it is probably more to the point to expect Ga³⁺ to have five-coordination inasmuch as Fe³⁺ does (Adelskold, 1938; Braun, 1957)† and Ga³⁺ is known to have both four- and six-coordination to O²⁻ ions.

After ascertaining that the structure of YGaO₃ was the same as that of LuMnO₃, the work from that point on should have been straightforward. However, this was not the case. The reasons for this are given in the text. The Al³⁺ ion has five-coordination in a hexagonal YAlO₃, the structure (Bertaut & Mareschal, 1963) of which is different from that of hexagonal YGaO₃ and LuMnO₃.

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† CeGaO₃ prepared by solid-state reaction had also been reported (Keith & Roy, 1954).
material was then reground, repelletized and retired for deduced from these photographs are given in Table 1.

X-ray powder photography

X-ray powder photographs of the polycrystalline materials were taken with Cr Kα radiation and Norelco 114-6 cm diam. powder cameras. The lattice constants deduced from these photographs are given in Table 1.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>a (Å)</th>
<th>c (Å)</th>
<th>c/a</th>
<th>Vol. (Å³)</th>
<th>ρ0 (g cm⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R</td>
<td>(±0.002)</td>
<td>(±0.004)</td>
<td>(±0.001)</td>
<td>(±0.3)</td>
<td>(±0.005)</td>
</tr>
<tr>
<td>Y</td>
<td>6.065</td>
<td>11.615</td>
<td>1.915</td>
<td>370.0</td>
<td>5.564</td>
</tr>
<tr>
<td>Ho</td>
<td>6.065</td>
<td>11.651</td>
<td>1.921</td>
<td>371.2</td>
<td>7.588</td>
</tr>
<tr>
<td>Er</td>
<td>6.041</td>
<td>11.676</td>
<td>1.933</td>
<td>369.0</td>
<td>7.695</td>
</tr>
</tbody>
</table>

Single crystal photography

Initially, Buerger precession camera photographs were taken of a 0.05 mm thick YGaO₃ crystal, 0.5 mm in largest dimension, with Pd-filtered Ag Kα radiation. The reflections were very sharp. The diffraction symmetry is 6/mmm; systematic absences occur for reflections h0l, l = 2n + 1. Reflections with l = 2n + 1 are mostly weaker than those with l = 2n. There are many other nonsystematic absences. For l = 0, and l = 2n + 1, all reflections with h − k = 3n are absent. For l = 2n, n ≠ 0, almost all reflections are present.

The diffraction symmetry and systematic absences lead to P6₃/mcm (D₆h) and P6₃cm (C₆h) and P6c2 (D₃h) as probable space groups. The structure analysis indicates that P6c2cm is most probable.

Single crystal intensity data

A crystal of YGaO₃ was ground to a sphere of diameter 0-14 mm with a modified (Schuyff & Hulscer, 1968; Crandall, 1970) Bond (1951) sphere grinder. The crystal was oriented with the use of the Buerger precession camera and transferred by means of a Supper crystal transfer device to another goniometer head so that the hexagonal c axis was the rotation axis. The crystal had lattice constants a = 6.065 ± 0.002, c = 11.615 ± 0.004 Å. The formula weight of YGaO₃ is 206.622; the unit-cell volume is 370.01 Å³; with six formula units per unit cell, the X-ray density is 5.564 g cm⁻³. For Mo Kα radiation, the linear absorption coefficient, μ, is 370-23 cm⁻¹. For the 0.07 mm radius, μR = 2.6.

Intensities of independent reflections in the range 10° ≤ 2θ ≤ 65° were collected with a Buerger–Supper diffractometer automated by a Nova 1200 computer. Mo Kα radiation, Zr–Y balanced filters and a scan rate of 1° min⁻¹ were used. Background counts were taken at 1° the scan time on both sides of the peak for each filter. Lorentz–polarization–Tunell and absorption factors (Bond, 1959) were applied; relative |F₀|² are put out by the Nova computer on paper tape as well as printed on-line by the teletype. Absorption corrections had a range of about a factor of two. In all, 266 independent intensities were collected, of which 91 were below threshold.

Structure refinement

Refinement was carried out with the least-squares program of Busing, Martin & Levy (1962), modified by Ibers, Johnson, Ellison & Levy to include site occupancy refinement (not used in this work) and the contribution from the imaginary parts of the scattering factors. The scattering factors were those of Tokonami (1965) for O²⁻ and those of Cromer & Waber (1965) for Y³⁺ and Ga³⁺. Corrections for the real and imaginary parts (see below) of anomalous dispersion (Cromer, 1965) were also applied. Weighting of the observed structure amplitudes was done with the formula given in Colville & Geller (1971), A = 10-0, B = 5-0, C = 0-07, D = 20-0.

From the outset of the attempt at refinement, great difficulty was caused by large parameter correlations. These occurred not only between thermal parameters, and between positional parameters, but also, unfortunately, between positional and thermal parameters. Even when the discrepancy index R = Σ|F₀|−|F₁|/Σ|F₀| was already down to 0.04, convergence could not be attained. Oscillations in parameters occurred and physically impossible values of some of the oxygen thermal parameters were obtained. Corrections for the imaginary parts of the anomalous dispersion showed that the crystal was actually aligned with the polar axis pointing into the goniometer head; that is, the data taken all have negative l; the corrections were first introduced when R(=Σ|F₀|−|F₁|/Σ|F₀|) was 0.049. When the values for Ga and Y were introduced as positive, R increased to 0.065. When introduced as negative, R decreased to 0.043. The introduction of these corrections appeared also to improve the situa-
tion with regard to the convergence of the $O(3)$ (Table 2) $z$ parameter.

Various aspects of the structure were considered in an attempt to resolve the dilemma. Only the $O(1)$, $O(2)$ and Ga$^{3+}$ atoms (Table 2) contribute to reflections with $l = 2n + 1$. However, not many of these have intensities above threshold (see above) and use of these reflections only would not eliminate some of the largest parameter interactions. It was thought that possibly the higher angle reflections, not receiving significant contributions from the oxygens, might be contributing errors which were preventing convergence of the oxygen parameters. Therefore a calculation was made at a data cut-off of $2\theta = 55^\circ$. This did not improve the situation and we returned to use of the full data.

Finally, to conclude the work, a decision was made to hold certain of the oxygen thermal parameters constant. The values were chosen according to how they had appeared in the various cycles. In the case of $O(1)$ and $O(2)$ atoms, they are averages. In all, it was necessary to hold nine oxygen thermal parameters and one Ga thermal parameter constant. Thus it should be understood that the standard errors given in Table 2 for the varied parameters and those for the interatomic distances (calculated with the Busing, Martin & Levy (1964) program) given in Table 3 are conditional. As will be shown later, the results are plausible. For the interatomic distances with very small standard error, the results are essentially independent of the error in the positional parameter because the component of the distance involving such parameters is very small.

A table giving the comparison between calculated and observed structure amplitudes (absolute values) may be obtained on request from the first author.*

* Parameters held constant. The Ga $z$-parameter is arbitrarily fixed at 0-0000 because the structure is polar.

### Table 3. Interionic distances, Å (and conditional standard errors), in hexagonal YGaO$_3$

<table>
<thead>
<tr>
<th>Distance</th>
<th>Average (Å)</th>
<th>Standard Error (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Ga-O(1)$</td>
<td>1.82 (20)</td>
<td>0.009 (3)</td>
</tr>
<tr>
<td>$Ga-O(2)$</td>
<td>1.84 (20)</td>
<td>0.009 (3)</td>
</tr>
<tr>
<td>$Ga-O(3)$</td>
<td>2.02 (3)</td>
<td>0.009 (3)</td>
</tr>
<tr>
<td>$Ga-O(4)$</td>
<td>2.06 (5)</td>
<td>0.009 (3)</td>
</tr>
<tr>
<td>Average</td>
<td>1.96 (11)</td>
<td>0.009 (3)</td>
</tr>
<tr>
<td>$Y(1)-O(1)$</td>
<td>2.31 (19)</td>
<td>0.009 (3)</td>
</tr>
<tr>
<td>$Y(1)-O(2)$</td>
<td>2.33 (18)</td>
<td>0.009 (3)</td>
</tr>
<tr>
<td>$Y(1)-O(3)$</td>
<td>2.46 (31)</td>
<td>0.009 (3)</td>
</tr>
<tr>
<td>$Y(1)-O(4)$</td>
<td>2.33 (20)</td>
<td>0.009 (3)</td>
</tr>
<tr>
<td>Average</td>
<td>2.33 (20)</td>
<td>0.009 (3)</td>
</tr>
</tbody>
</table>

### Discussion

A description of the structure is given by Yakel et al. (1963) [see also Goodenough & Longo (1970)]. The structure consists of six layers of hexagonally co-ordinated rather loosely packed oxygen ions in an $ABCACB$ stacking sequence. The gallium ions are situated near the centers of every other oxygen triangle in the $A$ layers (consisting of $O(3)$'s and $O(4)$'s). The Y$^{3+}$ ions are situated in interstices in two layers at approximately $+c/4$, i.e. between $B$ and $C$ layers of oxygens and are surrounded by seven-coordination polyhedra. There are two crystallographically non-equivalent Y$^{3+}$ ions but both have similar surroundings. Each is equidistant from three $O(1)$ and from three $O(2)$ ions; $Y(1)$ has a near $O(3)$ neighbor at 2.46 Å, and $Y(2)$ a near $O(4)$ neighbor at 2.54 Å. Around each of the Y$^{3+}$ ions, the $Y-O(1)$ and $Y-O(2)$ distances are nearly equal (Table 3); this differs from the situation in LuMnO$_3$. The two average Y–O distances differ by 0.01 Å which is not statistically significant. The average of all Y–O distances (Table 3) is 2.33 ± 0.05 (3σ) Å. The average six coordination Y–O distance in Y$_2$O$_3$ is 2.28 Å (Herman, Lohrmann & Philipp, 1928–1932; Fert, 1962). In yttrium iron garnet

### Table 2. Parameters and standard errors for hexagonal YGaO$_3$

Parameters not given in decimal notation are fixed by the space group. The form of the temperature factor is $T = \exp \left[-(k^2 \beta_{11} + k^2 \beta_{22} + l^2 \beta_{33} + 2hk \beta_{13} + 2kl \beta_{23} + 2hl \beta_{12})\right]$.  

<table>
<thead>
<tr>
<th>Position</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
<th>$\beta_{11}$</th>
<th>$\beta_{22}$</th>
<th>$\beta_{33}$</th>
<th>$\beta_{12}$</th>
<th>$\beta_{13}$</th>
<th>$\beta_{23}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y(1)</td>
<td>2(a)</td>
<td>0</td>
<td>0</td>
<td>0.2716 (5)</td>
<td>0.0077 (7)</td>
<td>= $\beta_{11}$</td>
<td>0.0009 (1)</td>
<td>= $\beta_{11}$</td>
<td>0</td>
</tr>
<tr>
<td>Y(2)</td>
<td>4(b)</td>
<td>$\frac{1}{3}$</td>
<td>$\frac{1}{3}$</td>
<td>0.2347 (3)</td>
<td>0.0057 (3)</td>
<td>= $\beta_{11}$</td>
<td>0.0011 (1)</td>
<td>= $\beta_{11}$</td>
<td>0</td>
</tr>
<tr>
<td>Ga</td>
<td>6(c)</td>
<td>0.3376 (8)</td>
<td>0</td>
<td>0.0000*</td>
<td>0.0090*</td>
<td>0.0094*</td>
<td>0.0009 (1)</td>
<td>= $\beta_{11}$</td>
<td>0</td>
</tr>
<tr>
<td>O(1)</td>
<td>6(c)</td>
<td>0.3104 (30)</td>
<td>0</td>
<td>0.1578 (21)</td>
<td>0.0135*</td>
<td>0.0030*</td>
<td>0.0025*</td>
<td>= $\beta_{11}$</td>
<td>0.0006 (11)</td>
</tr>
<tr>
<td>O(2)</td>
<td>6(c)</td>
<td>0.6394 (29)</td>
<td>0</td>
<td>0.3419 (18)</td>
<td>0.0135*</td>
<td>0.0030*</td>
<td>0.0025*</td>
<td>= $\beta_{11}$</td>
<td>0</td>
</tr>
<tr>
<td>O(3)</td>
<td>2(a)</td>
<td>0</td>
<td>0</td>
<td>0.4837 (25)</td>
<td>0.0030*</td>
<td>= $\beta_{11}$</td>
<td>0.0006 (11)</td>
<td>= $\beta_{11}$</td>
<td>0</td>
</tr>
<tr>
<td>O(4)</td>
<td>4(b)</td>
<td>$\frac{1}{3}$</td>
<td>$\frac{1}{3}$</td>
<td>0.0161 (22)</td>
<td>0.0111 (32)</td>
<td>= $\beta_{11}$</td>
<td>0.0013 (11)</td>
<td>= $\beta_{11}$</td>
<td>0</td>
</tr>
</tbody>
</table>

* Parameters held constant. The Ga $z$-parameter is arbitrarily fixed at 0-0000 because the structure is polar.
(Geller & Gillé, 1957, 1959), the average eight-coordination Y–O distance is 2.40 Å. The average of these two averages is 2.34 Å in good agreement with the average seven-coordination Y–O distance in hexagonal YGaO₃. Linear extrapolation to a hypothetical 12-coordination distance gives 2.64 Å, in very good agreement with the value 2.63 Å, predicted from the crystal structure calculations. The shorter ones are those to the pyramid apices in the Ga₃⁺ coordination distance gives 2.64 Å in very good agreement with the value, 2.63 Å, predicted from studies of the perovskite-like crystals involving rare-earth ions (Geller, 1957b).

The Ga³⁺ ions have five-coordination; the coordination polyhedron is a trigonal bipyramid. The longer Ga³⁺–O²⁻ distances (Table 3) are those in the A layer; the shorter ones are those to the pyramid apices in the B and C layers. The differences between the short and long distances are rather large. The average octahedral and tetrahedral Ga³⁺–O²⁻ distances in β-Ga₂O₃ (Geller, 1960) are 2.00 and 1.83 Å, respectively. The average of these is 1.915 Å, much smaller than the average Ga³⁺–O²⁻ distance in hexagonal YGaO₃. In fact, the Ga³⁺–O²⁻ distances in hexagonal YGaO₃ and tetrahedral Ga⁴⁺–O²⁻ distances in fβ-Ga₂O₃ (Geller, 1957b) are isostructural with the orthomanganites, these two averages is 2.34 Å in good agreement with the value, 2.63 Å, predicted from studies of the perovskite-like crystals involving rare-earth ions (Geller, 1957b).

The in YGaO₃ is probably somewhat larger than in YMnO₃, mainly because of the longer c axis of the former.

This structure can go into the centrosymmetric one belonging to space group P6₃/mmc (D₃d) without drastic ionic movements. The O(1) and O(2) ions would move into the single equipoint set k (ideal values of parameters x,y) the Ga³⁺ ions would be in the g positions (ideal x = 1/3), the Y³⁺ ions would be in the special positions a and d, and the O(3) and O(4) ions would be in special positions b and c, respectively. The transitions of YMnO₃ and YbMnO₃ to the centrosymmetric structure appear to be first order and occur at 660 and 700–725°C respectively (Ismailzade & Kizhaev, 1965). At room temperature, the deviations of the structures of LuMnO₃ and of YGaO₃ from the centrosymmetric one are large and readily seen in the structure factor data. In the YGaO₃ this was ascertained in initial calculations.

We thank P. M. Skarstad for helpful discussion and G. F. Ruse for assistance with the high-temperature experiments. The section in Landolt–Börnstein entitled Crystallographic and Magnetic Properties of Perovskite and Perovskite-Related Compounds written by Goodenough & Longo (1970) deserves special acknowledgement because of its usefulness throughout this study.

References

Etude Structurale par Microscopie Electronique des Phases 'de Type Bronzes Oxygénés de Tungstène Quadratiques' des Systèmes AM₂O₆–M₂O₅
(M = Ta, Nb ; A = Eu II, Sr, Pb)

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An electron microscopy study of 'tungsten bronze' type oxides in AM₂O₆–M₂O₅ (M = Ta, Nb; A = Eu II, Sr, Pb) systems gives evidence of two types of superstructure. Crystals with orthorhombic superstructure 17 x 17 Å, mainly observed in ANb₂O₆ compounds, show quasi-periodic twin bands. Crystals with orthorhombic superstructure 12 x 36 Å, observed in compounds containing more niobium or tantalum AO.₂₅M₂O₅ and AgNb₃₄O₉₄, show superstructure domains. A study of domain and fault boundaries is made in the last case. In some crystals of A₉Nb₃₄O₉₄, both superstructures appear close together: this is interpreted as an order–disorder phenomenon.

Introduction


Il nous a donc semblé intéressant d'étudier, par microscopie électronique, les relations structurales entre les phases du type bronze de Magnéli des systèmes AO–M₂O₅ (A = Sr, Pb, Eu II ; M = Ta, Nb). Les composés étudiés au cours de ce travail correspondent à trois formulations: AM₂O₆, AO.₂₅M₂O₅ et A₉M₃₄O₉₄.

Techniques expérimentales

La synthèse chimique des composés observés en microscopie électronique a été effectuée suivant les techniques opératoires décrites précédemment (Fayolle et al., 1975; Francombe & Lewis, 1958). Pour chaque com-