

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 *P*6₃*cm* with *a* = 6.065 (2), *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, 1957*a*) 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 prepared at high pressures (Marezio, Remeika & Dernier, 1966, 1968).

In the course of the high-temperature experiments (Geller, Curlander & Ruse, 1974), new hexagonal RGaO₃ phases were obtained. These phases are isostructural with LuMnO₃ and other RMnO₃, R = Ho, Er, Tm, Yb, Y (Yakel, Koehler, Bertaut & Forrat, 1963). The hexagonal RMnO₃ have been shown to be antiferromagnetic (*e.g.* Bertaut & Mercier, 1963) and ferroelectric (Bertaut, Forrat & Fang, 1963; Bokov, Smolenskii, Kizhaev & Myl'nikova, 1964; Ismailzade & Kizhaev, 1965).

There are some interesting aspects of these materials: The Mn³⁺ ion has the unusual five (trigonal bipyramidal) coordination to O²⁻ ions. Yakel *et al.* (1963) were not certain of the structure; they found high correlations among parameters and although convergence was claimed, the values of some thermal parameters were physically impossible. It was not known whether the LuMnO₃ crystal on which the work was done was a single domain and the possibility that twinning could be indicating a higher symmetry space group was not completely eliminated; for the data measured,

the discrepancy index $\sum||F_o|^2 - |F_c|^2| / \sum|F_o|^2$ 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, 3*d*⁴, of Mn³⁺ is considerably different from that, 3*d*¹⁰, 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 (Adelsköld, 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, 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 ($\sum||F_o|^2 - |F_c|^2| / \sum|F_o|^2 = 0.07$), convergence could not be attained when all 29 positional and thermal parameters were allowed to vary. The crystal on which the data were taken is

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† CeGaO₃ prepared by solid-state reaction had also been reported (Keith & Roy, 1954).

† 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.

very likely single domain: application of the imaginary parts of the dispersion correction markedly improved agreement for several reflections and seemed to reduce the difficulty of convergence somewhat. To bring the work to a conclusion, it was necessary to hold some of the thermal parameters constant during the final least-squares cycles.

Experimental

Specimen preparation

Equimolar proportions of Y_2O_3 and Ga_2O_3 , both of 99.99% purity with weights corrected for volatile matter (Geller, Williams, Sherwood & Espinosa, 1961), were ground together in an agate mortar, then pelletized and fired for one hour at 1000°C. The material was then reground, repelletized and refired for eight hours at 1400°C. The material was then melted in argon in an iridium crucible inductively heated to >1950°C. The melt was then cooled at a rate of 30°C min⁻¹ to ~1700°C where solidification occurred, after which the power was abruptly cut off. The largest crystals were approximately 1 × 0.5 × 0.5 mm in size.

X-ray powder photography

X-ray powder photographs of the polycrystalline materials were taken with Cr $K\alpha$ radiation and Norelco 114.6 cm diam. powder cameras. The lattice constants deduced from these photographs are given in Table 1.

Table 1. Unit-cell parameters of hexagonal $RGaO_3$ compounds

R	a (Å) (±0.002)	c (Å) (±0.004)	c/a (±0.001)	Vol. (Å ³) (±0.3)	ρ_x (gcm ⁻³) (±0.005)
Y	6.065	11.615	1.915	370.0	5.564
Ho	6.065	11.651	1.921	371.2	7.588
Er	6.041	11.676	1.933	369.0	7.695

Single crystal photography

Initially, Buerger precession camera photographs were taken of a 0.05 mm thick $YGaO_3$ crystal, 0.5 mm in largest dimension, with Pd-filtered Ag $K\alpha$ 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 $h-k \neq 3n$ are absent. For $l=2n$, $n \neq 0$, almost all reflections are present.

The diffraction symmetry and systematic absences lead to $P6/mcm$ (D_{6h}^3), $P6_3cm$ (C_{6v}^3) and $P\bar{6}c2$ (D_{3h}^2) as probable space groups. The structure analysis indicates that $P6_3cm$ is most probable.

Single crystal intensity data

A crystal of $YGaO_3$ was ground to a sphere of diameter 0.14 mm with a modified (Schuyff & Hulscher, 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 $a=6.065 \pm 0.002$, $c=11.615 \pm 0.004$ Å. The formula weight of $YGaO_3$ 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 $K\alpha$ radiation, the linear absorption coefficient, μ , is 370.23 cm⁻¹. For the 0.07 mm radius, $\mu R=2.6$.

Intensities of independent reflections in the range $10^\circ \leq 2\theta \leq 65^\circ$ were collected with a Buerger-Supper diffractometer automated by a Nova 1200 computer. Mo $K\alpha$ radiation, Zr-Y balanced filters and a scan rate of 1° min⁻¹ were used. Background counts were taken at $\frac{1}{6}$ the scan time on both sides of the peak for each filter. Lorentz-polarization-Tunell and absorption factors (Bond, 1959) were applied; relative $|F_o|^2$ 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 $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ 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 $R (= \sum ||F_o| - |F_c|| / \sum |F_o|)$ 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 Ga³⁺ 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.* The discrepancy index (excluding the 300 reflection) is 0.040. For $\sum||F_o^2|-|F_c^2||/\sum|F_o|^2$ the value is 0.072. The standard error of an observation of unit weight is 0.93.

* This table has also been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31097 (2 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. Parameters and standard errors for hexagonal YGaO₃

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

Position	<i>x</i>	<i>y</i>	<i>z</i>	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Y(1)	2(<i>a</i>)	0	0	0.2716 (5)	0.0077 (7)	$=\beta_{11}$	0.0009 (1)	$=\frac{1}{2}\beta_{11}$	0
Y(2)	4(<i>b</i>)	$\frac{1}{3}$	$\frac{2}{3}$	0.2347 (3)	0.0059 (3)	$=\beta_{11}$	0.0011 (1)	$=\frac{1}{2}\beta_{11}$	0
Ga	5(<i>c</i>)	0.3376 (8)	0	0.0000*	0.0090 (4)	0.0094*	0.0009 (1)	$=\frac{1}{2}\beta_{11}$	0.0002 (2)
O(1)	6(<i>c</i>)	0.3104 (30)	0	0.1578 (21)	0.0135*	0.0030*	0.0025*	$=\frac{1}{2}\beta_{11}$	0.0020*
O(2)	5(<i>c</i>)	0.6394 (29)	0	0.3419 (18)	0.0135*	0.0030*	0.0025*	$=\frac{1}{2}\beta_{11}$	0.0020*
O(3)	2(<i>a</i>)	0	0	0.4837 (25)	0.0030*	$=\beta_{11}$	0.0006 (11)	$=\frac{1}{2}\beta_{11}$	0
O(4)	4(<i>b</i>)	$\frac{1}{3}$	$\frac{2}{3}$	0.0161 (22)	0.0111 (32)	$=\beta_{11}$	0.0013 (11)	$=\frac{1}{2}\beta_{11}$	0

* 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 YGaO₃

Ga-O trigonal bipyramid			
Ga-O(1)	1.840 (24)	O(1)-O(3)	2.664 (27)
Ga-O(2)	1.842 (20)	(2) O(1)-O(4)	2.763 (37)
Ga-O(3)	2.018 (3)	O(2)-O(3)	2.738 (24)
(2) Ga-O(4)	2.056 (5)	(2) O(2)-O(4)	2.806 (27)
Average	1.962 (11)	(2) O(3)-O(4)	3.522 (2)
		O(4)-O(4)	3.502 (1)
		Average	3.010 (22)
Y(1)-O polyhedron			
(3) Y(1)-O(1)	2.301 (19)	(3) O(1)-O(1)	3.261 (32)
(3) Y(1)-O(2)	2.335 (18)	(3) O(2)-O(2)	3.789 (30)
Y(1)-O(3)	2.463 (31)	(6) O(1)-O(2)	2.963 (17)
Average	2.339 (20)	(3) O(2)-O(3)	2.738 (24)
		Average	3.143 (24)
Y(2)-O polyhedron			
(3) Y(2)-O(1)	2.277 (15)	(3) O(1)-O(1)	3.628 (18)
(3) Y(2)-O(2)	2.309 (13)	(3) O(2)-O(2)	3.367 (13)
Y(2)-O(4)	2.539 (25)	(6) O(1)-O(2)	2.924 (29)
Average	2.328 (16)	(3) O(1)-O(4)	2.763 (37)
		Average	3.121 (25)

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 coordinated 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 Y³⁺ ions are situated in interstices in two layers at approximately $\pm c/4$, *i.e.* between *B* and *C* layers of oxygens and are surrounded by seven-coordination polyhedra. There are two crystallographically non-equivalent Y³⁺ 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 Y³⁺ ions, the Y-O(1) and Y-O(2) distances are nearly equal (Table 3); this differs from the situation in LuMnO₃. 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 $2.33 \pm 0.05(3\sigma)$ Å. The average six coordination Y-O distance in Y₂O₃ is 2.28 Å (Heriman, Lohrmann & Philipp, 1928-1932; Fert, 1962). In yttrium iron garnet

(Geller & Gilleo, 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 studies of the perovskite-like crystals involving rare-earth ions (Geller, 1957*b*).

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 average Ga³⁺–O²⁻ distance in hexagonal YGaO₃ is much closer to the average octahedral distance in β-Ga₂O₃ than to the tetrahedral one.

In the case of the manganese compounds, a transition to an orthorhombic perovskite-like phase at high pressure and temperature has been reported (Waintal & Chenavas, 1967*a, b*). Results of high-pressure experiments on the rare-earth and yttrium gallium oxides are in accord with this.

Yakel *et al.* (1963) have speculated that the orthorhombic phase is the high-temperature one. It does appear from our work that this is also the case for the Ga³⁺ compounds. In this case we have found that both phases exist at high temperatures for Ho and Er, but we have not been able to prepare the gallium perovskites of Tm, Yb, Lu and Y, even though Y³⁺ has very nearly the same size as Ho³⁺. However, the Tm, Yb, Lu and Y gallium perovskites have been prepared at high pressure (Marezio *et al.*, 1966, 1968). Thus this is a case in which the high-temperature phase is also the high-pressure phase.

As mentioned earlier, the hexagonal rare-earth orthomanganites are ferroelectric (Bertaut *et al.*, 1963; Bokov *et al.*, 1964; Ismailzade & Kizhaev, 1965; Bertaut & Lissalde, 1967). At room temperature, the coercive fields for these crystals are 15–20 kV cm⁻¹; spontaneous polarizations are 4–5 μC cm⁻² (Bokov *et al.*, 1964). Because the hexagonal gallium compounds are isostructural with the orthomanganites, these should also be ferroelectric. A test must await the growth of larger crystals. The displacement of charge 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/mcm* (*D_{6h}³*) without drastic ionic movements. The O(1) and O(2) ions would move into the single equipoint set *k* (ideal values of parameters $\frac{1}{3}, 0, \frac{5}{12}$), the Ga³⁺ ions would be in the *g* positions (ideal $x = \frac{1}{3}$), 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.

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Etude Structurale par Microscopie Electronique des Phases 'de Type Bronzes Oxygénés de Tungstène Quadratiques' des Systèmes $\text{AM}_2\text{O}_6\text{-M}_2\text{O}_5$ (M = Ta, Nb ; A = Eu^{II} , Sr, Pb)

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An electron microscopy study of 'tungsten bronze' type oxides in $\text{AM}_2\text{O}_6\text{-M}_2\text{O}_5$ (M = Ta, Nb; A = Eu^{II} , Sr, Pb) systems gives evidence of two types of superstructure. Crystals with orthorhombic superstructure 17×17 Å, mainly observed in ANb_2O_6 compounds, show quasi-periodic twin bands. Crystals with orthorhombic superstructure 12×36 Å, observed in compounds containing more niobium or tantalum $\text{AO} \cdot 2.5\text{Nb}_2\text{O}_5$ and $\text{A}_9\text{Nb}_{34}\text{O}_{94}$, show superstructure domains. A study of domain and fault boundaries is made in the last case. In some crystals of $\text{A}_9\text{Nb}_{34}\text{O}_{94}$, both superstructures appear close together: this is interpreted as an order-disorder phenomenon.

Introduction

Ce travail fait suite à l'étude des oxydes ternaires de 'type bronzes de tungstène quadratiques' entreprise précédemment au laboratoire (Deschanvres, Leparmentier & Raveau, 1970, 1972; Deschanvres, Desgardin & Raveau, 1972; Fayolle, Studer, Desgardin & Raveau, 1975). Les résultats obtenus dans le cas des systèmes $\text{SrM}_2\text{O}_6\text{-M}_2\text{O}_5$ et $\text{PbM}_2\text{O}_6\text{-M}_2\text{O}_5$ (Deschanvres, Desgardin & Raveau, 1972; Francombe & Lewis, 1958) pour lesquels M est le tantale ou le niobium, et la synthèse récente de composés analogues d'euporium divalent (Fayolle *et al.*, 1975; Desgardin, Fayolle & Raveau, 1973) mettent en évidence de nombreuses phases dont la parenté avec la structure 'bronze de tungstène' ne fait aucun doute. Cependant, à l'exception du niobate PbNb_2O_6 dont la structure a été déterminée à partir d'un monocristal (Labbé, Frey & Allais, 1973), les études par diffraction X de ces phases effectuées sur poudre, ne permettent pas d'apporter des renseignements suffisants pour la

connaissance de la maille réelle et conduisent dans certains cas à des résultats divergents. De plus, les études des composés du système $\text{Nb}_2\text{O}_5\text{-WO}_3$ (Allpress, 1969, 1972; Iijima & Allpress, 1974) de structure apparentée au 'bronze de tungstène quadratique' laissent prévoir pour ce type de composés l'existence de défauts analogues.

Il nous a donc semblé intéressant d'étudier, par microscopie électronique, les relations structurales entre les phases du type bronze de Magnéli des systèmes $\text{AO-M}_2\text{O}_5$ (A = Sr, Pb, Eu^{II} ; M = Ta, Nb). Les composés étudiés au cours de ce travail correspondent à trois formulations: AM_2O_6 , $\text{AO} \cdot 2.5\text{M}_2\text{O}_5$ et $\text{A}_9\text{M}_{34}\text{O}_{94}$.

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-