Double Oxides of Gallium and Niobium

BY P. L. GAI AND J. S. ANDERSON

Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QR, England

(Received 5 August 1975; accepted 16 August 1975)

A combination of lattice-imaging electron microscopy and powder X-ray diffraction methods has been used to identify the ternary oxide phases and their structures in the system gallium oxide–niobium oxide. In addition to GaNbO$_4$, GaNb$_{11}$O$_{29}$, isostructural with Ti$_2$Nb$_{10}$O$_{29}$ and GaNb$_9$O$_{124}$, isostructural with TiNb$_2$O$_{29}$, are equilibrium phases. GaNb$_{11}$O$_{29}$, isostructural with TiNb$_2$O$_{29}$, can exist as coherently intergrown lamellae in GaNb$_{11}$O$_{29}$. Extended defects observed in low-temperature preparations are discussed.

In a study of the ternary compounds formed between Nb$_2$O$_5$ (and Ta$_2$O$_5$) and the oxides of the trivalent metals, Iyer & Smith (1967) reported the existence of a compound GaNb$_{11}$O$_{29}$, to which they assigned the orthorhombic cell dimensions $a=3.81$, $b=20.67$, $c=28.62$ Å, space group Cmc$_2$1. The composition of their preparation was based on analogy with the series of compounds LaNb$_2$O$_{14}$ formed by the lanthanides (Mason, 1964; Dyer & White, 1964; Bodiot, 1968, 1969). The cell dimensions were determined on a single crystal picked from the preparation, and a potentially dangerous assumption was made: that this crystal had the same composition as the whole preparation, even though no evidence was advanced that the product was monophasic. The structure was not solved.

Since $a$ [in Iyer & Smith's (1967) assignment] clearly corresponds to one coordination polyhedron (a typical octahedron diagonal length) it appeared that the essentials of the crystal structure should be deducible by the methods of real-space crystallography, from the lattice image observed in [100] projection. Lattice images at once showed that the formula assigned by Iyer & Smith (1967) was incorrect and that material of composition Ga$_2$O$_{a1.5}$Nb$_2$O$_5$ must be diphasic. By combining lattice imaging with the usual diffraction techniques, the structural chemistry of the system Ga$_2$O$_3$–Nb$_2$O$_5$ has been elucidated and shown to involve GaNbO$_4$ and, at higher Nb$_2$O$_5$ contents, a succession of ‘block structure’ double oxides.

Experimental

Materials were prepared from Johnson–Matthey ‘Specpure’ Ga$_2$O$_3$ and Nb$_2$O$_5$. Mixtures with Ga$_2$O$_3$:Nb$_2$O$_5$ = 1:0.5, 1:1, 1:2, 1:3, 1:5, 1:11 and 1:49 were well ground and fired at 1300°C in sealed Pt capsules for 50–100 h. In addition, one preparation (1:5) was carried out at 1000°C for 50 h. X-ray diffraction patterns were recorded in a Hagg–Guinier focusing camera with Cu K$_\alpha$ radiation.

For lattice imaging, samples were finely ground, dispersed on carbon films, and examined with a Siemens Elmiskop 102, at 100 kV and, usually, × 700 000 magnification. Crystal flakes with thin edges (< 100 Å) were oriented so that the short axis was exactly parallel to the electron beam, and micrographs were recorded at around 900 Å defocus with an objective aperture to include all diffracted beams out to approximately 0.35 Å$^{-1}$. Under these conditions, the image contrast approximates closely to the projected charge density in the crystal and can be interpreted directly in terms of the projected positions of the heavy atoms.

Results

GaNb$_{11}$O$_{29}$

As noted by Iyer & Smith (1967), and as follows from the large unit cell of at least one of the compounds in the system, all preparations Ga$_2$O$_3$.xNb$_2$O$_5$ ($x \geq 2$) gave X-ray diffraction patterns very rich in lines, in which it is difficult to detect with certainty the lines arising from some second phase. For all these samples, the electron diffraction patterns of many crystals were typical of the niobium oxide ‘block’ structures, and over the range 2 < $x$ < 11 those crystals from 1300°C preparations furnished identical lattice images, typified by Fig. 1. It is evident that this is indeed a block structure, with columns measuring (3 x 4) octahedra in cross section, linked in infinite zigzag ribbons. It is isostructural with the orthorhombic modifications of Ti$_2$Nb$_{10}$O$_{29}$ and Nb$_{12}$O$_{29}$, and the cell dimensions reported by Iyer & Smith (1967) relate to this material, since they agree well (apart from interchanged labelling of axes) with Wadsley's (1961) data. In the subsequent discussion we shall adopt Wadsley's axial labelling, taking the short cell dimension as $b$. Since, in the family of block structures there is a direct relation between structure and composition, this phase can be unambiguously formulated as GaNb$_{11}$O$_{29}$. In agreement with this, the X-ray diffraction pattern of Ga$_2$O$_3$.11Nb$_2$O$_5$ could be completely indexed in terms of the M$_{12}$O$_{29}$ structures, whereas close examination revealed the presence of additional lines in the diffraction pattern of Ga$_2$O$_3$.5Nb$_2$O$_5$.

Crystals from the 1000°C preparation also furnished lattice images identifiable as the (3 x 4)$_\infty$ block structure
of GaNb₁₁O₂₉, but predominantly of the monoclinic modification (Fig. 2). Thus GaNb₁₁O₂₉, like other known (3 x 4)₀₀ block-structure compounds, is diomorphic, with the orthorhombic mode of linking columns as the structure stable at high temperatures.

In the analogous system, Al₂O₃-Nb₂O₅, Layden (1963) reported the existence of phases with compositions close to Al₂O₃·9Nb₂O₅ and Al₂O₃·25Nb₂O₅, which Trunov, Kovba & Pol'shchikova (1968) identified as Al₁Nb₁₂O₃9 and Al₀₅Nb₂₄₄O₆₂ respectively. Tilloca (1973) confirmed the existence of monoclinic Al₁Nb₁₂O₃9 and also reported the existence of both monoclinic and orthorhombic GaNb₁₁O₂₉, but without giving any details. Our work shows that his phase II in the Ga₃O₉-Nb₂O₅ system was correctly identified and establishes its structure.

Since octahedrally coordinated Ga³⁺ enters into the (3 x 4)₀₀ block structure, it is probable that other block structure phases MO₄ (M = Ga + Nb; 2·417 ≤ x < 2·500) will exist. Tilloca (1973) found only two intermediate phases between Nb₂O₅ and MnNbO₄ in both the Al and Ga systems, but, apparently misinterpreting the experimental evidence in the TiO₂-Nb₂O₅ system, he assigned to his phase I the composition M₀·₅Nb₁₄·₅O₃₇ (M = Al, Ga), with the (5 x 3)₀₀ structure known for MgNb₁₄O₃₉F₂. Fig. 3 shows a lattice image from our 1:49 preparation. This is identical with the lattice image from TiNb₂₄O₆₂, a (3 x 4)₀₀ structure, and proves the existence of Ga₂O₃·Nb₂₄·₅O₆₂, as proposed by Trunov et al. (1968). In principle, it seems likely that ordered intergrowth phases between the GaNb₁₁O₂₉ and Ga₁₀₅Nb₂₄·₄O₆₂ structures, and between Ga₀₅Nb₂₄·₄O₆₂ and H-Nb₂O₅ could be prepared. These parts of the phase diagram have not been explored by electron microscopy and, from the work of Allpress (1970) on the TiO₂-Nb₂O₅ system, it is likely that the requisite ordering processes would be very sluggish.

**Defects in GaNb₁₁O₂₉**

After annealing at 1300°C, the crystals of orthorhombic GaNb₁₁O₂₉ were very perfect. However, both the formation reaction from the constituent oxides and the subsequent ordering are dependent upon cation diffusion processes and proceed much more slowly at 1000°C. The material prepared at the lower temperature showed extensive domains of disorder in many crystals.

Lattice images from such crystals show features similar to those found by Iijima, Kimura & Goto (1973) in slightly oxygen-deficient Nb₂O₅, and identified by them as arising from point defects. Fig. 4 shows a lattice image in which contrast anomalies attributable to point defects are indicated by the arrows. Extended defects and domains of disorder are shown in Figs. 5 and 6; the structure of relevant portions of Fig. 5 is drawn out in Fig. 7. In both micrographs, the areas M are composed of the monoclinic modification of GaNb₁₁O₂₉ in one orientation; the areas T are also of the monoclinic form, but with the orientation rotated through 90°. In extensive work, we have frequently ob-
Fig. 1. Lattice image of orthorhombic GaNb$_{11}$O$_{29}$ prepared at 1300°C.
Fig. 2. Monoclinic GaNb$_{11}$O$_{29}$: lattice image of 1000°C preparation.

Fig. 3. Lattice image of GaNb$_{49}$O$_{124}$. 
Fig. 4. GaNb$_{11}$O$_{29}$: contrast anomalies indicative of point defects in the 1000 ℃ preparation.
Fig. 5. Indeterminate boundary between twin orientations (M and T) of monoclinic GaNb₁₋₅O₁₉. Faults in semicoherent boundary labelled D₁ to D₆. X - coherently intergrown lamellae of GaNb₅O₁₄ structure.

Fig. 6. Faulted twin boundary and intergrowth of GaNb₃O₁₄.
to be juxtaposed across the closure gap. The layers of sites must necessarily be canted and buckled, as was first recognized by Iijima (1973).

In Figs. 5 and 6 the files of columns marked $X$ are of particular interest. These are files of $(3 \times 3)$ columns, corner-sharing at the same cation level, as in TiNb$_2$O$_7$, and constituting lamellar intergrowths of a different composition. The composition of these lamellae necessarily corresponds to GaNb$_2$O$_4$, the compound supposedly prepared by Iyer & Smith (1967). We obtained no evidence that this is capable of existence either as a pure structure or in extended domains, but it can be formed, presumably as a metastable structure, in the form of Wadsley defects, in low-temperature reactions.

**GaNbO$_4$**

Since GaNb$_{1.5}$O$_{29}$ is still an abundant constituent in Ga$_2$O$_3$, 2Nb$_2$O$_5$, it is evident that it coexists with some compound rich in Ga$_2$O$_3$. The diffraction pattern of the 1:1 preparation, which contained all the supernumary diffraction lines observed for $2 < x < 5$, could be completely indexed analytically, by de Wolff's methods, in terms of a monoclinic structure with $a=11.77$, $b=3.749$, $c=6.25$ Å, $\beta=107.6^\circ$. Comparison with the recorded data for AlNbO$_4$ ($a=12.13$, $b=3.726$, $c=6.46$ Å, $\beta=107.2^\circ$) makes it evident that the 1:1 preparation is monophasic and consists of GaNbO$_4$, isostructural with the Al compound.

Ga$_2$O$_3$.0.5Nb$_2$O$_5$ was biphasic, the second phase being identified as $\beta$-Ga$_2$O$_3$. It follows that GaNbO$_4$ is the only compound intermediate between Ga$_2$O$_3$ and the block structure phases.

P.L.G. thanks the S.R.C. for financial support.

**References**


