

Crystal Structure of β -Ga₂O₃

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The crystal structure of β -Ga₂O₃ has been determined from single-crystal three-dimensional x-ray diffraction data. The monoclinic crystal has cell dimensions $a=12.23\pm 0.02$, $b=3.04\pm 0.01$, $c=5.80\pm 0.01$ Å and $\beta=103.7\pm 0.3^\circ$ as originally reported by Kohn, Katz, and Broder [Am. Mineral. 42, 398 (1957)]. There are 4 Ga₂O₃ in the unit cell. The most probable space group to which the crystal belongs is C_{2h}^2-C2/m ; the atoms are in five sets of special positions $4i: (000, \frac{1}{2}, 0) \pm (x0z)$. There are two kinds of coordination for Ga³⁺ ions in this structure, namely tetrahedral and octahedral. Average interionic distances are: tetrahedral Ga—O, 1.83 Å; octahedral Ga—O, 2.00 Å; tetrahedron edge O—O, 3.02 Å; and octahedron edge O—O, 2.84 Å. Because of the reduced coordination of half of the metal ions, the density of β -Ga₂O₃ is lower than that of α -Ga₂O₃ which has the α -corundum structure. Also the closest approach of two Ga³⁺ ions in β -Ga₂O₃ is 3.04 Å which is considerably larger than the closest approach of metal ions in the sesquioxides with the α -corundum-type structure and, in agreement with the results of thermodynamic meas-

urements, the β phase appears to be the structurally more stable one.

The average Ga—O distances in the structure seem to account for the fact that although the Ga³⁺ ion is substantially larger than the Al³⁺ ion its quantitative preference for tetrahedrally coordinated sites when substituted for Fe³⁺ ion in the iron garnet is very nearly the same as that of the Al³⁺ ion.

The structure accounts for a recent result obtained by Peter and Schawlow from paramagnetic-resonance measurements on Cr³⁺-ion-doped β -Ga₂O₃, namely that the Cr³⁺ ion substitutes for the Ga³⁺ ions in a single set of equivalent octahedral sites.

The magnetic aspects of the β -Ga₂O₃ structure are discussed and it is shown that a possible Fe₂O₃ isomorph could be expected to be at least antiferromagnetic with a Néel temperature of about 700°K. Furthermore, a knowledge of the β -Ga₂O₃ structure and of the nature of site preferences of the Ga³⁺ and Fe³⁺ ions in the garnet lead to a prediction regarding the structure of the ferrimagnetic crystals of formula Ga_{2-2x}Fe_xO₃ recently discovered by Remeika

INTRODUCTION

MUCH attention has recently been given the sesquioxides of the 3d elements particularly in regard to their magnetic nature. Several of these have the α -Al₂O₃ (α -corundum) structure.¹ Crystals of α -Al₂O₃ doped with small amounts of magnetic ions are not only of scientific interest but have important application as MASER materials. Trivalent gallium with 3d¹⁰ configuration is nonmagnetic and therefore a Ga₂O₃ crystal doped with a magnetic ion is also of scientific and possibly technological interest.

In these Laboratories paramagnetic-resonance studies by Peter and Schawlow² on Cr³⁺-ion-doped β -Ga₂O₃ crystals prepared by Remeika³ indicated that the Cr³⁺ ions had replaced Ga³⁺ ions in crystallographically equivalent octahedral sites. If the Cr³⁺ ions had entered crystallographically nonequivalent octahedral sites, this certainly would have been detected. On the other hand, it would not have been simple to detect tetrahedrally coordinated Cr³⁺ ions.

Since Kohn, Katz, and Broder had shown⁴ that the unit cell of β -Ga₂O₃ contained 8 Ga³⁺ ions, then, as will be shown in detail later, these ions must be in at least two sets of crystallographically nonequivalent positions. Because there seemed little reason to expect the Cr³⁺

ions to prefer one set of octahedral sites to another and because the Cr³⁺ ion shows an exclusive preference for octahedral coordination, (see, for example, footnotes in references 5–7) it appeared reasonable to speculate that the Ga³⁺ ions had two types of coordination in β -Ga₂O₃. If this speculation proved sound, we would have the first clear-cut case in which a *pure* sesquioxide contained octahedrally and tetrahedrally coordinated metal ions in the same structure.

With the present interest in the 3d transition-metal oxides, it would seem worthwhile to determine the structures of any of those yet unknown. (Indeed there now appears to be good reason to refine *known* structures of these oxides to provide needed accuracy for theoretical considerations.) Such knowledge could be important to our understanding of the crystal chemistry of the ions involved. For example, the Fe³⁺ and Ga³⁺ ions with spherical electronic configurations 3d⁵ and 3d¹⁰, respectively, have both octahedral and tetrahedral coordination in the garnets {Y₃}[Fe₂](Fe₃)O₁₂ and {Y₃}[Ga₂](Ga₃)O₁₂ and in solid solutions of one of these in the other.⁵ Both the Ga³⁺ and Al³⁺ ions are smaller than the Fe³⁺ ion, but the Ga³⁺ is substantially larger than the Al³⁺ ion.⁸ Yet when these ions are substituted for the Fe³⁺ ion in the garnets they show very nearly the same quantitative preference for tetrahedral sites.^{5,9} The present investigation appears to clarify this observation.

The structure of β -Ga₂O₃ also accounts for its behavior

¹ R. W. G. Wyckoff, *Crystal Structures*, Vol. II (Interscience Publishers Inc., New York). See also Z. Krist., Strukturbericht 1, 240 (1931); L. Pauling and S. B. Hendricks, J. Am. Chem. Soc. 47, 781 (1925); W. H. Zachariasen, Z. Krist., Strukturbericht 2, 310 (1937).

² M. Peter and A. L. Schawlow, Bull. Am. Phys. Soc. Ser. II, 5, 158 (1960).

³ J. P. Remeika, J. Appl. Phys. 31, 263S (1960); See also Conference on Magnetism and Magnetic Materials, Detroit, Michigan, November, 1959, Paper No. S4.

⁴ J. A. Kohn, G. Katz, and J. D. Broder, Am. Mineral. 42, 398 (1957).

⁵ M. A. Gilileo and S. Geller, Phys. Rev. 110, 73 (1958).

⁶ S. Geller, J. Appl. Phys. 31, 30S (1960).

⁷ S. Geller, C. E. Miller, and R. G. Treuting, Acta Cryst. 179 (1960).

⁸ S. Geller, Acta Cryst. 10, 248 (1957).

⁹ S. Geller, J. Phys. Chem. Solids (to be published).