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Notes

On the Structure of β-Ga_2O_3

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The deviation from the symmetry $2/m$ to 1 of β-Ga_2O_3 as reported by Wolten and Chase must be very small. It is apparently not measurable by X-ray intensity differences, by EPR of both Fe^{3+}- and Cr^{3+}-doped β-Ga_2O_3, by Mössbauer effect spectroscopy of Fe^{3+}-substituted β-Ga_2O_3, or by optical and microwave resonance spectroscopy. Second harmonic generation, as measured by the Kurtz–Perry technique, and pyroelectricity are absent. It is pointed out also that single crystals of high-pressure phase $Ga_{2-x}In_xO_3$ have been reported to be isostructural with the monoclinic β-Ga_2O_3.

Recently, this journal contained an article by Wolten and Chase (*1*) which gave evidence that the space group of β-Ga_2O_3 is $P1$. The purpose of this note is to point out other published results which have not detected this lower symmetry, implying that the deviation from the higher symmetry reported earlier (*2*) is undoubtedly very small.

In the earlier report (*2*), it was pointed out that a single crystal of β-Ga_2O_3 with the *b*-axis along the long direction gave diffraction symmetry $2/m$. Deviation, if any, from this symmetry must be *very* small, at least not observable from the X-ray photographs which have been carefully reexamined in light of the Wolten and Chase paper. Thus any *real* deviation from $2/m$ would be very difficult, perhaps impossible, to ascertain from the X-ray photographic data. There is the possibility that counter techniques applied to a good single crystal might detect a deviation, but it is not highly probable.

There are other cases that are at least somewhat similar to that under discussion: Yttrium iron garnet below its Curie temperature, for example, is rhombohedral, but this cannot be detected by X-rays, and in the refinement (*3*) of the crystal structure of this garnet at room temperature, it was assumed to be cubic. In the case of yttrium iron garnet, however, the main evidence comes from magnetic measurements.

In the case of β-Ga_2O_3, no measurement of the physical properties of the crystals other than those measured by Wolten and Chase confirms their result. In the earlier paper (*2*), it was pointed out that paramagnetic resonance studies of Cr^{3+}-doped β-Ga_2O_3 (*4*) did not show the presence of crystallographically nonequivalent octahedral sites, which would be a requirement of the space group $P1$. It is noteworthy that in a ferrimagnetic garnet which has a [100] "easy" direction, and which "looks" cubic to X-rays, Mössbauer spectroscopy distinguishes the nonequivalent tetrahedral Fe^{3+} ions (*5*). However, it does not resolve the three sets of nonequivalent sites in orthorhombic $(Mn_{1-x}Fe_x)_2O_3$, $x = 0.025$ and 0.060 (*6*). In the first case, one observes magnetic hyperfine spectra, whereas the second case has electric quadrupole split spectra only. On the other hand, X-ray diffraction readily shows that the $(Mn_{1-x}Fe_x)_2O_3$ phases are orthorhombic below the crystallographic transition temperatures (*6*).

There have been numerous other investi-

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gations on crystals of β-Ga_2O_3, or on crystals related thereto, since the publication of the earlier paper (*2*). None of these has indicated a deviation from the monoclinic structure. A number of additional EPR investigations have been carried out on Fe^{3+}-doped β-Ga_2O_3 (*7*) and on Cr^{3+}-doped β-Ga_2O_3 (*8*) which confirm only two sets of sites for the cations in the crystal. This is also the case for a Mössbauer effect spectroscopy investigation (*9*) of Fe^{3+}-substituted β-Ga_2O_3. Tippins has performed optical and microwave measurements (*11*) and EPR measurements (*12*) finding no discrepancy with the monoclinic structure. It has been found (*10*) that solid solutions with formula $Ga_{2-x}In_xO_3$ prepared at high pressure have the β-Ga_2O_3 structure as reported earlier (*2*). The failure (*1*) of the SHG technique to detect polarity in the crystals is particularly interesting. The SHG technique (*13*) is a very sensitive one and has detected noncentrosymmetry in a number of crystals earlier thought to be centrosymmetric. Wolten and Chase (*1*) have also reported that a test for pyroelectricity was negative.

The primary evidence for the acentric triclinic symmetry of β-Ga_2O_3 is its morphology (*1*). Optical and SEM studies (*1*) support the assignment of the lower symmetry to β-Ga_2O_3. Because all the other physical measurements point to the higher symmetry, it is likely that the deviation from the more symmetric structure is very small indeed. This is the conclusion to be drawn regarding this question, raised by Wolten and Chase (*1*).

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