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Comments

Comments are short papers which comment on papers of other authors previously published in the **Physical Review**. *Each Comment should state clearly to which paper it refers and must be accompanied by a brief abstract. The same publication schedule as for regular articles is followed, and page proofs are sent to authors.*

Comment on "Optical and electron paramagnetic resonance studies of Fe impurities in yttrium aluminum garnet crystals"

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In this paper, we examine the relative concentrations of Fe^{+2} and Fe^{+3} in yttrium aluminum garnet and their distribution between octahedral and tetrahedral sites. We suggest that by examining the tetrahedral iron absorption peaks at 407 and 415 nm, the hypothesis of substantial shifting of Fe^{+3} from tetrahedral to octahedral sites when annealed between 600 and 1100 °C and the conversion of substantial amounts of Fe^{+3} to Fe^{+2} when annealed in a reducing atmosphere can be analyzed.

In a recent paper, Chen *et al.*[1] have examined the properties of Fe^{+3} impurities in yttrium aluminum garnet. They have come to the following conclusions:

(1) Based on both electron paramagnetic resonance (EPR) and optical absorption measurements, in as-grown yttrium-aluminum garnet (YAG), there is about as high a concentration of Fe^{+2} as there is Fe^{+3}. Annealing in reducing atmospheres (N_2 atmosphere) can convert all the ions to Fe^{+2}; the reverse annealing in O_2 converts ions to Fe^{+3}.

(2) Based on the EPR experiments, there appears to be a shift of Fe^{+3} from tetrahedral to octahedral sites, independent of annealing atmosphere, which begins at 600 °C. Since the optical charge-transfer absorption band at 255 nm does not change at annealing temperatures less than 1100 °C, Chen *et al.* postulate that this charge-transfer band is due to oxygen-to-iron charge transfer where the iron can be in tetrahedral or octahedral sites and can absorb with approximately the same oscillator strengths.

While we do not disagree with either their results or their conclusions, we would like to compare these results to our results[2,3] and suggest possible experiments to further confirm their measurements.

(1) In a set of optical measurements on deliberately doped Fe^{+3} YAG crystals grown via the floating-zone crystal-growth method from polycrystalline feed rods at the Materials Processing Center at MIT (ranging from 0.1% to 10% iron doping in the initial powder preparation) annealed in atmospheres at 1300 °C ranging from O_2 ($P_{O_2}=1$) to mixtures of CO_2/CO (with partial pressures of oxygen as low as 10^{-14}), we were unable to observe the presence of Fe^{+2} or Fe^{+4} through optical measurements; the expected infrared absorption of Fe^{+2} and 600-nm absorption of Fe^{+4} as given in Refs. 4–7 was not observed. The Fe^{+3} peaks (internal *d-d* transitions) remained constant in absorption strength. Also, electrical conductivity measurements indicated that the concentration of Fe^{+3} ions remained fixed throughout the aforementioned annealing conditions.

The discrepancy between our results and those of Chen *et al.* are not surprising. Background impurities will certainly be different between crystals grown by different methods in different laboratories. If we assume that our crystals had a greater percentage of aliovalent background impurities, then the Fe^{+3} concentration could be fixed in our crystals and variable in those of Chen *et al.* Moreover, our crystals were doped with considerably higher concentrations of iron than were those of Chen *et al.* (with trace amounts of iron). If the iron ions interact, then the effects observed by Chen *et al.* may be concentration dependent.

(2) The changing of Fe^{+3} from tetrahedral to octahedral sites at low temperatures (600 K) is very interesting. Similar measurements by us[2] on Ni^{+3} and Ni^{+2} indicated that even at high temperatures (1300 °C) when the nickel changed its valence state, it nevertheless maintained its initial growth site. Thus, when grown as Ni^{+3} in Ni:YAG, the nickel remained octahedral even when converted to Ni^{+2} by reducing at 1300 °C. On the other hand, when Ni^{+2} was introduced in the growth state in Ni:Zr:YAG, it went partially into tetrahedral sites.

To further confirm their results, we would like to suggest a further optical absorption measurement. Several

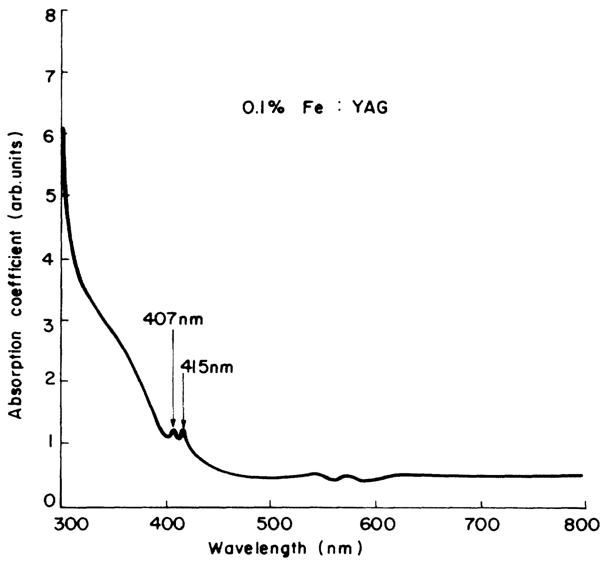

FIG. 1. Absorption spectrum of 0.1% Fe:YAG; the percentage of iron is based on the initial powder preparation.

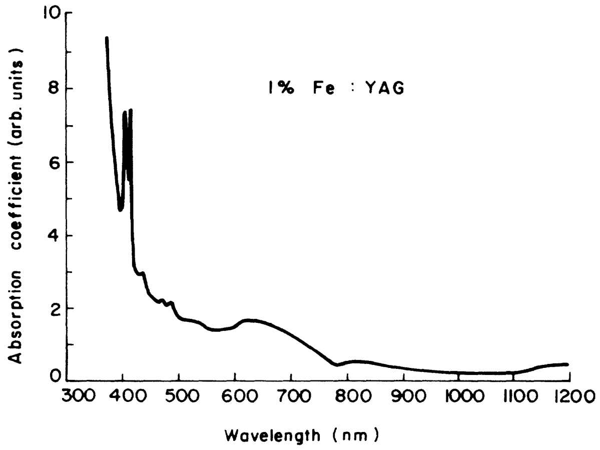

FIG. 2. Absorption spectrum of 1% Fe:YAG; the percentage of iron is based on the initial powder preparation.

researchers have determined[2,3,8,9] that Fe^{+3} in tetrahedral sites in YAG have a characteristic doublet at 407 and 415 nm. These peaks can be observed both in YAG grown with 0.1% and 1% iron concentrations in the melt, resulting (in our crystals) in 0.02% and 0.2% iron concentrations in the crystals. As can be seen in Figs. 1 and 2, the doublet can be clearly seen. Chen *et al.*[1] have reported that they have available a crystal containing 0.3 at.% iron. By observing the magnitude of the absorption doublet, they should be able either to confirm the overall increase of the Fe^{+3} concentration at high temperatures (>1100 K) in oxidizing atmospheres and the shift of Fe^{+3} from octahedral to tetrahedral sites at annealing temperatures (>600 K) or to determine the iron concentration dependence of such effects.

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