

## SHORT COMMUNICATIONS

### SITE SYMMETRY OF $\text{Eu}^{3+}$ IN FLUX-GROWN ZIRCON

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It is well known that the lanthanides replace  $\text{Zr}^{4+}$  ions in natural zircon;<sup>1</sup> the charge compensating mechanism is unknown as natural material always contains many trace impurities. We have studied the fluorescence of  $\text{Pr}^{3+}$  and its distribution in natural zircon,<sup>2</sup> but flux-grown crystals containing added lanthanides were also used to furnish comparison data. In this note we report on the emission from zircons grown in flux melts cooled at varying rates and show that the  $\text{Eu}^{3+}$  ions can occupy three sites of different symmetries.

A great deal of recent work has centered on  $\text{Eu}^{3+}$ -doped phosphors having the zircon structure, usually prepared by high temperature ceramic or flux melt techniques. Yttrium vanadate,  $\text{YVO}_4$ , is a typical example in which the  $\text{Eu}^{3+}$  ion substitutes for  $\text{Y}^{3+}$  and emission spectra have shown<sup>3</sup> that the site symmetry is strictly  $D_{2d}$ . In this case there is no problem of maintaining electrical neutrality, whereas this requirement in  $\text{Eu}^{3+}$ -doped zircon could mean that compensating ions in the proximity of the  $\text{Eu}^{3+}$  ion produce localized distortions that change the site symmetry.

A number of investigators have used the visible emission from  $\text{Eu}^{3+}$  to study the local site symmetry when the ion is solvated in solution, complexed with ligands, or substituted in inorganic crystal lattices.<sup>4</sup> The transitions  ${}^5D_0-{}^7F_0$ ,  ${}^5D_0-{}^7F_1$ , and  ${}^5D_0-{}^7F_2$  are of particular interest as they can each reveal some important feature of the crystalline field acting on the ion. The  ${}^5D_0-{}^7F_0$  transition is normally forbidden unless the site symmetry allows a linear term to be included in the crystal field expansion thereby relaxing this prohibition.<sup>5</sup> When this occurs the emission will be a single line that cannot be split unless the  $\text{Eu}^{3+}$  ions are situated in sites of different symmetry. The intensity of the  ${}^5D_0-{}^7F_1$  transition should not vary very much when the surroundings are changed as it is a magnetic dipole transition. It has been used as a reference in a study of  $\text{Eu}^{3+}$  emission from some garnets.<sup>6</sup> The  ${}^5D_0-{}^7F_2$  transition

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<sup>1</sup> Deer, W. A., Howie, R. A., and Zussman, J., "Rock Forming Minerals." Vol. 1, p. 59. (Longmans: London 1962.)

<sup>2</sup> Fielding, P. E., unpublished data.

<sup>3</sup> Brecher, C., Samelson, H., Lempicki, A., Riley, R., and Peters, T., *Phys. Rev.*, 1967, **155**, 178.

<sup>4</sup> Crosswhite, H. M., and Moos, H. W., "Optical Properties of Ions in Crystals." (Interscience: New York 1967.)

<sup>5</sup> Blasse, G., and Bril, A., *Philips Res. Rep.*, 1966, **21**, 368.

<sup>6</sup> Blasse, G., and Bril, A., *J. chem. Phys.*, 1967, **47**, 5442.

is classed as a hypersensitive one as its intensity relative to the  ${}^5D_0-{}^7F_1$  transition is strongly influenced by the disposition and nature of the surrounding ions. The spectra reproduced in this note are of powdered samples cooled to 77°K, excited with 3650-Å Hg radiation, and not corrected for the S20 response of the photomultiplier. The half-widths of all the emission lines are about 8  $\text{cm}^{-1}$  except the intense one at 16745  $\text{cm}^{-1}$ , in this case (Fig. 1(c)) the 16753  $\text{cm}^{-1}$  line is only just resolved and contributes to the total half-width of 13  $\text{cm}^{-1}$ . The spectrum in Figure 1(a) is for zircon grown in a flux cooled at the rate of 2°/hr from 1400°C to 900°C, during which time the temperature regulation was about  $\pm 1^\circ\text{C}$ . The spectra in Figures 1(b) and 1(c) are for crystals grown by cooling at 5°/hr, the temperature regulation being no better than  $\pm 10^\circ\text{C}$ . Spectrum 1(b) was recorded immediately after the conclusion of the growth run and 1(c) 3 months later.

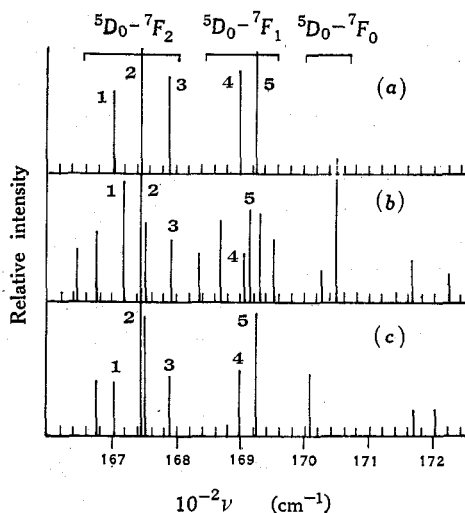


Fig. 1.—Emission spectra of  $\text{ZrSiO}_4 + \text{Eu}^{3+}$ , 3650-Å Hg excitation.

(a) Flux cooled 2°/hr;

(b) flux cooled 5°/hr;

(c) same after 3 months.

The structure shown in Figure 1(a) is in agreement with that predicted by the selection rules for  $\text{Eu}^{3+}$  in a  $D_{2d}$  site except that the  ${}^5D_0-{}^7F_2$  transition should consist of only two lines instead of the three actually detected. This extra line could be due to a  ${}^5D_1-{}^7F_4$  transition that might be expected on the basis of a comparison with the more detailed study of  $\text{Eu}^{3+}$  in  $\text{YVO}_4$ .<sup>3</sup> The spectrum is also explicable if the  $D_{2d}$  symmetry is reduced to  $S_4$  as the result of a slight distortion of the eightfold coordination polyhedron.<sup>7</sup> The spectra of Figures 1(b) and 1(c) quite clearly consist of spectrum 1(a) plus emission from  $\text{Eu}^{3+}$  ions occupying two other types of sites. The relative intensities of the  ${}^5D_0-{}^7F_1$  lines in Figures 1(a) and 1(c) near 17000  $\text{cm}^{-1}$  indicate that one particular site was highly populated during growth but it annealed out on standing, presumably changing to  $D_{2d}$  or  $S_4$  sites. The other site is also associated with the extra lines in the 17200  $\text{cm}^{-1}$  and 16700  $\text{cm}^{-1}$  regions as it appears quite stable. The nature of these sites can only be surmised on the basis of the selection

<sup>7</sup> Brecher, C., Samelson, H., and Lempicki, A., *J. chem. Phys.*, 1965, **42**, 1081.

rules which allow the  ${}^5D_0-{}^7F_0$  transition in the case of a  $C_{2v}$  site having eightfold coordination or a  $C_{4v}$  site with ninefold coordination. The results also emphasize the degree of regulation that must be achieved in furnaces used for growing crystals from flux melts if multiple site occupancy is to be avoided.

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