

Mollwo-Ivey relation between peak color-center absorption energy and average oxygen ion spacing in several oxides of group-II and -III metals*

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A simple relationship similar to that reported by Mollwo and Ivey relating peak absorption energy to the lattice parameter in the alkali halides has been noted for several oxides of group-II and -III metals, including BeO, Al₂O₃, MgAl₂O₄, Y₃Al₅O₁₂, and most of the cubic alkaline-earth oxides. Instead of the lattice parameter, the average oxygen spacing, which may be defined independent of crystal structure, is taken here as the independent variable.

The author recently measured optical-absorption spectra in pure single crystals¹ of two oxides MgAl₂O₄ (spinel) and Y₃Al₅O₁₂ (YAG) which had been irradiated² at room temperature with moderate fluences ($\sim 3 \times 10^{16} \text{ nvt}$) of 14-MeV neutrons.

The spectra appeared strikingly reminiscent of those which have been reported for other neutron-irradiated oxides including BeO,³ Al₂O₃,⁴ and MgO along with the other cubic alkaline-earth oxides.⁵

The points of similarity include the following: all the spectra include one prominent peak in the near-uv or visible range with several subsidiary peaks, usually at longer wavelengths; the predominant peaks (with the possible exception of YAG) have similar shapes in all the oxides listed; and the efficiencies of coloration (assuming equal oscillator strengths) per neutron for YAG and spinel are similar to the other compounds (where comparison is feasible).

In pursuing the possibility that the similarity might extend to the defects responsible for the absorption peaks, it was noted that the peak wavelength varies systematically with the oxygen density of the respective compounds as shown in Fig. 1, where the photon energy at peak absorption is plotted as a function of (oxygen density)^{-1/3}. The points (excluding BaO) are rather well fitted by a quadratic relation (actually the lines $E = 42.6a^{-2}$ and $E = 44.4a^{-2} - 3.5a^{-1}$ fit the points about equally well; the latter bends toward the point for BaO, which was not included in the least-squares analysis). This relationship is similar to those noted by Mollwo⁶ and Ivey⁷ for the alkali halides as discussed by Wood and Fröhlich,⁹ and to that discussed by Hayes and Stoneham¹⁰ for the alkaline-earth oxides. For the alkali halides, the *F* center is responsible for the absorption peak, and for the cubic alkaline-earth oxides the evidence is strong¹¹ for a similar role for the *F*⁺ center. There is considerable indirect evidence^{12,13} that the peak in Al₂O₃ is due to an *F*-type center.

If the *F*⁺ center were assumed to be responsible

for the main absorption peak in all these oxides, a plausible theoretical explanation along the lines of that of Wood⁸ could be proposed for the observed relationship. Despite the variety of structures represented the oxygen ions, being generally larger than the cations, and tending to have close-packed structures, would determine the scaling parameter. Since the *F*⁺ electron is rather localized, the varying details of the potentials corresponding to the different cation arrangements around the anion vacancy in the various structures might be expected to have only a second-order effect on the lowest transition energies.

The relatively larger size of the barium ion compared to the oxygen is responsible for the departure of this datum from the observed empirical curve, as already discussed by Hayes and Stoneham.¹⁰

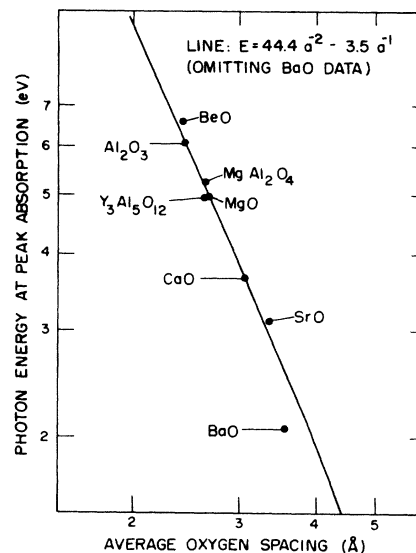


FIG. 1. Photon energy corresponding to the wavelength at maximum absorption vs average oxygen spacing, given by (oxygen density)^{-1/3}.

It would be interesting to test the general validity of the observed relationship with other oxides of the group-II and -III metals. Neutron-irradiated Y_2O_3 has been examined in this context, and no prominent band was observed, at the predicted wavelength (300 nm) or otherwise. The sample was cloudy, and this led to wavelength-dependent scattering which precluded measurements below 240 nm, at which wavelength either the shoulder of a band or an edge was just starting to rise above background.

Thus it is not clear whether the band of interest is missing altogether or is just at the wrong wavelength.

There exist a number of other mixed oxides which could be investigated, some of them of interest for technical applications in which identification of point defects is desirable. The observed relationship, if generally valid, would be helpful in this context as has been the case for the alkali halides.

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¹The samples, of nominal 99.99% purity, were obtained from Union Carbide Crystal Products Div., San Diego, Calif. The lack of prominent absorption bands in the unirradiated samples suggests that the purities may be better than nominal.

²The irradiations were performed at the RTNS (Rotating Target Neutron Source) at the Lawrence Livermore Laboratory, Calif.

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