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Optical Spectra of $Y_3Al_5O_{12}$ and $YAlO_3$ in VUV

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The optical properties of $Y_3Al_5O_{12}$ (YAG) single crystals in the fundamental region have been studied till now by Glen A. Slack *et al.*[1] and N. S. Rooze *et al.*[2] alone. Similarly, in the case of $YAlO_3$ (YAP), only single paper by V. N. Abramov *et al.*[3] came to our attention since the advent of the pure single crystals in 1969.[4] The information obtainable from them was not sufficient for our luminescence research[5] and hence we report here briefly on the spectra of the near-normal reflectivity in VUV region (5 ~ 40 eV) and of absorption in the tail region (2 ~ 8 eV) of single crystals of YAG and YAP at room temperature.

The spectra were measured with polarized light from the Seya-Namioka type 1 m grating (1200 lines/mm) spectrometer at the Synchrotron Radiation Laboratory, and the tail spectrum of YAG was taken with natural light from the McPherson 50 cm grating (600 lines/mm) spectrometer at the Institute for Solid State Physics (ISSP). The spectra of the air UV region down to 2 eV were measured with natural light of the Hitachi 330 automatic recording spectrophotometer in the Matsushita Research Institute Tokyo, Inc.

Specimen surfaces were prepared by the mechanical polishing followed by etching off the surface layers in hot H_3PO_4. {111}-surfaces were used for YAG. In the earlier two of the preliminary reports,[6-8] data were found to include the wavelength shift of about 10 Å or so at 1600 Å; this is corrected in this report.

Figure 1 shows the absorption spectra of

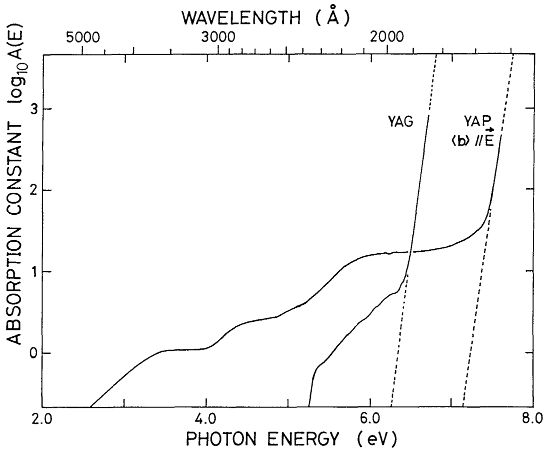

Fig. 1. The absorption spectra in the tail region of YAG and YAP at room temperature, here $A(E)$ is expressed in unit of cm^{-1}.

YAG and YAP, $\langle b \rangle \| E$, in the tail region, E being the electric field of light. The specimens ranged 1 mm ~ 20 μm in thickness. Each spectrum $A(E)$ shows a steep rise beyond the photon energy $E \sim 6.4$ eV and ~ 7.4 eV, respectively, for YAG and YAP. This part is conceived to be due to the absorption intrinsic to each species, the spectral behaviour of which is shown by the broken lines. The absorptions seen in the lower energies are due to impurities. The whole spectral behaviour of YAG is almost similar to ref. 1 (M28 curve), and the absorption becomes negligible already $\lambda \gtrsim 2400$ Å. Contrasting to this, the extrinsic absorptions of YAP tail down into the visible region, and this causes ingots to tint brown.

The reflectivity spectra are shown in Fig. 2. The absolute values are determined referring to the refractive indices,[9,10] and the reflectances calculated therefrom are shown by the dotted curves. One will note that each spectrum consists of three parts: the 1st part lies in the region of 7 ~ 15 eV, and the 2nd and 3rd parts in the regions 15 ~ 25 eV and above 25 eV, respectively. The 3rd part is most likely due to the inner core transitions of Y^{3+}, the transitions from $4p^6$ to $4p^5$ (4d+5s) lines over the region of 26.1 ~ 34.84 eV in a free ion state,[12] as interpreted in ref. 7.

The spectral structure seen in the first two regions are conceived to be due to the transitions from the O^{2-} $2p^6$ valence band(s) to the conduction bands mainly originating from the

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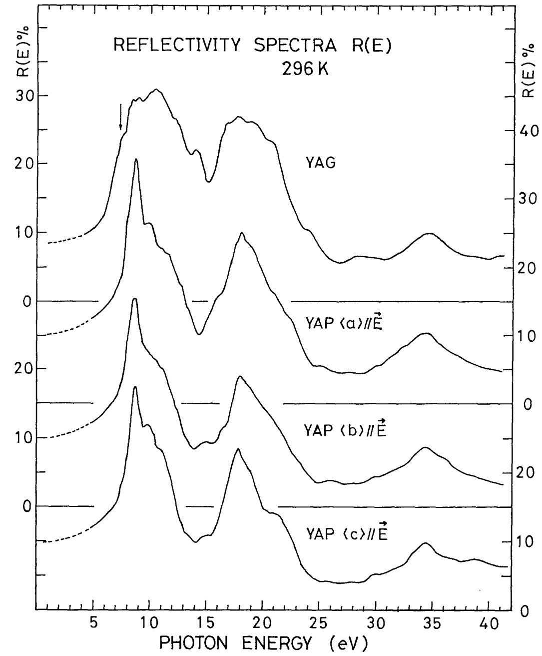

Fig. 2. The reflectivity spectra of YAG and YAP single crystals at room temperature.

3s, 3d,$\cdots$ levels of Al^{2+} and 4d, 5s,$\cdots$ levels of Y^{2+}. The basis on which this valence band transition is conducted is due to a large loss peak occurring around 23 eV where the inner core transitions set in. Because of the proximity of the 4d and 5s shell levels in Y^{2+} ion,[12,13] the lowest lying conduction band from Y^{2+} will be made up of the 4d–5s mixing orbitals, while those from Al^{2+} will be the 3s orbital. The lowest lying shoulder in the YAG spectrum, indicated by an arrow around 7.3 eV in Fig. 2, has been identified with the exciton transitions by Rooze *et al.*[2] who inferred the transitions to occur in $(AlO_4)^{-5}$. It is conceived, however, that an alternative interpretation is possible to be made referring to the spectrum of Y_2O_3.[14] Contrasting to YAG, such a distinct structure of the exciton transition is hardly observed on the reflectivity spectra of YAP at room temperature. One may notice, however, a shoulder around 8.0 eV on the reflectivity spectrum. This photon energy corresponds to the cross-over point of the Urbach rule as well as the peak position found in the excitation spectrum study of Ce^{3+} emission.[6] Similarly, the photon energy of 7.0 eV plays the same role in YAG.

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13) See, for example, G. Herzberg: *Atomic Spectra and Atomic Structure* (Dover, 1944) p. 148.
14) in preparation.