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Effects of Ce$^{3+}$ energy level structure on absorption and luminescence properties of Ce-doped YAlO$_3$, Y$_3$Al$_5$O$_{12}$, and LaAlO$_3$ single crystals

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We investigate the spectra and scintillation properties of Ce:YAlO$_3$, Ce:Y$_3$Al$_5$O$_{12}$, and Ce:LaAlO$_3$. For Ce:YAlO$_3$, the excitation spectrum is very similar with the absorption spectrum; for Ce:Y$_3$Al$_5$O$_{12}$ and Ce:LaAlO$_3$, the excitation spectra are different from the absorption spectra. Further, Ce:YAlO$_3$ has better scintillation performance than Ce:Y$_3$Al$_5$O$_{12}$; whereas Ce:LaAlO$_3$ has not demonstrated scintillation performance to date. We also provide reasonable explanations for these experimental phenomena from the viewpoint of energy level structure.


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Fig. 1. Absorption, fluorescence, and excitation spectra of Ce-doped YAP, YAG, and LAP single crystals. (a) Absorption spectrum of Ce:YAP; (b) fluorescence and excitation spectra of Ce:YAP; (c) absorption spectrum of Ce:YAG; (d) fluorescence and excitation spectra of Ce:YAG; (e) absorption spectrum of Ce:LAP; (f) fluorescence and excitation spectra of Ce: LAP.

peak is at 319 nm when we choose 416 nm as the emission peak. The peak position and intensity ratio of the absorption spectrum are totally different with those of the excitation spectrum for Ce:LAP.

Spectral properties are determined from the energy level structure; therefore, the abovementioned phenomena can be explained from the Ce$^{3+}$ energy level structure in the three crystals as shown in Fig. 2.

Figure 2(a) shows the Ce$^{3+}$ energy level structure in YAP crystal[8]. Absorption intensity is generally determined from the oscillation factor. Except the 290-nm absorption band, the absorption intensity increases with the increase of absorption wavelength. The absorption intensity at 290 nm is the highest in all five absorption bands, indicating that the absorption transition at 290 nm has the highest oscillation intensity. On one hand, excitation intensity is determined from the non-recombination probability between the excited 5d energy level and the lowest energy level. On the other hand, the non-recombination probability decreases exponentially with the increase of energy space. In normal condition, the excitation intensity decreases with the decrease of the excitation wavelength. Therefore, except for the 290-nm excitation being higher than the 302-nm excitation, other excitation intensities are in accordance with the abovementioned rule. The absorption intensity at 290 nm is higher than that at 302 nm. Moreover, the non-recombination probability between these two highest energy levels is high because of the small energy gap; thus, the 290-nm excitation is higher than the 302-nm excitation. The energy space between the two lowest 5d energy levels is only 1 500 cm$^{-1}$, which means the non-recombination probability can reach up to $10^6$[9]. In that case, the excitation intensity becomes proportional with the absorption intensity. Therefore, the absorption spectrum is very similar with the excitation spectrum for Ce:YAP.

Figure 2(b) shows the Ce$^{3+}$ energy levels structure in YAG crystal[10]. The energy space between the two 5d higher energy levels is 14 641 cm$^{-1}$. The probability of non-recombination relaxation between these two energy levels is very low. Although the absorption intensity at 225 nm is higher than that at 340 nm, the excitation intensity at 225 nm is much lower than that at 340 nm when the emission peak is 539 nm.

Figure 2(c) shows the Ce$^{3+}$ energy levels structure in LAP crystal[10]. We have investigated the position relation between Ce$^{3+}$ energy levels and conduction band (CB)[11]. The two higher 5d energy levels of Ce$^{3+}$ are located above the bottom part of the CB of LAP, and the lowest 5d energy level of Ce$^{3+}$ is located below the bottom part of the CB of LAP. The luminescence under 246, 214 nm, and higher energy excitations was either weakened or quenched. There are two important reasons behind these phenomena. One is that the nonradiative relaxation of excited electron from the second lowest energy level (40 650 cm$^{-1}$) to the lowest energy level (31 546 cm$^{-1}$) has very low probability due to the large energy difference (9 104 cm$^{-1}$) of the two lowest 5d energy levels of Ce$^{3+}$ in LAP; the other is that the two higher 5d excited states of Ce$^{3+}$ ion overlap with the conduction Fig. 2. Ce$^{3+}$ energy level structures in different crystals. (a) Ce:YAP, (b) Ce:YAG, and (c) Ce:LAP.
band. Thus, most of these 5d electrons situated at the two higher energy level of Ce$^{3+}$ can enter into the CB of LAP through the 5d energy level resonant with the CB and then vanish with holes through the nonradiative decay process. Thus, Ce:LAP may not be suitable for scintillation application. We believe this is an important reason why, to date, there are no scintillation properties reported about Ce:LAP.

The light yield of Ce:YAP is higher than that of Ce:YAG\cite{5}. This phenomenon can also be explained from the Ce$^{3+}$ energy level structure shown in Figs. 2(a) and (b). Under high-energy ray excitation, many thermalized electron-hole pairs are created in Ce-doped crystals\cite{12}. There are mainly two kinds of energy transfer to luminescence center: e-h and excitonic excitations. The excitonic mechanism of the energy transfer to luminescence centers occurs less often than recombination (e-h recombination) luminescence in inorganic crystals\cite{13}. As a luminescence center, a Ce$^{3+}$ ion is transformed into a Ce$^{4+}$ ion by capturing an electron. In comparison, the recombination energy of the e-h can easily be transferred to the Ce$^{3+}$ ion, then the Ce$^{3+}$ ion is excited from the 4f ground state to the 5d excited state. The 5d excited state is composed of different sub-levels. In general condition, the Ce$^{4+}$ ion is relaxed from the 5d higher energy level to the 5d lower energy level, then 5d-4f luminescent transition will appear. For Ce:YAP, the energy space between the two nearest 5d energy levels is smaller than that of Ce:YAG, and as such, the probability of 5d-4f luminescent transition for Ce:YAP is higher than that for Ce:YAG.

By comparing the Ce$^{3+}$ energy level structures among YAP, YAG, and LAP crystals, it can be concluded that the energy space between the two nearest 5d sub-levels of Ce$^{3+}$ is a critical parameter influencing the shape of the excitation spectrum. For a certain 5d higher sub-level, although the absorption intensity of the 4f-5d transition is high, if there exists a larger energy space between this and other 5d lower sub-levels, then the excitation intensity becomes very low. According to the same rule, the energy space between the nearest two 5d sub-levels of Ce$^{3+}$ is an important factor in determining the light yield of scintillators.

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