

Effects of Ce^{3+} energy level structure on absorption and luminescence properties of Ce-doped YAlO_3 , $\text{Y}_3\text{Al}_5\text{O}_{12}$, and LaAlO_3 single crystals

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We investigate the spectra and scintillation properties of Ce:YAlO₃, Ce:Y₃Al₅O₁₂, and Ce:LaAlO₃. For Ce:YAlO₃, the excitation spectrum is very similar with the absorption spectrum; for Ce:Y₃Al₅O₁₂ and Ce:LaAlO₃, the excitation spectra are different from the absorption spectra. Further, Ce:YAlO₃ has better scintillation performance than Ce:Y₃Al₅O₁₂; whereas Ce:LaAlO₃ 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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Ce³⁺-doped single crystals are very important luminescent materials widely used in medical imaging, astrophysics, high energy physics, and other fields^[1]. Ce:YAlO₃ (YAP) and Ce:Y₃Al₅O₁₂ (YAG) single crystals are two famous scintillation crystals^[2,3]. In related research, light yield is an important performance index for a scintillation crystal under high-energy excitation^[4]. The light yield of Ce:YAP is higher than that of Ce:YAG^[5]. However, no explanation has yet to be provided for this phenomenon. The scintillation properties of Ce:LaAlO₃ (LAP) have not yet been reported, although it has similar composition and structure with Ce:YAP^[6]. In the research of Ce-doped YAP, YAG, and LAP single crystals, we observed other interesting phenomena: firstly, the excitation spectrum is very similar with the absorption spectrum for Ce:YAP; secondly, for Ce:YAG, the peak position of excitation spectrum is correspondent with that of the absorption spectrum, but the peak to peak ratio is different; thirdly, for Ce:LAP, the excitation spectrum is totally different from the absorption spectrum. In fact, the spectral properties are determined from the energy level structure. In this letter, we investigated the effects of Ce³⁺ energy level structure on the absorption and luminescence properties of Ce-doped YAP, YAG, and LAP single crystals.

Ce-doped YAP, YAG, and LAP single crystals were grown using the Czochralski technique. The concentrations of Ce³⁺ ions in YAP, YAG, and LAP single crystals were about 0.30, 0.04, and 0.28 atm%, respectively. Detailed information about the growth process can be found in our previous works^[6,7].

Absorption spectra and fluorescence spectra were measured using spectrophotometer (V-570 type ultraviolet/visible/near-IR, JASCO, Japan) and fluorescence spectrometer (FP-6500/6600, JASCO, Japan). The wavelength range of the absorption spectra was

from 190 to 1200 nm, the light sources were deuterium (190 to 350 nm) and halogen (340 to 1200 nm) lamps, and the spectral resolution was 1 nm. For fluorescence spectra measurement, the excitation light source was a xenon lamp, with a wavelength range of 220–750 nm and spectral resolution of 1 nm. Ce³⁺ concentration was determined from the inductively coupled plasmas atomic emission spectroscopy (Advantage-type ICP-AES, Thermol Company, USA). All measurements were performed at room temperature.

Five Ce³⁺ characteristic absorption peaks at 220, 238, 275, 290, and 302 nm are observed, all of which correspond with the 4f-5d transitions of Ce³⁺ in YAP single crystal (Fig. 1(a)). Figure 1(b) shows the excitation and fluorescence spectra of Ce:YAP; the fluorescence peak is at 368 nm, and the excitation peaks are at 220, 238, 275, 290, and 302 nm when we choose 368 nm as an emission peak. The shape and peak position of the absorption spectrum are very similar with those of the excitation spectrum for Ce:YAP.

However, for Ce:YAG and Ce:LAP, different cases are observed. In the absorption spectrum of Ce:YAG, three Ce³⁺ characteristic absorption peaks at 225, 340, and 458 nm are observed, which correspond with the 4f-5d transitions of Ce³⁺ in YAG single crystal (Fig. 1(c)). Moreover, the fluorescence peak is at 539 nm, and the excitation peaks are at 225, 340, and 460 nm when we choose 539 nm as an emission peak. In fact, the peak position at the absorption spectrum is very similar with that of excitation spectrum for Ce:YAG. However, the intensity ratio between 225 and 340 nm shows opposite absorption and excitation spectra. For Ce:LAP, three Ce³⁺ characteristic absorption peaks at 214, 246, and 314 nm are observed, which correspond with the 4f-5d transitions of Ce³⁺ in LAP single crystal (Fig. 1(e)). The fluorescence peak is at 416 nm, and the excitation

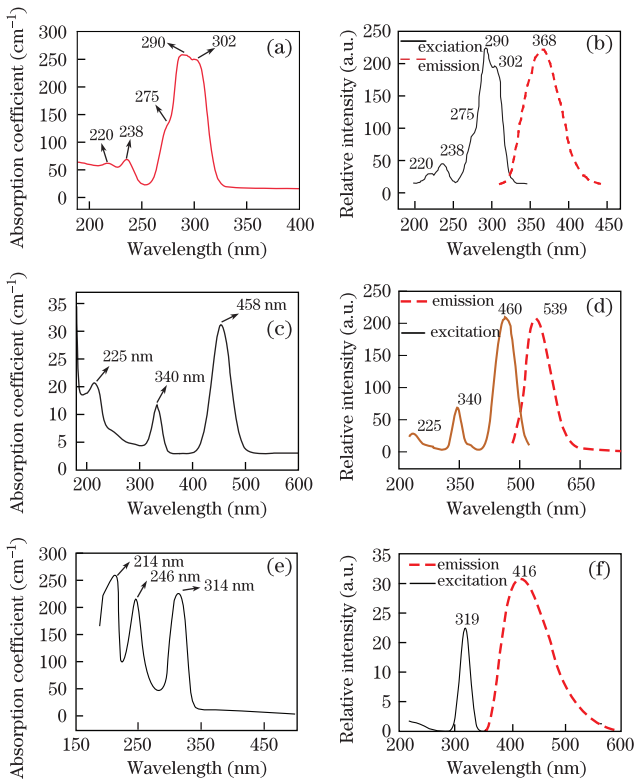


Fig. 1. Absorption, fluorescence, and excitation spectra of Ce-doped YAP, YAG, and LAP single crystals. (a) Absorption spectrum of Ce:YAP; (b) fluorescence and excitation spectra of Ce:YAP; (c) absorption spectrum of Ce:YAG; (d) fluorescence and excitation spectra of Ce:YAG; (e) absorption spectrum of 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 Ce³⁺ energy level structure in the three crystals as shown in Fig. 2.

Figure 2(a) shows the Ce³⁺ 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 5d 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 10⁶^[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 Ce³⁺ 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 Ce³⁺ energy levels structure in LAP crystal^[10]. We have investigated the position relation between Ce³⁺ energy levels and conduction band (CB)^[11]. The two higher 5d energy levels of Ce³⁺ are located above the bottom part of the CB of LAP, and the lowest 5d energy level of Ce³⁺ 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 Ce³⁺ in LAP; the other is that the two higher 5d excited states of Ce³⁺ ion overlap with the conduction

Fig. 2. Ce³⁺ 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^[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^[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^[13]. As a luminescence center, a Ce^{3+} ion is transformed into a Ce^{4+} ion by capturing a hole, after which the Ce^{4+} ion is transformed into a Ce^{3+} ion again 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^{3+} ion is relaxed from the 5d higher energy level to the 5d lowest 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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