

Spectral properties and energy transfer in YAlO_3 crystals doped with Ce ions and Mn ions

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We report the luminescence properties and decay profiles of Ce:YAlO₃, Mn:YAlO₃, and Ce,Mn:YAlO₃ crystals grown by Czochralski method. The spectroscopic properties show that both Mn²⁺ ions and Mn⁴⁺ ions exist in Mn:YAlO₃ and Ce,Mn:YAlO₃ crystals. The Mn²⁺ ions have a broad emission band of 60 nm in Mn-doped YAlO₃ crystal at 530 nm. The luminescence spectra also indicate that there is significant energy transfer between Ce³⁺ and Mn⁴⁺ in Ce,Mn:YAlO₃ crystal. Because of the energy transfer, the first decay component in Ce,Mn:YAlO₃ decreases from 24.5 to 10.8 ns, which is much faster than that of Ce:YAlO₃.

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In recent years, the yttrium orthoaluminate (YAlO₃) crystal is a widely useful host material with such diverse applications as optical recording media, scintillators, and solid state lasers. YAlO₃ doped with manganese was shown to be a promising material for holographic recording and optical data storage^[1,2]. As a scintillator, Ce:YAlO₃ has many attractive properties, such as fast decay, high light yield, and good energy resolution^[3-5]. YAlO₃ crystals doped with Mn ions and Ce ions have been reported^[6], and it is revealed that the valence of Mn ions in the Ce,Mn:YAlO₃ crystal is changed, but the mechanism of interactions between Mn ions and Ce ions in YAlO₃ is not clear yet. In this letter, we study the luminescence properties and decay profiles of YAlO₃ crystal doped with Mn ions and Ce ions.

YAlO₃ has a distorted perovskite structure^[7] that belongs to the orthorhombic P_{nma} space group with parameters of $a = 0.5180$ nm, $b = 0.7375$ nm, $c = 0.5330$ nm. Because of the distortion, the coordination number of Y³⁺ is close to 8, and the ionic radius of Y³⁺ is 0.1019 nm. Al³⁺ sites in YAlO₃ have almost ideal octahedral symmetry with an ionic radius of 0.0535 nm. The Ce³⁺ ions (0.103 nm) enter the YAlO₃ lattice, substituting for Y³⁺ ions. Mn²⁺ ions (0.096 nm) and Mn⁴⁺ ions (0.053 nm) may provide charge compensation for each other, substituting for Y³⁺ ions and Al³⁺ ions, respectively.

In this letter, Ce:YAlO₃, Mn:YAlO₃, and Ce, Mn:YAlO₃ crystals are grown with the dimensions of $\Phi 55 \times 150$ (mm) (Ce:YAlO₃) and $\Phi 25 \times 60$ (mm), respectively. The luminescence properties and decay kinetics of the crystals are investigated. The Mn⁴⁺ ions display the emission peaking at 714 nm, while the Mn²⁺ ions display the emission peaking at 530 nm. Because of energy transfer between Ce³⁺ and Mn⁴⁺, the emission intensity of Mn⁴⁺ ions at 714 nm becomes much stronger, and the Ce³⁺ ions show considerable faster decay time in comparison with the result of Ce:YAlO₃. The fast decay

component of Ce,Mn:YAlO₃ is only 10.8 ns, less than half of that of Ce:YAlO₃. This makes Ce,Mn:YAlO₃ attractive in the application of scintillators with ultrashort decay time.

To grow Ce:YAlO₃, Mn:YAlO₃, and Ce,Mn:YAlO₃ crystals, the materials was prepared with highly pure Y₂O₃(5N), Al₂O₃(5N), MnO₂(3N), and CeO₂(4N), in concentrations of (Ce:YAlO₃) 0.1 at.-%; (Ce,Mn:YAlO₃) 0.1 at.-%, 0.5 at.-%; (Mn:YAlO₃) 0.5 at.-%, respectively. The distribution coefficients of Mn and Ce in YAlO₃ crystal are estimated as 0.11^[8] and 0.5 respectively. The crystals were grown by the Czochralski method with radio frequency induction heating iridium crucible. The temperature-control apparatus was EURO THERM 818 controller/programmer with a precision of ± 0.5 °C. The wriggly distance of pulling apparatus was less than 1 μ m. The growth atmosphere was N₂. The crystals were grown by using b -direction YAlO₃ single crystal seeds with dimensions of 4.5 \times 4.5 \times 20 (mm). The pulling rate was 1–2 mm/h after the crystal diameter reached a certain value, and the crystal was rotated at a rate of 10–30 rpm during growth. The details were described in Ref. [9]. As-grown Ce,Mn:YAlO₃ crystal has pinkish color, while Mn:YAlO₃ crystal is orange. The photographs of the crystals are shown in Fig. 1.

Samples for optical measurements were cut into polished plates being 10 \times 10 \times 2 (mm) in dimensions. Luminescence spectra and lifetime were measured with LS-55 fluorescence spectrometer from Perkin-Elmer. Transmission spectra were taken with the ultraviolet/visible (UV/Vis) spectrophotometer (Mode V-570, JASCO). The X-ray excited luminescence (XEL) spectra were measured on an X-ray excited spectrometer under the same condition (35 kV, 20 mA) at room temperature, and the spectra were obtained by SBP300 grating monochromator and Hamamatsu CR131 photomultiplier tube (PMT) with the data acquired by computer. Decay time measurements (1–5000 ns) were performed under ultrashort

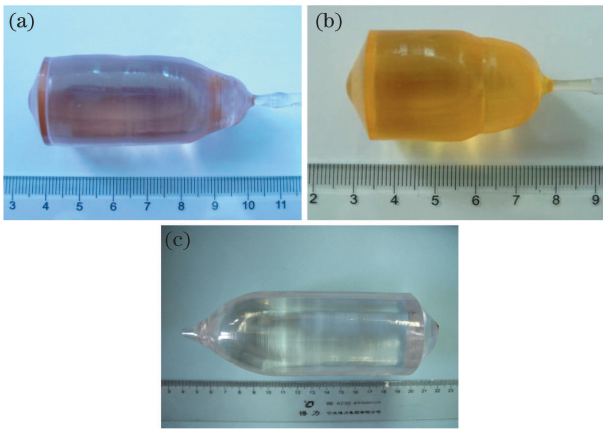


Fig. 1. Photographs of as-grown (a) Ce,Mn:YAlO₃, (b) Mn:YAlO₃, and (c) Ce:YAlO₃ crystals.

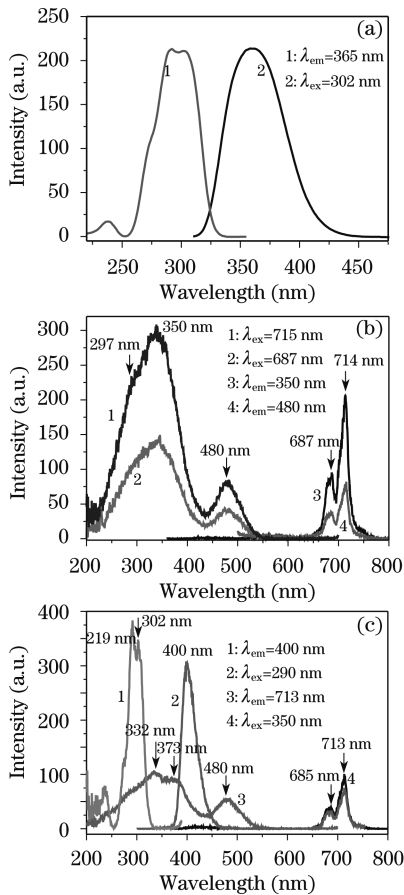


Fig. 2. Excitation and emission spectra of (a) Ce:YAlO₃, (b) Mn:YAlO₃, and (c) Ce,Mn:YAlO₃ crystals.

pulsed X-ray (30 kV) and detected by photomultiplier XP2020Q at 295 K, and the system impulse response for the facility was less than 120 ps^[10].

The luminescence properties of Ce:YAlO₃, Mn:YAlO₃, and Ce,Mn:YAlO₃ crystals are presented in Fig. 2. The emission band of Ce:YAlO₃ crystal peaking at 365 nm and the excitation bands peaking at 290 and 302 nm are due to 5d–4f transition of Ce³⁺ ions. The emission band of Mn:YAlO₃ and Ce,Mn:YAlO₃ peaking at 714 nm are assigned to ²E–⁴A₂ transition of Mn⁴⁺ ions, and the emission peaking at 685 nm is the anti-Stokes vibronic side band^[6]. The excitation

bands at 332, 373, and 480 nm ($\lambda_{em} = 714$ nm) are assigned to ⁴A₂→⁴T₁(⁴F), ⁴A₂→⁴T₁(⁴P), and ⁴A₂→⁴T₂ Mn⁴⁺ transitions, respectively^[11]. The Ce³⁺ emission of Ce,Mn:YAlO₃ peaks at 400 nm, the red shift of the emission band can be attributed to the low transmission of the sample in the region of 330–375 nm. The transmission spectra of the samples are shown in Fig. 3, indicating the 480-nm absorption of Mn:YAlO₃ and Ce,Mn:YAlO₃ due to ⁴A₂→⁴T₂ Mn⁴⁺ transition.

The XEL spectra of the samples are shown in Fig. 4. The luminescence spectra of Ce³⁺ and Mn⁴⁺ ions excited by X-ray are similar to those in Fig. 2. The broad bands peaking at 530 nm in both Mn:YAlO₃ and Ce,Mn:YAlO₃ are due to ⁴T₁→⁶A₁ Mn²⁺ transition^[6].

Figures 1 and 2 show apparent spectral overlapping between Ce³⁺ luminescence and Mn⁴⁺ excited spectra in the 320–420 nm region, indicating that there are energy transfer between Ce³⁺ and Mn⁴⁺. In Fig. 4, the strength of 530-nm Mn²⁺ emission of Mn:YAlO₃ and Ce,Mn:YAlO₃ are similar, but Ce,Mn:YAlO₃ has much stronger emission at the peak of 714 nm. Considering the same experiment condition of the XEL spectra measurement and the same concentration of Mn ions, the enhancement of the emission at 714 nm can be attributed to the energy transfer from Ce³⁺ ions.

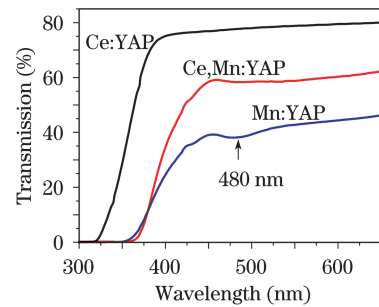


Fig. 3. Absorption spectra of Ce:YAlO₃, Mn:YAlO₃, and Ce,Mn:YAlO₃ crystals.

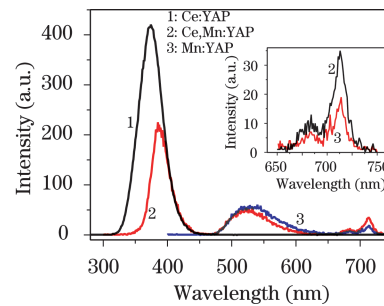


Fig. 4. XEL spectra of Ce:YAlO₃, Mn:YAlO₃, and Ce,Mn:YAlO₃ crystals.

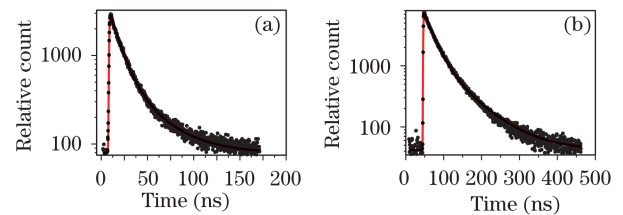


Fig. 5. Decay kinetics of (a) Ce,Mn:YAlO₃ and (b) Ce:YAlO₃ crystals.

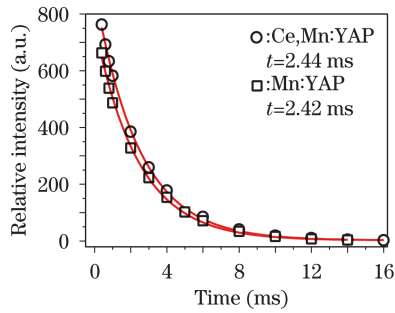


Fig. 6. Luminescence kinetics of Mn:YAlO₃ and Ce,Mn:YAlO₃ crystals.

Table 1. Parameters of Decay Time of Ce:YAlO₃, Mn:YAlO₃, and Ce,Mn:YAlO₃ Crystals

Crystal	τ_1 (ns)	τ_2 (ns)	I_1 (%)	I_2 (%)
Ce:YAlO ₃	24.5	75.8	59.4	40.6
Ce,Mn:YAlO ₃	10.8	34.6	57.6	42.4
Mn:YAlO ₃	None	None	None	None

The decay curves under pulsed X-ray excitation are shown in Fig. 5. The decay time was calculated using the following approximation of decay curve:

$$S(t) = y_0 + \sum_{i=1}^N \frac{1}{2} I_i \tau_i^{-1} \exp \left[-\tau_i^{-1} \left(t - T_0 - \frac{1}{4} \tau_i^{-1} \sigma^2 \right) \right] \times \left\{ 1 - \operatorname{erf} \left[\frac{1}{2} \tau_i^{-1} \sigma - (t - T_0) / \sigma \right] \right\}, \quad (1)$$

where N is the fitted number of multi-exponential approximation of the decay curve, τ_i is the mean time, I_i is the relative intensity for component i , y_0 is the background, and σ is the system impulse response. The decay time results are listed in Table 1. The decay curves of Ce:YAlO₃ and Ce,Mn:YAlO₃ are approximated by the sum of two exponentials with decays $\tau_1=24.5$ ns and $\tau_2=75.8$ ns, and $\tau_1=10.8$ ns and $\tau_2=34.6$ ns, respectively. The result of Ce:YAlO₃ is similar to those reported^[3], and the slow component may be caused by defects in the sample^[12]. However, the decay time of Ce,Mn:YAlO₃ shows a significant decrease, especially, the first component decreases from 24.5 to 10.8 ns. The shortening of decay time of the Ce³⁺ emission can be caused by the presence of non-radiative energy transfer, which confirms the energy transfer between Ce³⁺ and Mn⁴⁺. For the interaction between Ce³⁺ and Mn⁴⁺, the energy may transfer from Ce³⁺ 5d excited levels to the ⁴T₁(⁴F), ⁴T₁(⁴P), and ⁴T₂ Mn⁴⁺ energy levels, then to the ²E level of Mn⁴⁺, and finally the ²E-⁴A₂ Mn⁴⁺ transition with the emission peaking at 687–714 nm.

The decay time measurement of Mn:YAlO₃ has no readout (Table 1), which indicates that the broad band peaking at 530 nm is very slow. The luminescence decays of Mn⁴⁺ ($\lambda_{\text{ex}} = 350$ nm) at 714 nm in Mn:YAlO₃ and Ce,Mn:YAlO₃ are depicted in Fig. 6, both nearly to be 2.4 ms.

In conclusion, Ce:YAlO₃, Mn:YAlO₃, and Ce,Mn:

YAlO₃ crystals have been grown by Czochralski method. The characteristics of photoluminescence and XEL, and the lifetime of the crystals are studied at room temperature. The luminescence properties show the existence of Mn²⁺ ions and Mn⁴⁺ ions in Mn:YAlO₃ and Ce,Mn:YAlO₃ crystals. The Mn⁴⁺ ions have the emission peaking at 714 nm, and the Mn²⁺ ions emission peaking at 530 nm. The results of spectra and decay time measurements show that there is significant energy transfer between Ce³⁺ and Mn⁴⁺ ions in Ce,Mn:YAlO₃. Because of the energy transfer, Ce,Mn:YAlO₃ has much stronger emission at the peak of 714 nm and faster decay time than those observed in Mn:YAlO₃ and Ce:YAlO₃ samples, respectively. The fast decay component of Ce,Mn:YAlO₃ decreases from 24.5 to 10.8 ns, thus the luminescence decay in the material is distinctly shortened, and this may be hopeful to improve the properties of Ce-doped scintillator in terms of time efficiency. In addition, for better understanding of the spectroscopic properties of Ce,Mn:YAlO₃, it will be helpful to compare the characteristics of Y₃Al₅O₁₂ doped with Mn ions and Ce ions in the future.

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