



Effects of growth atmosphere and annealing on luminescence efficiency of YAP:Ce crystal

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ABSTRACT

YAlO₃:Ce³⁺ (YAP:Ce) single crystals were successfully grown by the Czochralski method. The effects of growth atmosphere and annealing on the luminescence efficiency of YAP:Ce crystals were investigated. The mechanism of self-absorption of YAP:Ce crystal was discussed which was confirmed to be one of the factors that influenced the luminescence efficiency. Comparison of samples grown in different atmosphere showed that reducing atmosphere has great advantages on reducing the self-absorption and improving the luminescence intensity of YAP:Ce crystals.

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1. Introduction

Yttrium aluminium perovskite doped with Cerium (YAP:Ce) is a well known scintillation material with many attractive properties, such as fast decay (20–100 ns), high light yield (about 20,000 photons/MeV) and good energy resolution (~4% at 662 keV) [1–7]. These properties have made YAP:Ce a material of choice for many applications, including medical diagnostics, multi-detector systems and charged heavy ions detections [7–12].

It is well established that the scintillation performances of Ce-doped yttrium aluminate crystals depend strongly on the method of crystal growth and heat treatments [13–15]. Luminescence efficiency is one of the main scintillation properties which will be affected by charge carrier capture, nonradiative transitions and self-absorption of luminescence [14,16]. Charge carrier capture caused by electron traps can greatly decrease the luminescence efficiency of YAP:Ce by competing with prompt energy transfer to the luminescence centers [17,18]. Nonradiative transitions will result in the luminescence quenching of YAP:Ce by energy transfer from Ce³⁺ ions to quenching centers [19]. Self-absorption occurs when photons emitted are trapped by luminescence centers or other defects, which will decrease the light yield of Y (Lu) AP:Ce crystals [14,20]. However, the factors that influence the self-absorption of

YAP:Ce crystals and the specific mechanism are still not clear and have never been analyzed in the previous literature.

In this paper, the effects of crystal growth atmosphere and heat treatment processes on the luminescence efficiency and self-absorption characterization of YAP:Ce crystals were investigated. The mechanism of the self-absorption of YAP:Ce crystal and the relationship between self-absorption with annealing temperature and atmosphere were discussed. Comparison of YAP:Ce crystals grown in different atmosphere indicated that Ar–H₂ atmosphere has great advantages on suppressing the self-absorption and improving the luminescence intensity.

2. Experimental

The crystals were grown by the traditional Czochralski (Cz) method with radio frequency induction heating iridium crucible. The chemicals of Y₂O₃, Al₂O₃ and CeO₂ with purity of 99.999% were used. The raw materials were weighed according to the following chemical reaction equation Ce_{0.003}Y_{0.997}AP and synthesized by solid-state reaction. The reducing growth was performed under the mixture of Ar and H₂ (4–10 vol.%). The crystals were grown by using <101> direction YAP single crystal seeds with dimensions of 4.5 mm × 4.5 mm × 20 mm. The pulling rate was 1 mm/h after crystal diameter reached a certain value, and the crystal was rotated at a rate of 10–20 rpm during growth. The samples grown in inert condition were annealed in the 1200–1550 °C range in air and reducing atmosphere, respectively.

The crystal samples were cut from the as-grown crystal with dimensions of 15 mm × 15 mm × 2 mm and 15 mm × 15 mm × 0.36 mm, respectively. The room temperature optical transmittances of the samples were recorded by the UV/VIS Spectrophotometer (Mode V-570, JASCO). A FP-6500/6600 Spectrofluorometer was used to acquire the room temperature emission spectra for YAP:Ce crystals. The infrared transmission spectra of YAP:Ce crystals were measured on PerkinElmer FTIR Spectrum GX Optica.

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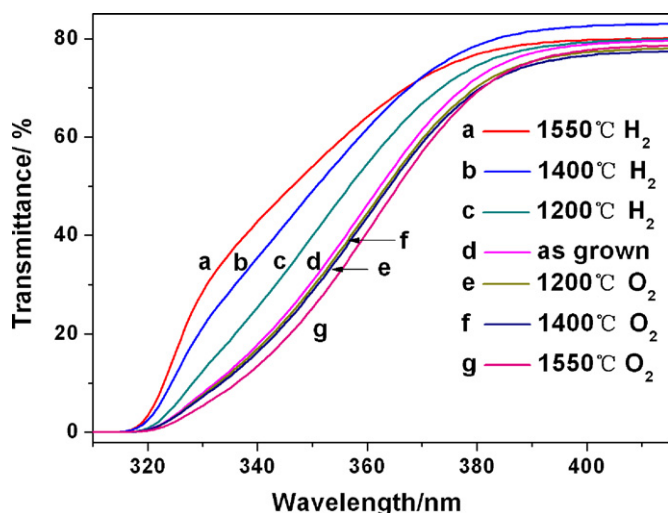


Fig. 1. Transmittance spectra of YAP:Ce crystals with different annealing condition.

3. Results and discussion

The transmittance spectra of YAP:Ce samples annealed in different atmosphere are shown in Fig. 1. It can be seen that the transmittance edge of the samples grown in inert condition shift to shorter wavelength side with the increase of the annealing temperature in H_2 atmosphere, while the transmittance edge shift to the opposite side in air atmosphere. This phenomenon indicates that there may be an inherent relationship between the shifting of transmittance edge and the valence variation of doping ions. Considering the quenching effect of tetravalent Ln ions [21] and the broad absorption band of Ce^{4+} near 280–300 nm found in sulfuric acid solutions [22], we propose that Ce^{4+} may be the main reason resulting in the self-absorption of YAP:Ce crystal and the shifting of transmittance edge. In YAP crystal, there is charge transfer (CT) transition between Ce^{4+} and the ligands. Because of the distortion of YO_{12} polyhedron in YAP, the coordination number of Ce^{4+} in YAP crystal is eight [23], and the center of CT absorption band can be approximately calculated by the following formula [21]:

$$\sigma = [\chi(X) - \chi(M)] \times 30,000 \quad (1)$$

where σ is the center of the CT absorption band; $\chi(X)$ is the optical electronegativity of the anion and $\chi(M)$ is the uncorrected optical electronegativity of the ligands. We get $\sigma = 33,000 \text{ cm}^{-1}$ (303 nm), for $\chi(O^{2-}) = 3.2$ and $\chi(Ce^{4+}) = 2.1$ [21].

Since Ce^{4+} can be restrained in reducing atmosphere, we grow a 0.3 at.% YAP:Ce crystal in Ar- H_2 atmosphere and compare it with crystal (0.3 at.%) grown in inert atmosphere. The transmittance edge of the sample grown in reducing condition shifts nearly 30 nm to the blue side (shown in Fig. 2), and the luminescence intensity of this sample improve significantly under excitation of 300 nm (shown in Fig. 3).

The absorption spectra of YAP:Ce samples grown in different atmosphere are shown in Fig. 4, the absorption peaks at 302, 291, 274, 237 and 219 nm are contributed by the d-f transitions of Ce^{3+} ions. The different absorption spectrum of YAP:Ce crystals grown in inert atmosphere versus sample grown in reducing atmosphere is shown in Fig. 5, there is an obvious different absorption peak near 281 nm with the full width half maximum (FWHM) nearly 105 nm, which confirms the charge transfer transition of Ce^{4+} ions in YAP:Ce.

The emission spectra of YAP:Ce have two components corresponding to transitions from the lowest d level to the ground manifolds $^2F_{7/2}$ and $^2F_{5/2}$ of the Ce^{3+} , and the spectra can be

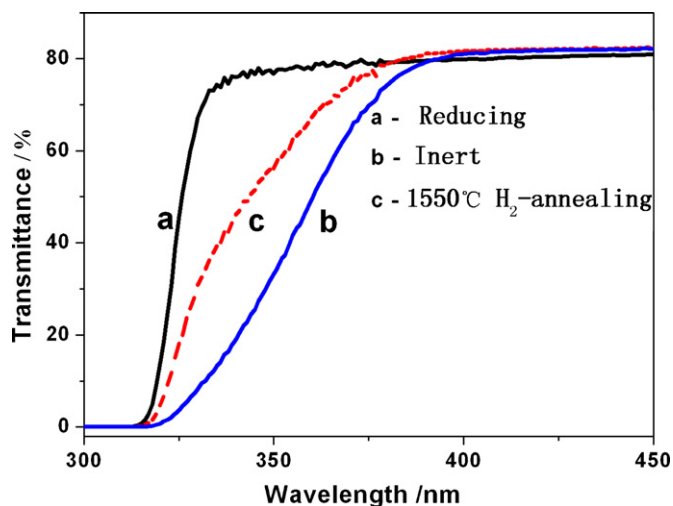


Fig. 2. Transmittance spectra of YAP:Ce crystals: (a) as-grown sample grown in reducing condition; (b) as-grown sample grown in inert condition; (c) 1550 °C H_2 -annealed sample grown in inert condition was presented for comparison.

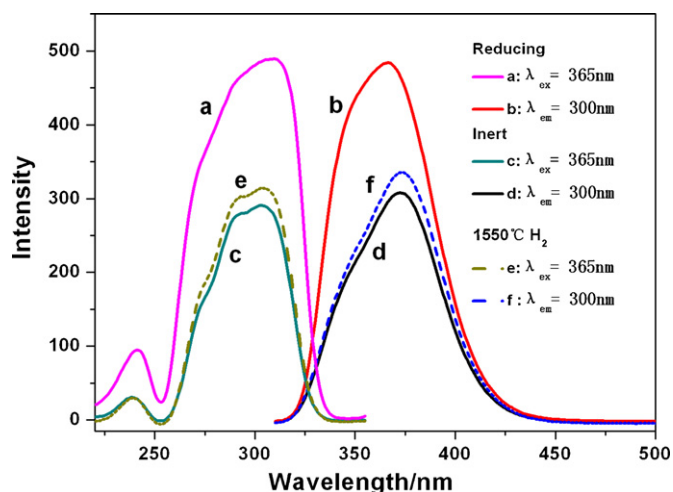


Fig. 3. Luminescence spectra of YAP:Ce crystals. 1550 °C H_2 -annealed sample grown in inert condition was presented for comparison.

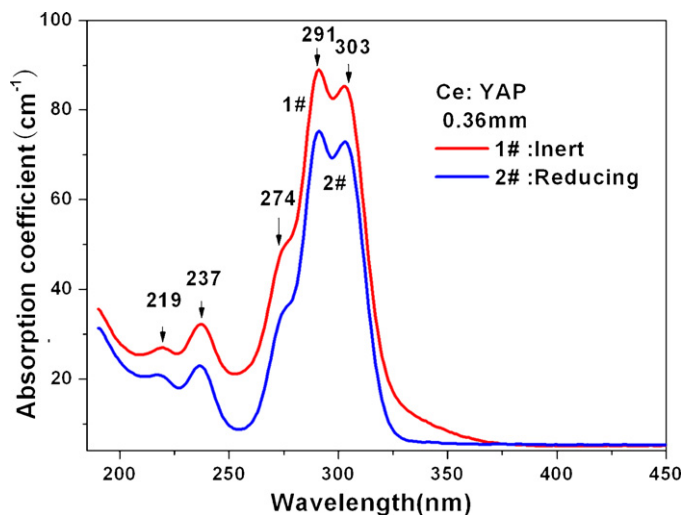


Fig. 4. The absorption spectra of YAP:Ce crystals grown in different atmosphere.

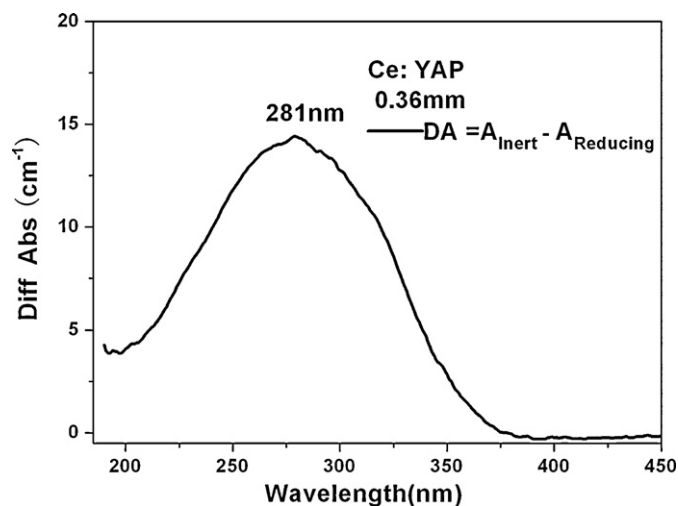


Fig. 5. The different absorption spectrum of YAP:Ce crystals grown in inert atmosphere versus sample grown in reducing atmosphere.

expressed by the Gaussian functions:

$$G_i = G_{0,i} \exp[-b_i(\lambda - \lambda_{\max,i})^2]$$

$$b_i = \left(\frac{2}{B_i}\right)^2 \ln 2 \quad (2)$$

where $i = 1, 2$; B_i stands for the FWHM of G_i . Two Gaussian bands are fitted by Eq. (2).

The two components of emission spectra of YAP:Ce grown in different conditions are shown in Fig. 6. They are peaking near 342 and 370 nm, respectively, but their intensities are different significantly. Due to the CT absorption band at 280–300 nm, the higher energy component ($G_{0,1}$) of sample grown in reducing atmosphere is twice stronger than that of sample grown in inert atmosphere. For the lower energy components near 370 nm, the intensity of sample grown in reducing atmosphere is 54% higher than that of sample grown in inert atmosphere. Since the component at 370 nm is far away from the CT absorption band of Ce^{4+} , the increase of emission intensity may be caused by valence state changing of Ce ions in the reducing growth atmosphere, and it is necessary to compare the Ce^{3+} content of samples.

Infrared transmission spectra of YAP:Ce crystals are shown in Fig. 7, and the bands at 2087, 2357, 2702 and 3260 nm can be ascribed to ${}^2F_{5/2} \rightarrow {}^2F_{7/2}$ transitions of Ce^{3+} ions. Due to the f–f transitions, Ce^{3+} emission can avoid extraneous distortion, and the log of the fractional transmission of intraconfigurational bands is linearly related to Ce^{3+} concentration [24]. Because the improvement of luminescence intensity can not be attributed to the increasing of Ce^{3+} ions with the similar Ce^{3+} concentration of the samples, we assume that the luminescence of Ce^{3+} ions in sample grown in inert condition may be quenched by complex defects associated with the small amount of Ce^{4+} ions, and the details of the quenching mechanism need further investigation.

4. Conclusions

YAP:Ce crystals have been grown in different atmosphere by the Czochraski method. Samples grown in inert condition were annealed in different atmosphere and temperature, and the corresponding transmittance and PL spectra of these samples were measured. The study revealed that the self-absorption of YAP:Ce crystals related with different annealing condition was caused by Ce^{4+} ions, which had a broad charge transfer absorption band (105 nm) near 280–300 nm. Therefore, the self-absorption of YAP:Ce crystals could be decreased by minimizing the concentra-

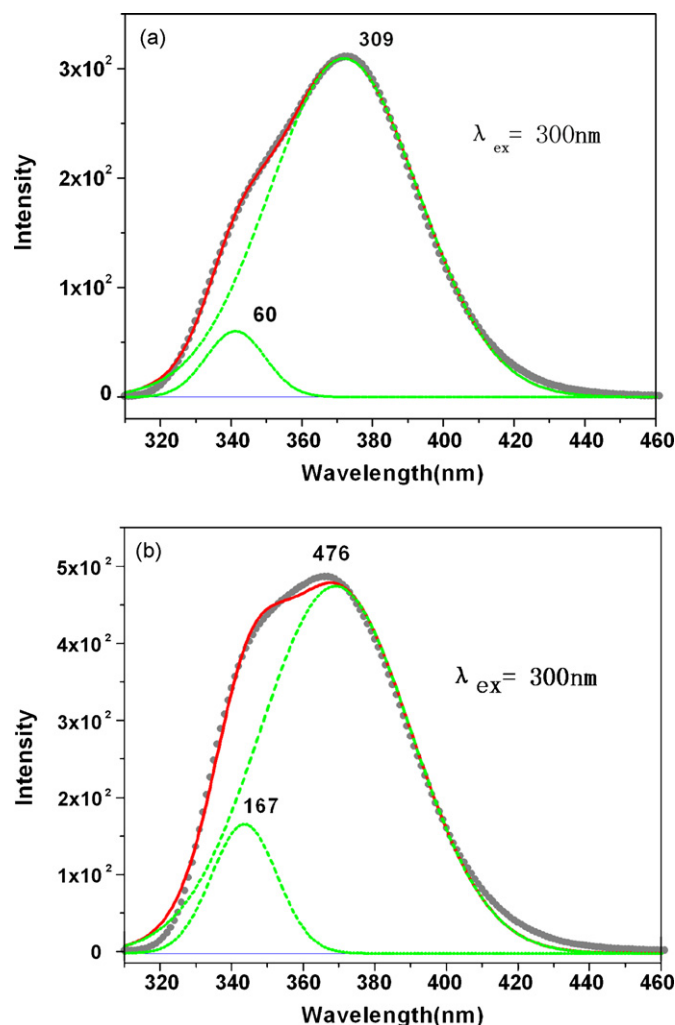


Fig. 6. Emission spectra of YAP:Ce crystals grown in different condition. Dots stand for data points, broken curves for two Gaussian components for the fit to the dots, and a full curve represents their sum. (a) Crystal grown in inert atmosphere and (b) crystal grown in reducing atmosphere.

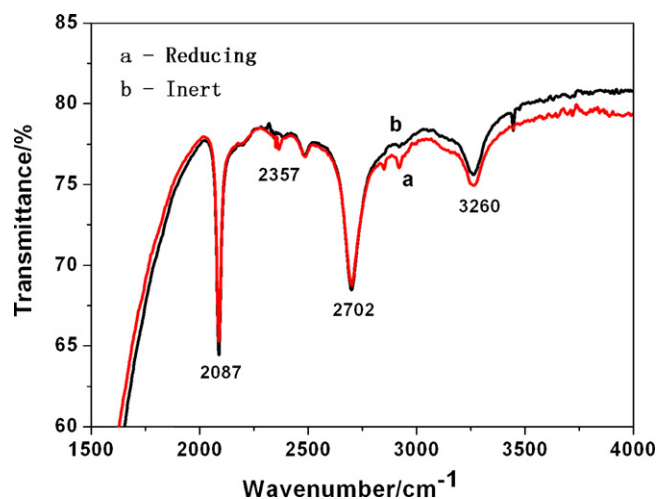


Fig. 7. Infrared transmission spectra of YAP:Ce crystals: (a) grown in reducing atmosphere; (b) grown in inert atmosphere.

tion of Ce^{4+} ions. Through the comparison of YAP:Ce crystals grown in different condition, it was found that reducing atmosphere can not only suppress the self-absorption with transmittance edge shifting nearly 30 nm to the blue side, but also increase the luminescence light output which is 54% higher than that of sample grown in inert condition.

Since YAP:Ce and LuAP:Ce are isostructural scintillator materials with similar properties, these results will help to improve the luminescence properties of LuAP:Ce crystals as well. Considering the same concentration of Ce^{3+} ions in the samples, the improvement of luminescence intensity of sample grown in reducing atmosphere may be due to the eliminating of complex defects related to Ce^{4+} ions, while the mechanism still needs further investigating.

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