Spectral properties of Ce^{3+} doped yttrium lanthanum oxide transparent ceramics*

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(Received 27 April 2009; revised manuscript received 21 July 2009)

Ce^{3+}-doped yttrium lanthanum oxide $(Y_{0.9}La_{0.1})_2O_3$ transparent ceramics is fabricated with nanopowders and sintered in H_2 atmosphere. The spectral properties of Ce:$(Y_{0.9}La_{0.1})_2O_3$ transparent ceramics are investigated. There appear two characteristic absorption peaks of Ce^{3+} ions at 230 nm and 400 nm, separately. It is found that Ce^{3+} ions can efficiently produce emission at 384 nm from $(Y_{0.9}La_{0.1})_2O_3$ transparent ceramic host, while the emission is completely quenched in Re_2O_3 (Re=Y, Lu, La) host materials.

Keywords: Ce^{3+} ion doped, spectral property, yttrium lanthanum oxide, transparent ceramics

PACC: 0765E, 7800, 8120L, 7630K

1. Introduction

Scintillators are used to convert high energy radiation into visible light which can be detected by conventional photomultiplier tubes. They have been widely used in many fields, such as nuclear medical imaging, high energy physics and nuclear physics, geophysical exploration, as well as some other industrial applications.[1,2] The 4f→5d transition allowed in trivalent rare earth ions owns the most possible luminescence mechanism, with a fast response time (10–100 ns) and a high light yield. Thus a large number of researches have been focused on Ce^{3+} ion, whose 4f→5d transition is electric dipole permitted. It has a short fluorescence lifetime, good time resolution, and can be coupled with the delicate absorption wavelength of photomultiplier tubes and silicon photodiodes. Consequently, doping Ce^{3+} ions is a major way to achieve fast response inorganic scintillating materials. It has long been known that the emission efficiency of 5d→4f transition of Ce^{3+} varies widely and randomly with the host lattice. Many studies have shown that in some host (e.g. Lu_2SiO_5), Ce^{3+} produces emission with high quantum efficiency, while in the other host lattices (e.g. Y_2O_3, Lu_2O_3, La_2O_3, etc.), Ce^{3+} emission is completely quenched, even at low temperatures.[3,4]

The hosts of Ce^{3+}-doped inorganic scintillating materials covers rare earth sesquioxide Re_2O_3, aluminate compounds $Re_3Al_5O_{12}$ (ReAG), $ReAlO_3$ (ReAP)[5] (Re=Y, Lu, Gd, etc.), and silicate compounds Re_2SiO_5, $Re_2Si_2O_7$.[6] However, in a number of hosts, such as Y_2O_3, La_2O_3, Lu_2O_3, and La_2O_2S, the emission of Ce^{3+} is completely quenched.[3] In marked contrast to them, Ce^{3+} exhibits a very high quantum efficiency in some large band gap hosts such as Lu_2SiO_5, within the spectral range of near-UV or blue light. G. Blasse[7,8] discussed some possible quenching mechanisms of Ce^{3+} ion, including large Stokes shift, electron transfer and photoionization. Recently, the discussion has been focused on the photoionization which is mainly about the correlation between the luminescence efficiency and the band gap energy of host material. A bit different location of the lowest cerium 5d electronic level relative to the host conduction band will influence the luminescence efficiency drastically.[3] At the same time, Ce^{3+} doping concentration is low in some systems, because the radius of Ce^{3+} ion (101 pm) is larger than those of Re^{3+} (Re=Y, Lu, Gd, etc.) ions. As the radius of Ce^{3+} ion is similar to that of La^{3+} ion, it is easy for Ce^{3+} ion to replace the site of La^{3+} ion in $(Y_{0.9}La_{0.1})_2O_3$ ceramics, which makes it possible to dope Ce^{3+} heavily.

In this paper, the spectral properties of Ce-doped $(Y_{0.9}La_{0.1})_2O_3$ transparent ceramics are investigated and the emission mechanism is discussed.

*Project supported by the National Natural Science Foundation of China (Grant No. 60578041), and the Shanghai Leading Academic Disciplines (Grant No. S30107).

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2. Experimental procedure

The Ce^{3+}-doped and undoped yttrium lanthanum oxide $(Y_{0.9}La_{0.1})_2O_3$ transparent ceramics were fabricated with commercial nanopowders (Rare-Chem. Hi-Tech Co., Ltd) and sintered at 1650–1700 °C for 25 h in H_2 atmosphere. The nanopowder size is 20–30 nm. Ce^{3+} ions concentration is 0.5 at%. The phase composition of the sintered specimen was identified by x-ray diffraction (Model D/MAX-3C, Rigaku, Japan), its microstructure was observed with optical microscope (BX60, OLYPMUS, Japan), the absorption spectra were measured with a spectrophotometer by using Xe light as pump source (Model V-570, JASCO) at room temperature. The fluorescence spectra were measured with a fluorescence spectrum analyzer (Fluorolog-3, Jobin Yvon Spex, France) at room temperature.

3. Results and discussion

Figure 1 shows the photographs of $(Y_{0.9}La_{0.1})_2O_3$ and Ce^{3+}:$(Y_{0.9}La_{0.1})_2O_3$ transparent ceramics (both are 2-mm thick). The undoped $(Y_{0.9}La_{0.1})_2O_3$ ceramics is colourless, while the Ce-doped $(Y_{0.9}La_{0.1})_2O_3$ transparent ceramics exhibits deep red. The specimen has high transparency and the letters under the specimens can be seen clearly.



Fig. 1. Photograph of Ce-doped and undoped $(Y_{0.9}La_{0.1})_2O_3$ transparent ceramics. Left: undoped; right: Ce-doped.

Figure 2 shows the optical microstructure photograph of Ce^{3+}:$(Y_{0.9}La_{0.1})_2O_3$ ceramics. It reveals that the specimen has uniform grains with an average grain size of about 20–30 μm and there are almost no pores between the grain boundaries.

Figure 3 shows the x-ray diffraction (XRD) pattern of Ce^{3+}:$(Y_{0.9}La_{0.1})_2O_3$ transparent ceramics. All peaks are corresponding to those of cubic Y_2O_3 phase. And no other phases were detected, which means that the La_2O_3 has been completely dissolved into Y_2O_3 lattice and a solid solution with cubic Y_2O_3 structure has been formed.

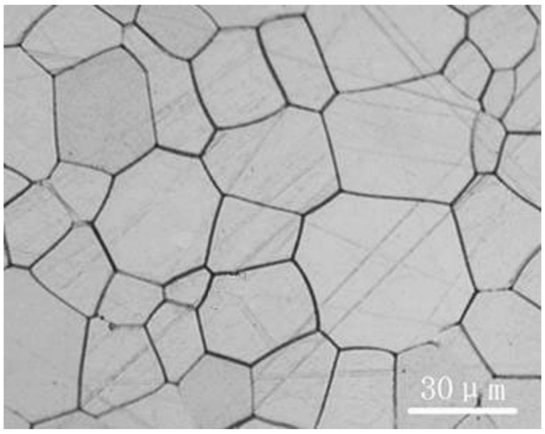


Fig. 2. Optical microscopic photograph of Ce^{3+}:$(Y_{0.9}La_{0.1})_2O_3$ ceramics.

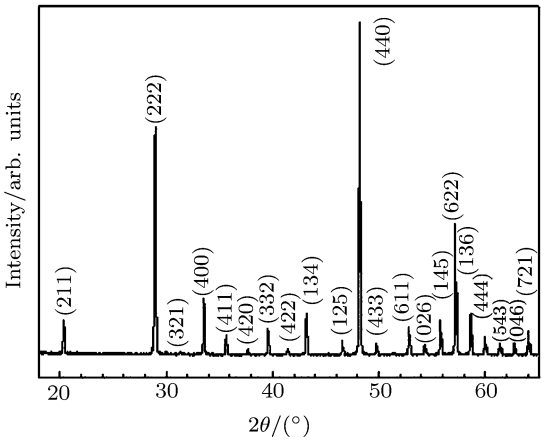


Fig. 3. X-ray diffraction profile of Ce^{3+}:$(Y_{0.9}La_{0.1})_2O_3$ ceramics.

The transmittance of the Ce:$(Y_{0.9}La_{0.1})_2O_3$ transparent ceramics is shown in Fig. 4. We can see that Ce:$(Y_{0.9}La_{0.1})_2O_3$ has high transmittance and the highest transmission reaches up to nearly 80%. However, the transmittance decreases remarkably in the visible region, which may be induced by its strong absorption in this region. The absorption spectra of Ce-doped and undoped $(Y_{0.9}La_{0.1})_2O_3$ transparent ceramics are presented in Fig. 5. There can be found one absorption peak centred at 223 nm in the undoped sample, two absorption peaks centred at 230 nm and 400 nm and an absorption shoulder at 518 nm in Ce^{3+} doped specimen. The strong absorption peaks of 223 nm in both samples are associated with the fundamental host absorption and the peaks centred at 230 nm and 400 nm are characteristic absorption peaks of Ce^{3+} ion and assigned to the lowest energy 4f→5d transitions of Ce^{3+} ion.[9] All these absorption features are similar to those of Ce:Y_2O_3 and Ce:Lu_2O_3 single crystals.[3,10]

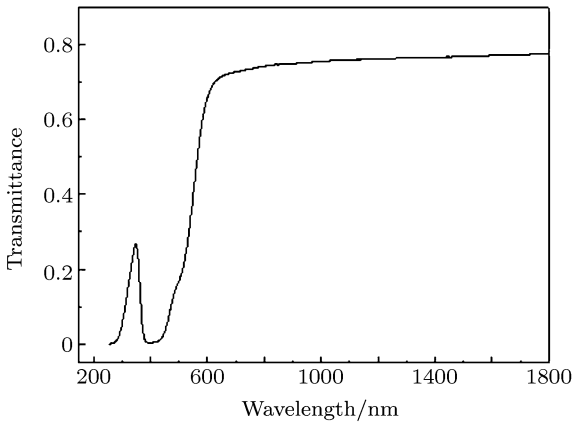


Fig. 4. Transmittance of Ce:$(Y_{0.9}La_{0.1})_2O_3$ transparent ceramics.

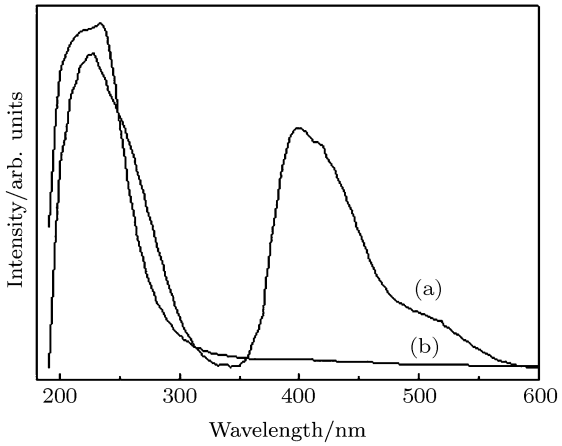


Fig. 5. Room temperature absorption spectra of Ce-doped and undoped $(Y_{0.9}La_{0.1})_2O_3$ ceramics (a): Ce-doped; (b): undoped.

Figure 6 shows the room temperature emission spectra of Ce:$(Y_{0.9}La_{0.1})_2O_3$ transparent ceramics stimulated at 290 nm. No luminescence of undoped $(Y_{0.9}La_{0.1})_2O_3$ transparent ceramics was detected in this condition. An efficient emission band was observed to have a peak at 384 nm. The emission band covers a wavelength range from 300 nm to 550 nm, with an FWHM (full width at half-maximum) of 222 nm. Under the same pump light, Ce:Re_2O_3 (Re=Y, Lu, La) is found to be able to quench emission completely, while Ce:$Lu_2(SiO_4)O$ and Ce:$Y_2(SiO_4)O$,[11] whose luminescence spectral properties are similar to Ce:$(Y_{0.9}La_{0.1})_2O_3$, can produce emission of ∼400 nm wavelength at high quantum efficiency. This means that Ce:$(Y_{0.9}La_{0.1})_2O_3$ is possible to become a fast response inorganic scintillating material. At the same time the strong absorption of Ce^{3+} at 400 nm wavelength will result in the strong reabsorption of the emission at 384 nm wavelength, which is one of the most important factor of emission quenched in Ce:Re_2O_3 (Re=Y, Lu, La) host materials.

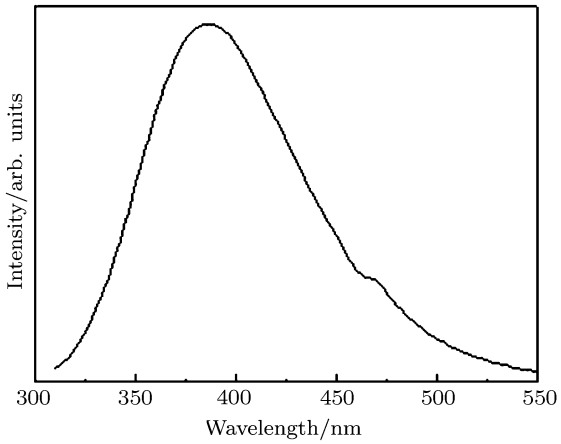


Fig. 6. Emission spectra of Ce:$(Y_{0.9}La_{0.1})_2O_3$ transparent ceramics at room temperature (λ_{ex} = 290 nm).

According to the spectrum rules,[12] 5d→4f luminescence transitions are permitted, which is characterized by a broad luminescence band, strong intensity and extra short decay lifetime. The crystal fields play an important role in 5d→4f transitions because 5d levels are outside the Ce atomic nucleus. M. Raukas *et al.*[3,4] suggested that luminescence efficiency was determined by small but crucial differences on the location of the lowest 5d level relative to the conduction band. It may be induced by the difference in radius between La^{3+} (R = 103 pm) and Y^{3+} (R = 89 pm), which will cause the distortion of lattice, the changes of the crystal field and the band gap. All these may cause the Ce^{3+} emission efficiency in $(Y_{0.9}La_{0.1})_2O_3$ ceramics to change. Further investigations on this will be performed in our future work.

4. Conclusion

Highly transparent Ce^{3+}-doped yttrium lanthanum oxide $(Y_{0.9}La_{0.1})_2O_3$ ceramics is fabricated. The highest transmission is nearly 80%. The Ce^{3+}-doped specimen has a strong characteristic absorption band of Ce^{3+} ions with two peaks at 230 nm and 400 nm, separately. An efficient luminescence of Ce^{3+} with a peak at 384 nm in Ce-doped $(Y_{0.9}La_{0.1})_2O_3$ ceramics is detected at room temperature, while no Ce^{3+} luminescence can be observed in other sesquioxde host materials, such as Re_2O_3 (Re=Y, Lu, La).

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