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Controlling optical temperature detection of $Ca_3Al_2O_6$: Yb^{3+},Er^{3+} phosphors through doping

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ABSTRACT

This work introduces a method to effectively improve optical temperature detection of novel $Ca_3Al_2O_6$:Yb^{3+},Er^{3+} through co-doping with Ba^{2+}, Mg^{2+}, Y^{3+}, La^{3+} and Lu^{3+} as well as the control of excitation power. The fluorescence intensity ratio of the green emissions at 526 nm and 551 nm in $Ca_3Al_2O_6$:Yb^{3+}-Er^{3+} was studied as a function of temperature in the temperature range from 298 K to 573 K. By analyzing the temperature dependent upconversion spectra, total emission intensity, ratios of fluorescence intensity, and sensitivity, the effect of doping ions on the optical temperature detection of $Ca_3Al_2O_6$:Yb^{3+}, Er^{3+} is studied. The relative and absolute temperature sensitivity of $Ca_3Al_2O_6$:Yb^{3+},Er^{3+} can be effectively enhanced by co-doping with Ba^{2+}, Mg^{2+}, Y^{3+}, La^{3+}, and Lu^{3+} ions and controlling excitation powers. The temperature sensitivity of $Ca_3Al_2O_6$:6%Yb^{3+}, 0.6%Er^{3+}, 1.2%Mg^{2+} can reach a maximum relative sensitivity of 0.0078 K^{-1} at 145 K, which is higher than the values in some reported works.

1. Introduction

Rare earth (RE) ions doped upconversion phosphors have been widely applied in solid-state lasers, three dimensional images and optoelectronics [1–7]. The main researches were focused on fluorides and oxides, since that host materials played an important role in upconversion emission process. Fluoride has low multiphonon relaxation rates, low phonon energy and great fluorescence quantum efficiency. However, it also has some obvious shortages, such as poor chemical stability, high cost, complex preparing processes and environment pollution. Compared with fluoride, oxide has better mechanical properties, and chemical stabilities [8–15]. The optical temperature sensitivity of Yb^{3+}-Er^{3+} co-doped materials has been extensively researched in matrices, for instance Al_2O_3 [16], ZrO_2 [17], Y_2O_3 phosphors [18,19], $Na_{0.5}Bi_{0.5}TiO_3$ ceramics [20], and TeO_2-WO_3 glass [21]. Among Yb^{3+}-Er^{3+} co-doped systems, a high-efficiency energy transfer from Yb^{3+} to Er^{3+}, due to Yb^{3+} emission ($^2F_{5/2}$-$^2F_{7/2}$) and Er^{3+} absorption ($^4I_{15/2}$-$^4I_{11/2}$) exist the large spectral overlap. Moreover, manufacturing costs and raw materials are generally low. Among the oxides, functional materials of $CaO{\cdot}Al_2O_3$ family have lately appealed to wide interests because of their potential applications in oxidants, light-emitting diodes (LEDs) and catalysts [22–26]. The calcium carbonate and aluminum oxide that used to synthesis of CaO-Al_2O_3 were large reserves, inexpensive and no environmental pollution. Among $CaO{\cdot}Al_2O_3$ family, the $Ca_3Al_2O_6$ crystallized is easy to form solid solution with metal oxides, due to $Pa\bar{3}$ is stable in space group [27]. However, the

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optical thermometry based on upconversion emissions has not been explored in $Ca_3Al_2O_6$ materials.

According to the crystal-field theory, the crystal field around Er^{3+} ions in hosts inevitably affects the emissions from the $^4S_{3/2}$ and $^4F_{9/2}$ excited states [28–30]. In some published works, the tuning of the upconversion emissions of Er^{3+} were realized by tailoring the crystal field around Er^{3+} ions. For examples, Liang et al. reported the Li^+ ions were add to Yb^{3+}/Er^{3+} codoped Y_2O_3 nano-crystals, and obtained the enhancement of the upconversion luminescence [31]. The lattice distortion of hosts is induced by dopant ions with small ionic radius and the crystal-field environment around Er^{3+} ions was affected strongly, which leads to increase in radiative transition probability from the excited state to the ground state of $^4I_{15/2}$ [32]. The $Ca_3Al_2O_6$ consists six different calcium sites, in which the site of Ca^{2+} has the high solubility with lanthanide ions [33]. The inner electric charge distribution of the $Ca_3Al_2O_6$ crystal nucleus can be modified by doping trivalent and divalent metal ions into the different Ca^{2+} sites. The optical temperature sensitivity of rare earth doped $Ca_3Al_2O_6$ solid solution will be also modified. It has sufficient space in the $Ca_3Al_2O_6$ framework to accommodate a certain amount of cations with different charges [34], which indicates that the luminescent property can be adjusted by doping metal ions in $Ca_3Al_2O_6$ system. In this paper, we study to modify the optical temperature sensitivity of $Ca_3Al_2O_6$:Yb^{3+}-Er^{3+} phosphors through co-doping with Ba^{2+}, Mg^{2+}, Y^{3+}, La^{3+} and Lu^{3+} and controlling excitation powers. The upconversion emission intensity and optical thermometry ability are greatly enhanced.

2. Experimental section

2.1. Material syntheses

All raw materials are $CaCO_3$ (AR), Al_2O_3 (99.99%), Yb_2O_3 (99.99%), Er_2O_3 (99.99%), BaO (AR), MgO (AR), Y_2O_3 (99.99%), La_2O_3 (99.99%), and Lu_2O_3 (99.99%). All the chemicals were used without any further purification. Using the solid-state reaction method to synthesize $Ca_3Al_2O_6$: Er^{3+}-Yb^{3+} and $Ca_3Al_2O_6$: Er^{3+}- Yb^{3+}-M^{n+} (M^{n+}=Ba^{2+}, Mg^{2+}, Y^{3+}, La^{3+} and Lu^{3+}) phosphors. The molar ratio of $Ca_3Al_2O_6$: Er^{3+}-Yb^{3+} sample is as follows: $12CaCO_3$-$7Al_2O_3$-$0.6Yb_2O_3$-$0.06Er_2O_3$. The molar ratios of $Ca_3Al_2O_6$: Yb^{3+}-Er^{3+}-M^{2+} samples are as follows: (12-x)$CaCO_3$- $7Al_2O_3$-$0.6Yb_2O_3$-$0.06Er_2O_3$-xMO, (M = Ba,Mg, x = 0.06, 0.12, 0.24, 0.36, 0.48, 0.6). The molar ratios of $Ca_3Al_2O_6$: Yb^{3+}-Er^{3+}-N^{3+} samples are as follows: (12-x) $CaCO_3$-$7Al_2O_3$-$0.6Yb_2O_3$-$0.06Er_2O_3$-yN_2O_3, (N=Y, La, Lu, y = 0.06, 0.12, 0.24, 0.36, 0.48, 0.6). The starting materials are entirely mixed and ground with alcohol for 1 h. The powder is subsequently sintered in a furnace for 12 h at 1350 °C. Finally, after cooling naturally, a series of samples for the white powder were obtained.

2.2. Characterization and optical measurements

The structures of the samples were studied by X-ray diffraction (XRD) using a X'TRA (Switzerland ARL) equipment equipped with Cu tube with K_α radiation at 1.54056 Å. The visible emissions were monitored using the Acton SpectraPro Sp-2300 Spectrophotometer with a photomultiplier tube equipped with 980 nm laser as the excitation sources. The different temperature spectra were monitored with the INSTEC HCS302 Hot and Cold System.

3. Results and discussion

Fig. 1 displays the XRD patterns of $Ca_3Al_2O_6$, the position and intensity of all diffraction peaks could be indexed to cubic $Ca_3Al_2O_6$ on account of the standard XRD pattern (JCPDS 38-1429), and no phase change occurs when Ba^{2+}, Mg^{2+}, Y^{3+}, La^{3+}, Lu^{3+} ions are doped into $Ca_3Al_2O_6$ respectively, which indicates that the $Ca_3Al_2O_6$ can be prepared by solid-state reaction method. Fig. 2 shows the unit cell of $Ca_3Al_2O_6$ and Ca^{2+} sites in the unit cell. The $Ca_3Al_2O_6$ unit cell contains 24 asymmetric units, and each one includes three Ca^{2+}, two Al^{3+} and six O^{2-}. There are six different Ca^{2+} sites in the lattice of $Ca_3Al_2O_6$. Ca3, Ca5 and Ca6 are all coordinated with six oxygen atoms forming distorted octahedral. While the Ca1, Ca2 and Ca4 are coordinated with 7, 8, and 9 oxygen atoms respectively [35]. It was reported that the effective ionic radius was dependent on the coordination numbers for the metal cation ions [36]. As for the Ca^{2+}, the effective ionic radiuses are $R_6 = 1.0$ Å, $R_7 = 1.06$ Å, $R_8 = 1.12$ Å, $R_9 = 1.18$ Å. The Yb^{3+} occupies the Ca4 site in the $Ca_3Al_2O_6$ lattice, due to the closer ionic radiuses between

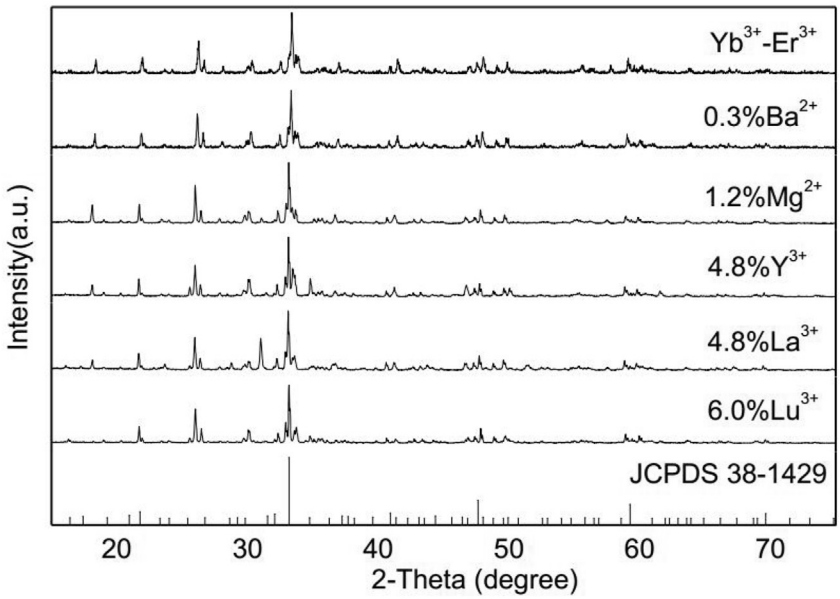

Fig. 1. XRD patterns of $Ca_3Al_2O_6$ doped with 6%Yb^{3+}-0.6%Er^{3+}, 6%Yb^{3+}-0.6%Er^{3+}-0.3%Ba^{2+}, 6%Yb^{3+}-0.6%Er^{3+}-1.2%Mg^{2+}, 6%Yb^{3+}-0.6%Er^{3+}-4.8%Y^{3+}, 6%Yb^{3+}-0.6% Er^{3+}-4.8%La^{3+} and 6%Yb^{3+}-0.6%Er^{3+}-6.0%Lu^{3+} and the JCPDS Card of $Ca_3Al_2O_6$ (38-1429).