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Novel single-component $CaLaAlO_4$:Tb^{3+}, Eu^{3+} phosphor for white light-emission

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ABSTRACT

Tb^{3+}/Eu^{3+} single and co-doped $CaLaAlO_4$ (CLA) phosphors were successfully prepared by solution combustion route. The luminescence properties of Tb^{3+} and Eu^{3+}, and the energy transfer (ET) from Tb^{3+} to Eu^{3+} were investigated. Microstructures are analyzed by X-ray diffraction and high-resolution scanning electron microscope (SEM) experiments. The sample shows single tetragonal structure. Under the excitation of 260 nm, CLA:Tb^{3+}, Eu^{3+} phosphors exhibited green emission corresponding to the f–f transition of Tb^{3+} ions and red emission bands corresponding to the f–f transition of Eu^{3+} ions, respectively. With appropriate tuning of the Tb^{3+}/Eu^{3+} ratio, tunable photoluminescence emission from blue-green to yellow and red is obtained in Tb^{3+} and Eu^{3+} co-doped CLA phosphors and emission spectrum covers the entire visible light region with comparable intensity, resulting in white emission. Moreover, the CLA:0.01 Tb^{3+}, 0.02Eu^{3+} assembly have Commission International del'Eclairage (CIE) chromaticity coordinates $x = 0.3277$ and $y = 0.3370$, which is close to the standard white-light color ($x = 0.333$ and $y = 0.333$), demonstrating its great potentials as single-component (single-phase) phosphors for white light emission. The maximum ET efficiency is found to be 63.77% for CLA:0.01 Tb^{3+}, 0.03Eu^{3+} phosphor.

1. Introduction

Phosphors that emit white light are imperative materials, which have been broadly applied in solid state lighting. The white light is a blended light of multicolor and perceived by human eyes as white light. There are two common approaches to white light generation: (i) blending three monochromatic sources (red, green and blue), or (ii) utilizing phosphors to convert UV or blue light into a mix of red, green and blue; or yellow and blue. In contrast, single-matrix phosphors can emit blue, green, and red lights that are potential white light sources because they offer greater luminescence efficiency and lower manufacturing costs compared to systems requiring multiple phosphors to accomplish the same effect [1]. Therefore, it is an urgent task to develop single-component (single-phase) phosphor that can produce white-light emission.

It is well-known that ET plays significant roles in the optical properties of luminescent materials both from theoretical and practical points of view. The generation of white light emission largely depends on the ET of excitation energy between RE ions. Furthermore, the ET from a large number of ion pairs has been investigated because of relatively bright room-temperature luminescence in the visible optical region. It is also known that the ET process might be affected by the presence of defects and/or carrier traps in the host lattice. Therefore, the trace co-dopant with different affinities has the potential to change the trap configuration and therefore to improve the efficiency significantly [2]. Tb^{3+}, frequently a green activator, has been investigated in detail in many hosts [3–5]. Additionally, it is clear that the Tb^{3+} acts as a good sensitizer to improve the luminescence efficiency of Eu^{3+} ions in $GdY(MoO_4)_3$ [6], $BiPO_4$ [7], $CaCO_3$ [8], $SrMg_2LaW_2O_{12}$ [9], $Ca_xSr_{1-x}Al_2O_4$ [10], $CaMoO_4$ [11], and Y_2O_3 [12] phosphors. Thus, the Tb^{3+} and Eu^{3+} ions could be used as efficient luminescent centers in practical devices.

$CaLaAlO_4$ (CLA) belongs to a wide family of compounds with general formula $ABCO_4$ (where A = Ca or alkaline earth divalent cation, B = La, Y or trivalent RE ion and C = Al, Ga or trivalent transition-metal cation). These types of materials crystallize in a perovskite-like phase with the tetragonal K_2NiF_4 structure [13,14]. Its crystal structure consists of interleaved layers with perovskite and rock-salt structure. The divalent A and trivalent B cations reside in nine fold coordinated sites with distorted C_{4v} symmetry due to the random occupation of neighboring sites by A^{2+} and B^{3+} ions. These complex oxides ($ABCO_4$) are versatile compounds which, when doped with different transition

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elements, result in materials with remarkable electric, magnetic [15], optical [16], and infrared [17] properties. Such types of materials doped with various transition-metal ions or RE ions are studied as laser materials [18,19]. Although there are some reports on the $CaYAlO_4:Tb^{3+}/Eu^{3+}$ [20], $CaYAlO_4:Tb^{3+}/Sm^{3+}$ [21], $SrLaAlO_4:Ho^{3+}/Er^{3+}$ [22], $LaCaAlO_4:Fe^{3+}$ [23], etc. To the best of our knowledge, Tb^{3+} and Eu^{3+} co-doped CLA phosphor for white light emission was not realized yet.

In this paper, the efficient ET from Tb^{3+} to Eu^{3+} in CLA compound was systematically investigated by the photoluminescence spectra and ET efficiency. It is found that the CLA: Eu^{3+} phosphor will have potential applications for w-LEDs as red phosphor and CLA: Tb^{3+}, Eu^{3+} codoped phosphor will have great potential as single-component (single-phase) phosphor for white-light emission.

2. Experimental procedures

2.1. Materials and synthesis

In this study, the solution combustion route by using urea has been employed for the synthesis of RE (RE = Tb^{3+} and Eu^{3+}) doped CLA phosphors. The starting materials for the sample preparation were Calcium nitrate [$Ca(NO_3)_2.4H_2O$], Lanthanum nitrate [$La(NO_3)_3.6H_2O$], Aluminum nitrate [$Al(NO_3)_2.9H_2O$], Europium oxide [Eu_2O_3], Terbium oxide [Tb_4O_7], and Urea [$CO(NH_2)_2$], all in analytical purity. All starting materials were weighed according to the desired stoichiometry. Nitrate form of RE were first obtained by dissolving the oxide form of corresponding RE into diluted nitric acid and warming these solutions at 50–60 °C for 10–15 min.

For each phosphor stoichiometric amounts of the nitrate precursors and urea were mixed and dissolved in minimum amount of doubly distilled water. This mixture kept onto a magnetic stirrer for 10–20 min at 80–100 °C to get uniform mixing and evaporation of water to form gel of precursors, and then the resulting gel was kept into a muffle furnace at an initiating combustion temperature of 500 ± 20 °C for the burning process. After all the liquid had evaporated, the reagents decomposed and released huge amounts of gases (oxides of nitrogen and ammonia). Due to the exothermic nature of this process, a huge amount of heat released, resulted in a flame that decomposed the reactants further with the evolution of large amount of gases. The flame lasted for nearly 60 s and the combustion process was completed within 5 min. As soon as the reaction was completed, the resulting white foamy and voluminous combustion products were cooled down to room temperature and were ground gently using a pestle mortar to get a fine powder. As-prepared samples were annealed at 900 °C for 2 h to improve its crystallinity. Then these samples were characterized.

2.2. Characterization methods

Phase and crystallinity of the prepared material were checked by a powder XRD pattern using PAN-analytical diffractometer with monochromatic Cu target radiation source ($\lambda = 1.54$ Å) operating at 40 kV, 30 mA in the 2θ range 10–80°. Powder morphology was studied using SEM at STIC, Kochi, India, (JEOL JSM-6390LV). Photoluminescence excitation and emission spectra of the prepared samples were recorded using a Shimadzu Spectrofluorophotometer (RF-5301 PC). All the measurements were performed at ambient temperature.

3. Results and discussion

3.1. Phase purity and morphology

The phase structure of the as-prepared powder sample was identified by XRD. The XRD pattern of 0.01 Tb^{3+}/0.02Eu^{3+} codoped CLA sample together with the JCPDS card no. 24–0206 are shown in Fig. 1. XRD pattern of prepared sample is well matched with standard data. It is obvious that this pattern can be basically indexed to the standard data for $CaLaAlO_4$ (JCPDS card no. 24–0206), revealing that the co-doped 0.01 Tb^{3+}/0.02Eu^{3+} ions did not causes any impurity or induce major changes in the host structure.

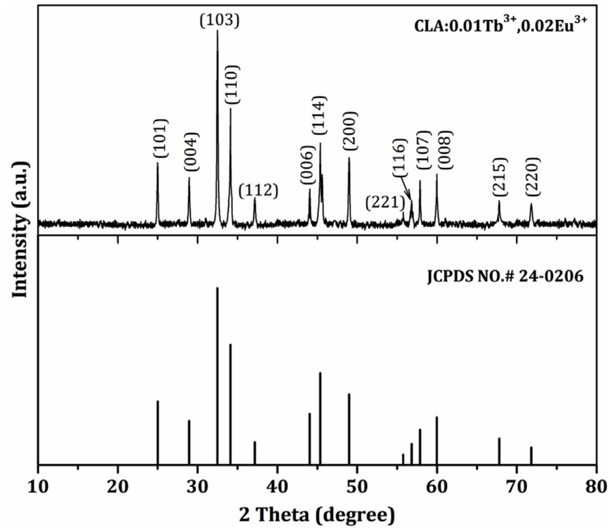

Fig. 1. XRD pattern of as-prepared CLA: 0.01 Tb^{3+}, 0.02Eu^{3+} phosphor and along with standard JCPDS card no. 24–0206.

Crystallinity, particle size and surface roughness of the prepared powder have strong effects on the photoluminescence. The surface morphology of the as-synthesized powder made via solution combustion synthesis is characterized by SEM. Fig. 2 exhibits the surface morphology of 0.01 Tb^{3+}/0.02Eu^{3+} codoped CLA phosphor. The micrographs show agglomerated, irregular shaped and sized particles. This irregularity of shape and size can be assigned to the irregular distribution of temperature and mass flow in the combustion process. The average grain size found to be about 200 nm.

3.2. Crystal structure

Fig. 3 shows the crystal structure of tetragonal $CaLaAlO_4$ (CLA) with space group *I4/mmm* (139). The lattice constants are a = b = 3.716 Å and c = 12.33 Å. There are two oxygen sites labeled by O(I) and O(II). The O(I) and Al atoms are positioned on the basal plane perpendicular to the *c* axis, forming short Al–O(I) bonds. The O(II) is located at the apical position of the AlO_6 octahedra, forming a long Al–O(II) bond. The distances Al–O(I) and Al–O(II) are 1.849 and 1.858 Å respectively [14,24], where O(I) and O(II) are the nearest and next-nearest O^{2-} ions to an Al^{3+} ion. Short-range ordering was found in this crystal [25], indicating predominantly disordered distribution of cation pairs formed by Ca^{2+} and La^{3+} ions. These pairs form different casual configurations, leading to a fluctuating crystal field at the Al^{3+} site. On the other hand, all cations are not bound into pairs, and there is still expected statistical fluctuation of the Ca^{2+}/La^{3+} ratio inside the crystal, since the Ca^{2+} and La^{3+} ions do not occupy regular positions in the lattice. The Ca^{2+}/La^{3+} ions are surrounded by nine nearest-neighbor oxygen ligand ions with C_{4v} symmetry. Site occupancy is expected to be determined mostly by considerations of ionic size. In consequence, Eu^{3+} or Tb^{3+} ions are expected to preferentially occupy Ca^{2+}/La^{3+} sites because the radius of Eu^{3+} (1.12 Å) and Tb^{3+} (1.095 Å) are closer to those of Ca^{2+} (1.18 Å) and La^{3+} (1.216 Å), and much larger than that of Al^{3+} (0.535 Å). In addition, the similar valency is the other advantageous factor to determine the site occupancy, which makes the La^{3+} ions in the CLA host preferentially be replaced by Eu^{3+} and Tb^{3+} ions.