Journal of Luminescence 152 (2014) 176–181

Contents lists available at ScienceDirect

Journal of Luminescence

journal homepage: www.elsevier.com/locate/jlumin

Full-color-emitting $CaYAl_3O_7:Pr^{3+},Ce^{3+}$ phosphor for near-UV LED-based white light

Sanjith Unithrattil [a], Kyoung Hwa Lee [a], Woon Jin Chung [b], Won Bin Im [a,*]

[a] School of Materials Science and Engineering, Chonnam National University, 300 Yongbong-dong, Buk-gu, Gwangju 500-757, Republic of Korea
[b] Institute for Rare Metals & Division of Advanced Materials Engineering, Kongju National University, Cheonan, Chungnam 330-717, Republic of Korea

ARTICLE INFO

Available online 15 November 2013

Keywords:
Solid-state lighting
Photoluminescence
Full-color emission
Rietveld refinement
Maximum entropy method

ABSTRACT

A full-color-emitting phosphor, $CaYAl_3O_7:Pr^{3+},Ce^{3+}$ was synthesized through conventional solid-state reaction. The structural properties of the phosphor were analyzed by Rietveld refinement, maximum entropy method, and luminescent properties were analyzed by co-activating with different rare earth ions. Photoluminescence spectra on excitation with 450 nm source were dominated by green band at 490 nm originating from $^3P_0 \rightarrow {}^3H_4$ transition of Pr^{3+} ions and less intense band at 617 nm due to $^1D_2 \rightarrow {}^3H_4$ transition. On codoping with Ce^{3+}, phosphor exhibits an additional broad band originating from $5d^1 \rightarrow 4f^1$ ($^2F_{7/2}$ and $^2F_{5/2}$) of Ce^{3+}, centered at around 540 nm due to efficient energy transfer from Pr^{3+} levels to Ce^{3+} levels. With this emission property we recommend $CaYAl_3O_7:Pr^{3+},Ce^{3+}$ as potential single-phase full-color-emitting phosphor for solid-state lighting applications.

1. Introduction

White LEDs based on the combination of a blue-emitting LED chip with broad band emitting yellow phosphor has been extensively used as a source of illumination over past several years [1,2]. The search for an ideal phosphor for the purpose has not reached anywhere beyond the $Y_3Al_5O_{12}:Ce^{3+}$ (YAG) phosphor, primarily due to its unparalleled efficiency. However the phosphor which has relatively weak emission in the red spectral region yields poor color rendering index, in combination with blue LEDs [3]. In order to improve the color rendering index of the combination, YAG phosphor in combination with red emitting phosphors was attempted [3,4]. These types of LEDs offer superior color uniformity, high color rendering index, but luminous efficacy of these white LEDs is low due to reabsorption of emission colors. As a solution of these, a single phased full-color emitting phosphors have been proposed [5–8].

Single phased full-color-emitting phosphors, by nullifying the chance for reabsorption of the light emitted by the blue, green or red phosphors improve the efficacy of the system. The most common strategy to develop such a phosphor is by codoping with suitable ions and utilizing the energy transfer from activators to coactivators [5,9]. However host compounds which can emit full-color spectrum when doped with specific activator ions are few in number. Among the full-color emitting phosphors, singly doped full-color-emitting phosphors are the most preferred ones as the energy loss in such phosphors could be the lowest possible, by avoiding the loss associated with inter-ionic energy transfer even though only very few host compounds are suitable for such kind of phosphors.

In this study, we have developed a single phased full-color-emitting phosphor, $Ca_{1-x-y}Pr_xM_yYAl_3O_7$ and investigated its structure and feasibility of emission with higher color rendering index. By coactivating $Ca_{1-x-y}Pr_xM_yYAl_3O_7$ with few broad band emitting ions M (M = Ce^{3+}, Tb^{3+}, Mn^{2+}) we have described its structure and optical properties in view of application in solid state lighting devices.

2. Experimental procedure

The $CaY_{1-x}Pr_xAl_3O_7$ phosphor was synthesized by conventional solid-state reaction method. The starting materials were $CaCO_3$ (Aldrich, 99.99%), Y_2O_3 (Aldrich, 99.99%), α-Al_2O_3 (Kojundo, 99.99%), Pr_6O_{11} (Aldrich, 99.99%), Tb_4O_7 (Aldrich, 99.99%) and MnO_2 (Aldrich, 99.99%). Raw materials in stoichiometric ratios were mixed using an agate mortar and pestle for about 1 h, with acetone as the dispersing medium. The dried mixture was then heated at various temperatures, ranging from 1300 to 1500 °C for 4 h in air at a heating rate of 5 °C min^{-1}. The compounds were then reduced by refiring at the same temperature in a reducing atmosphere of 5% H_2/N_2 gas. Finally the phosphor samples were prepared by pulverizing the product after naturally cooling down to room temperature.

Structural analysis of the samples was carried out using neutron diffraction data (HANARO Center, Korea Atomic Energy Research Institute, Korea) measured over an angular range

* Corresponding author. Tel.: +82 62 530 1715; fax: +82 62 530 1699.
E-mail address: imwonbin@jnu.ac.kr (W.B. Im).

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http://dx.doi.org/10.1016/j.jlumin.2013.11.039

$10^\circ \leq 2\theta \leq 100^\circ$, and was analyzed using General Structure Analysis System (GSAS) program [10]. Nuclear density of CYA phosphor, was analyzed using the maximum entropy method (MEM) based on the structural factors obtained from Rietveld refinement. The MEM analysis was carried out in $128 \times 128 \times 128$ pixels per lattice parameter using the program package (PRIMA) for neutron density distribution calculation by the MEM [11].

Luminescence properties were investigated using room temperature photoluminescence (PL) spectra measured on a Hitachi F-4500 fluorescence spectrophotometer over the wavelength range of 200–750 nm. Diffuse reflectance absorption spectra were recorded using a Thermo Scientific Evolution 220 UV–visible spectrophotometer in the wavelength range of 220–600 nm.

3. Results and discussion

Unit cell representation of $CaYAl_3O_7$ (CYA) crystal, which structurally belongs to the melilite structure group (tetragonal, $P\bar{4}2_1m$, S.G. # 113)[12] is shown in Fig. 1. The melilite group is composed of minerals which were widely investigated as laser materials and phosphors. These compounds have a general formula ABC_3O_7, where A is Ca, Sr, and Ba; B is La and Gd, Y; and C is Al and Ga. In the unit cell ($Z=2$) of CYA, Pr and Y atoms occupy only the 4e positions. Half of the 4e sites are expected to be filled by Ca atoms, and the other half by Y/Pr atoms. Ca/Y sites corresponding to polyhedra with 8-coordinations are likely to be substituted by Pr^{3+} ions. Al atoms occupy the 2a and 4e sites of the cell. Oxygen atoms distributed over the 2c, 4e, and 8f sites, are denoted as O(1), O(2), and O(3), respectively. Ca^{2+}/Y^{3+} ions are placed at the centers of the five-membered AlO_4^{5-} tetrahedra rings with unit linked at each corner. CYA consists of alternate cationic $(Ca/Y)_2$ and corner-sharing tetrahedral anionic Al_3O_7 layers, and features five-fold tunnels that accommodate the eight-coordinate Ca^{2+}/Y^{3+} as chains of cations, as shown in Fig. 1(b).

Rietveld refinement of $CaY_{0.7}Pr_{0.3}Al_3O_7$ structure using the neutron diffraction data is shown in Fig. 2. The profile R-factor, R_{wp} was 6.13% and the goodness-of-fit parameter (χ^2) was 4.74. No impurity phases were identified in the samples, irrespective of Pr^{3+} component. The unit cell parameters are a, $b=7.697(1)$ Å and $c=5.055(1)$ Å as listed in Table 1. Refined structural parameters of the $CaY_{0.7}Pr_{0.3}Al_3O_7$ crystals obtained from the structural refinement are tabulated in Table 2.

Maximum entropy method (MEM) is often considered as one of the versatile method to analyze the local structure of a crystal [13,14]. It has been reported that MEM analysis has many advantages in obtaining additional structural information from the diffraction data, independent of the structural model [15,16]. The local structure of the $CaY_{0.7}Pr_{0.3}Al_3O_7$ phosphor was investigated by the maximum entropy method using neutron diffraction pattern. The structural factors obtained from the Rietveld refinement was used as initial structural factors. The MEM analysis was carried out in $128 \times 128 \times 128$ pixels per lattice parameter. The final converged reliability factor (R_{WF}) was 1.68% for the $CaY_{0.7}Pr_{0.3}Al_3O_7$ powder sample, which was used to determine the nuclear densities of the constituent atoms. The final reliable R factors of MEM density is defined as

$$R_{WF} = \sqrt{\frac{\sum 1/\sigma^2 |F_0 - F_{MEM}|}{\sum 1/\sigma^2 |F_0|}} \quad (1)$$

where F_0 is the observed structure factor, σ is their estimated standard deviation, F_{MEM} is a structure factor estimated by the MEM analysis, and the summation is conducted over the reflections analyzed by the method.

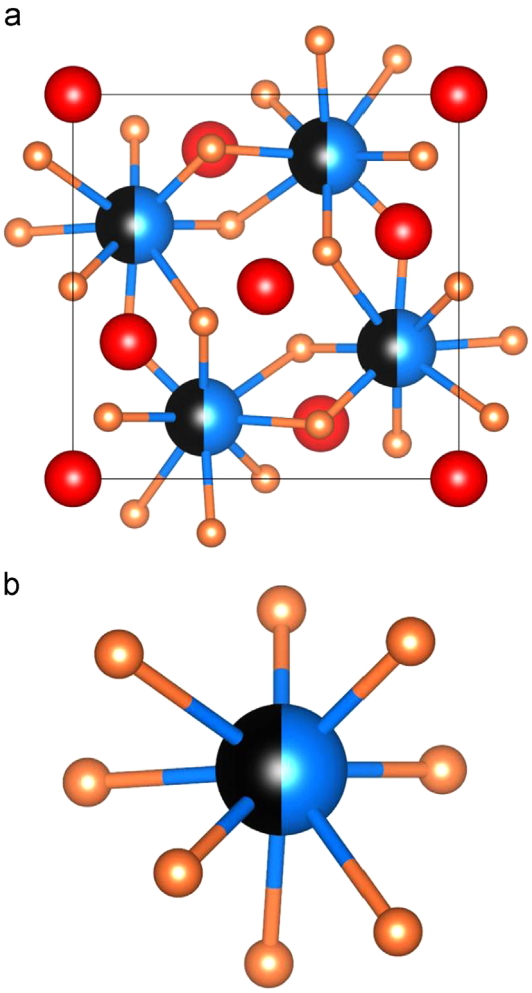

Fig. 1. (a) Unit cell representation of the crystal structure of $CaYAl_3O_7$ (CYA). Blue, black, red, and orange spheres represent Ca, Y, Al, and O atoms respectively. (b) Coordination geometry of $(Ca/Y)O_8$ is depicted. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

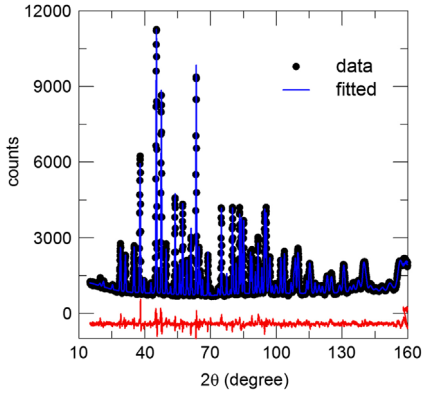

Fig. 2. Rietveld refinement of the neutron diffraction profile of $CaY_{0.7}Pr_{0.3}Al_3O_7$. Data (points) and fit (lines), the difference profile.

Nuclear density distribution of CYA:Pr^{3+} in the (2 0 0) plane shows the strong delocalization of the $Ca^{2+}/Y^{3+}/Pr^{3+}$ nucleus. The unit cell representation of the CYA:Pr^{3+} with a nuclear isosurface image is shown in Fig. 3(a) and the corresponding contour map depicting nuclear density along the (0 0 2) plane obtained by the MEM, is shown in Fig. 3(b). In the unit cell, the $Ca^{2+}/Y^{3+}/Pr^{3+}$ ions are randomly distributed on the 4e sites, with divalent and trivalent ions. Consequently, a number of antisite