Journal of Luminescence 192 (2017) 218–223

Contents lists available at ScienceDirect

Journal of Luminescence

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

Crystal structure characterization and up-conversion luminescent properties of $BaIn_2O_4$ phosphor

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ARTICLE INFO

Keywords:
Crystal structure
Up-conversion
$BaIn_2O_4$

ABSTRACT

Er^{3+} / Yb^{3+} doped $BaIn_2O_4$ up-conversion (UC) phosphors are synthesized and their UC luminescent properties are characterized. $BaIn_2O_4$ has *P*21/*c* space group but Rietveld refinement suggests it has twice smaller cell parameter (a = 10.3975 Å, *b* = 5.8295 Å, *c* = 14.4457 Å) and volume than previous reported structure. Refinement also reveals Er^{3+}/Yb^{3+} replaces In^{3+} ions in lattice because of the existence of InO_6 octahedra. In these $BaIn_2O_4$ phosphors, co-doping with Yb^{3+} ions changes the predominant UC emission from green ($^2H_{11/2}$, $^4S_{3/2}$ → $^4I_{15/2}$ of Er^{3+}) to red (about 665 nm, $^4F_{9/2}$ → $^4I_{15/2}$ of Er^{3+}). By controlling of Er^{3+}/Yb^{3+} concentrations, the $BaIn_2O_4$ phosphors have the potential of generating various UC spectra and color tunability. The pumping powers study shows two-photon process in these phosphors.

1. Introduction

Up-conversion (UC) phosphors have drawn lots of attentions recently due to their significant potential applications in light emitting displays, solid state lighting and biological labeling [1–3]. As spectral modification materials, UC phosphors show importance for converting photons with low energy to those of high energy by "merging" low energy photons [4–6]. Though fluoride-based compounds are considered as the most excellent UC phosphors due to their low phonon energy, oxide-based UC phosphors which have relative low phonon energy such as Y_2O_3 and Gd_2O_3 also are widely studied [7,8]. Nowadays highly efficient oxide UC phosphors are still demanded because they not only show good UC luminescent properties but also exhibit high chemical stability. Moreover, they always are easy to synthesize. Alkaline earth ions (Ca^{2+}, Sr^{2+}, and Ba^{2+}) have close ionic radius to lanthanide ions, inorganic compounds containing these ions are frequently used as UC host materials [9–11].

Kalinina et al. [12] established the phase diagram for BaO-In_2O_3 system previously, however the structure of $BaIn_2O_4$ still have some mysteries [12,13]. As a oxide compound, $BaIn_2O_4$ has good mechanical durability, chemical and thermal properties. As a semiconducting compound, $BaIn_2O_4$ demonstrates large potential as UC oxide-based host. Previous reports showed the possible space group of *P*21/*a* (ICSD #202986) for $BaIn_2O_4$ [14–16], means the crystallographic sites of In^{3+} ions in distorted InO_6 octahedra can be substituted by lanthanide ions such as Er^{3+} and Yb^{3+} [17–19]. As well known, Er^{3+} is important UC active ions which can emit green or red light [20–22], and Yb^{3+} is good sensitive ions due to its strong absorption in the near-infrared light region [23,24]. Therefor whether Er^{3+} and Yb^{3+} ions doped $BaIn_2O_4$ UC phosphors have low phonon energy and good UC luminescent properties is deserved to study. In this work, green and red emitting Er^{3+}/Yb^{3+} doped $BaIn_2O_4$ phosphors were synthesized. Crystal structure characterization as well as UC luminescent properties of these Er^{3+}/Yb^{3+} doped $BaIn_2O_4$ were studied in detail. The findings contribute to the complement of indate-based and oxide-based UC phosphors system, more importantly, open the possibility of Er^{3+}/Yb^{3+} doped $BaIn_2O_4$ as novel phosphors which can generate various UC spectra and color tunability.

2. Experimental

2.1. Sample preparation

Samples were prepared via solid-state reaction method. In a typical synthesis procedure, raw materials of $BaCO_3$(A.R.), In_2O_3(99.995%), Er_2O_3 (99.995%), Yb_2O_3(99.995%) were weighted according to

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http://dx.doi.org/10.1016/j.jlumin.2017.06.034
Received 28 November 2016; Received in revised form 1 May 2017; Accepted 17 June 2017
Available online 19 June 2017

stoichiometric ratio, and then mixed and ground thoroughly in an agate mortar. After that, the mixtures were transferred into alumina crucibles and sintered in muffle furnaces with different temperatures (1100–1500 °C, see Fig. S1). After these samples were cooled down to room temperature naturally, the resulted phosphors were fully ground again for the following measurements.

2.2. Characterization

The X-ray powder diffractometer (D8 Advance, Bruker Corporation, Germany, with Cu-Kα and linear VANTEC detector, λ = 0.15406 nm, 40 kV, 100 mA) was used for examine the crystal structure. Rietveld refinement was performed by using TOPAS 4.2 program. Raman spectra were collected using Raman Microscope (Horiba Jobin Yvon). Excitation wavelength was 633 nm with actual power of 46.0 μW. The UC luminescent spectra of the phosphors were recorded on a spectrophotometer (F-4600, Hitachi high technologies corporation, Tokyo, Japan) with an external power-controllable 980 nm semiconductor laser (Beijing Viasho Technology Company, Beijing, China) as the excitation source. The diffuse reflection spectra were measured on a UV-VIS-NIR spectrophotometer (Shimadzu UV-3600, Japan) attached to an integral sphere. All the tests were accomplished at room temperature.

3. Results and discussion

3.1. Crystal structure characterizations

Powder XRD Rietveld refinement was adopted to clarify the structure mysteries of these $BaIn_2O_4$ UC phosphors. First of all, crystal structure $BaIn_2O_4$ was solved previously in $P21/a$ space group and it was further transformed into space group $P21/c$ to get standard settings [25]. This structure was used as starting model for present Rietveld refinement which ended at R_B = 3.72% (Fig. 1a,b). Final crystal structure was checked by PLATON and by the internet service of IUCr which showed that there is nonspacegroup translation $a/2$. Therefore programs strongly recommended to halve cell parameter a, and to use new crystal structure with the same space group $P21/c$. New refinement ended at lower R_B = 3.49% and accounts the same peaks on the pattern by using twice less number of peaks (Fig. 1c). Difference Rietveld plots of both model look very similar (Fig. 1a,c), but new suggested model has twice smaller cell parameter and volume (Fig. 1b,d), twice smaller number of refinement parameters and it can be concluded that new model is better. There are two Ba^{2+} ions, four In^{3+} ions and eight O^{2-} ions in asymmetric part of new unit cell and this structure was determined as $P21/c$ space group (a = 10.3975 Å, b = 5.8295 Å, c = 14.4457 Å). It is important to note that some very small peaks at ~ 22 2θ° cannot be fitted and this is because Renninger-effect leads to the appearance of some weak peaks due to multiple diffractions from different planes inside of crystal [26,27].

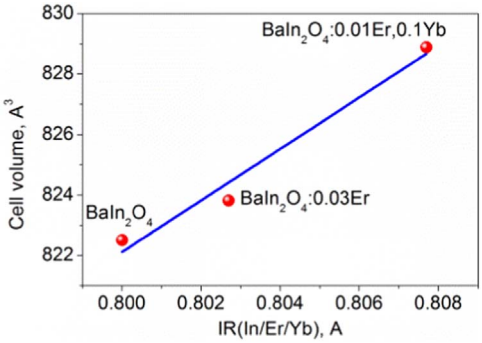

Fig. 2. Linear cell volume increasing per average ion radii IR(In/Er/Yb).

This solved model was used to make structure refinement of single Er^{3+} (0.03) doped and Er^{3+}/Yb^{3+} (0.01 / 0.1) co-doped $BaIn_2O_4$ phosphors. Linear increasing of cell volume per increasing concentration of doping elements (Fig. 2) proved the replacement of In^{3+} ions with small ion radii IR(In^{3+}, CN = 6) = 0.8 Å by bigger Er^{3+} and Yb^{3+} ions with IR(Er^{3+}, CN = 6) = 0.89 Å and IR(Yb^{3+}, CN = 6) = 0.868 Å, respectively. Therefore in models the sites of In^{3+} ion were occupied by random In^{3+} / Er^{3+} / Yb^{3+} ions with fixed occupations according to suggested chemical formulas (if Ba^{2+} were replaced, cell

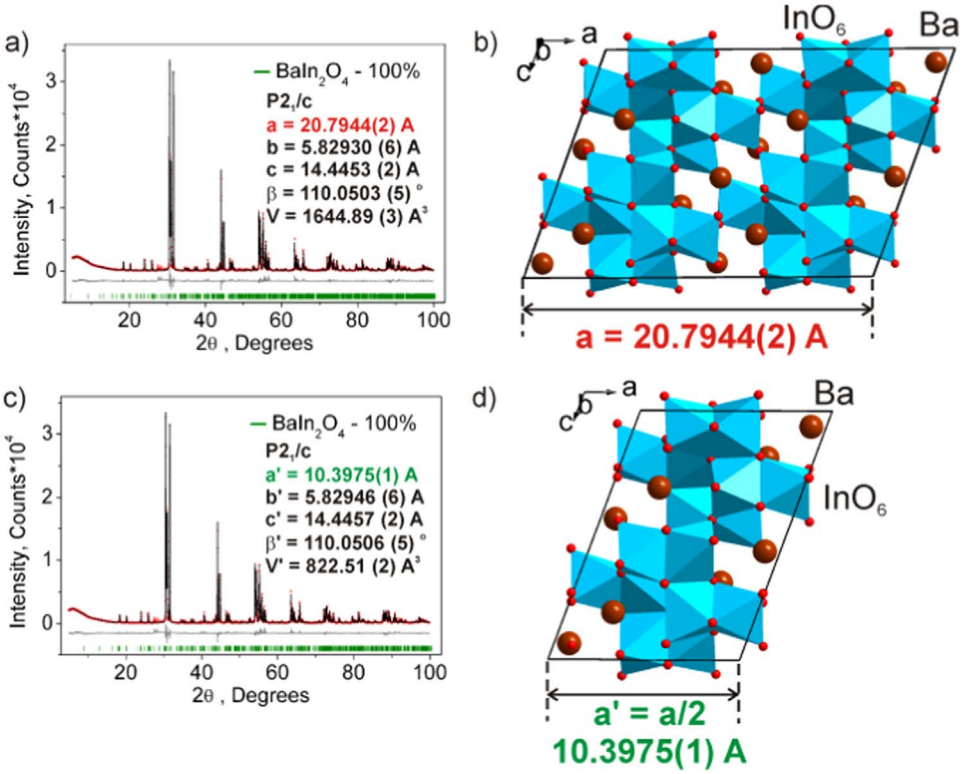

Fig. 1. XRD patterns and Rietveld plots of initial model (a) and new suggested model (c), and comparison initial crystal structure of $BaIn_2O_4$ (b) with new proposed structure (d).