



## Invited Article

Effect of Eu-doping on optical, structural and morphological properties of  $\text{BaI}_2 \cdot n\text{H}_2\text{O}$  powdersT. Salamakha <sup>a,\*</sup>, M. Buryi <sup>b</sup>, Y. Tratsiak <sup>a</sup><sup>a</sup> Research Institute for Physical Chemical Problems, Belarusian State University, Leningradskaya Str. 14, Minsk, Belarus<sup>b</sup> Institute of Physics of the Czech Academy of Science, Cukrovarnická 10/112, Prague, Czechia

## ARTICLE INFO

## Article history:

Received 29 December 2017

Received in revised form

5 February 2018

Accepted 19 February 2018

## Keywords:

Luminescence

EPR

 $\text{Eu}^{2+}$ 

Powders

Barium iodide

Scintillators

## ABSTRACT

The two-step approach to the  $\text{Eu}^{2+}$  doped  $\text{BaI}_2 \cdot n\text{H}_2\text{O}$  powders synthesis in Ar atmosphere from precursors containing different concentration of  $\text{Eu}^{3+}$  ions is reported. According to X-ray diffraction analysis the powders mainly consist of  $\text{BaI}_2 \cdot 2\text{H}_2\text{O}$  phase. Their morphological, structural and luminescent properties depend on the Eu-ions concentration. The luminescence spectra are composed of broad and strong emission band peaking at 420 nm, which was related to the  $\text{Eu}^{2+}$  5d–4f transition. Its intensity reaches maximum in the 2 at. %  $\text{Eu}^{2+}$  doped sample. Detailed analysis of the measured electron paramagnetic resonance spectra in the samples with different doping level confirms them belong to the  $\text{Eu}^{2+}$  ions substituting for the regular  $\text{Ba}^{2+}$  site in the  $\text{BaI}_2$  lattice. A sample exposed to the 330 nm UV irradiation exhibited an increase of the  $\text{Eu}^{2+}$  spectral intensity occurred exclusively due to the  $\text{Eu}^{3+}$  to  $\text{Eu}^{2+}$  transformation. No other signals either prior to or after the irradiation which might be attributed to the ions resided in e.g., interstitial positions or in any secondary phases were observed. Possible mechanisms of the  $\text{Eu}^{3+}$  stabilization in the host lattice with only divalent cation sites during the synthesis without additional treatment in reducing atmosphere are discussed as well.

© 2018 Elsevier B.V. All rights reserved.

## 1. Introduction

Scintillators are widely used in a variety of practical applications such as medical diagnostics, geological exploration, national security, high-energy physics, etc [1–3]. Rare-earth activated iodides of alkaline earth elements have been considered as attractive scintillation materials for quite a long time. Despite the potential scintillators application mentioned in the past century, they were not implied in practice due to low light yield and poor energy resolution. The interest in these compounds was renewed in the last decades when scintillators based on  $\text{SrI}_2:\text{Eu}$ ,  $\text{CaI}_2:\text{Eu}$  and  $\text{BaI}_2:\text{Eu}$  reached the 120000 photons/MeV, 110000 photons/MeV and 40000 photons/MeV light yield, respectively, with 3%, 8% and 8% energy resolution at 662 keV [4,5]. Even though these scintillators had several disadvantages, for instance, low  $Z_{\text{eff}}$  of  $\text{CaI}_2:\text{Eu}$ .  $\text{BaI}_2:\text{Eu}$  requires additional preliminary preparation of the raw materials [6]. However, namely the  $\text{BaI}_2:\text{Eu}$  among the whole family of alkaline-earth iodides is a promising material as a scintillator due to the highest  $Z_{\text{eff}}$  (54.1) [7] and the narrowest bandgap (3.2–5.0 eV

[7–11].

In the past tens of years, significant improvement in scintillators performance was achieved, first of all, due to the evolution of technologies for very pure raw materials (including low  $\text{H}_2\text{O}$  content, typically 100 ppm [12,13]) preparation and single crystals growth. The alkaline earth iodides exhibit structural anisotropy, which makes their large single crystals preparation problematic [14]. Transparent ceramics or glass ceramics are currently considered as the alternative to the single crystals, since structural anisotropy affects the preparation of such materials only to a limited extent [1]. However, in case of the transparent ceramics the search for powder compacting and sintering optimal conditions may require as great efforts as growing a single crystal. From this point of view, the preparation of glass ceramics based on alkaline-earth metals iodides seems to be the most attractive route to highly efficient scintillators. Glass-ceramics combines the glass transparency with the crystals efficiency (although still inferior) at a sufficiently lower production cost compare to the single crystals or ceramics [1]. It should be also noted that the glass matrix of the glass ceramics also protects iodide particles from environment [1,15,16]. Nevertheless, high requirements are imposed not only on the technical aspects of the production process but also on the

\* Corresponding author.

E-mail address: [solomakha.tanja@gmail.com](mailto:solomakha.tanja@gmail.com) (T. Salamakha).

quality of raw materials irrespectively of the material type (single crystals, ceramics, or glass-ceramics). It is noteworthy that powders are generally used as starting components in all cases. Thus, the development of the powder materials synthesis procedures and investigation of the synthesis conditions influence on the structure, morphology and luminescence of the powders to obtain the final product with desired properties are of great importance. Among the variety of different powders preparation methods the colloid chemistry one (sol-gel or co-precipitation) is the most flexible and promising [17,18]. However, since alkaline-earth iodides are hygroscopic, their issuance in aqueous solutions in the form of fine powders is challenging whereas precursors are more perspective [19]. This opens a number of advantages with respect to the method and conditions of the precursor synthesis. Using colloid-chemical approach the morphological, structural and luminescent properties of alkaline-earth iodides can be varied in a wide range [20,21]. Moreover, an activator addition at this point allows to reach its uniform distribution.

Therefore, the aim of the present work is to study the influence of the  $\text{Eu}^{2+}$  ions content on the  $\text{BaI}_2:\text{Eu}$  powders structural, morphological and luminescent properties. The samples were prepared employing the two-step approach involving the precursor powders preparation with co-precipitation method. The europium ions distribution and incorporation in the crystalline lattice were examined by electron paramagnetic resonance (EPR).

## 2. Experimental techniques

$\text{Ba}(\text{NO}_3)_2$ ,  $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{NH}_4\text{HCO}_3$  and  $\text{NH}_4\text{I}$  were used as starting materials. All reagents were of analytical grade.  $\text{BaI}_2:\text{Eu}$  was prepared in 2 stages: the first stage involved the synthesis of  $\text{BaCO}_3:\text{Eu}$  that was converted into  $\text{BaI}_2:\text{Eu}$  in the second stage [22].

**Precursor synthesis.**  $\text{BaCO}_3:\text{Eu}$  powder was obtained by a reverse precipitation. At first the required quantity of 0.1 M  $\text{Eu}(\text{NO}_3)_3$  solution was added into the acidified 0.25 M  $\text{Ba}(\text{NO}_3)_2$  solution.  $\text{Eu}(\text{NO}_3)_3$  was added in the amount corresponding to 0, 0.1, 0.5, 1, 1.5, 2, 3, 4 and 5 at. % of  $\text{Ba}^{2+}$  ions. The obtained mixture of nitrates was then added dropwise into 1.2 M solution of  $\text{NH}_4\text{HCO}_3$  under constant stirring. The resulting  $\text{BaCO}_3:\text{Eu}^{3+}$  precipitate was isolated by centrifugation, washed 2 times with distilled water and dried in air at  $80^\circ\text{C}$  for 12 h.

**$\text{BaI}_2:\text{Eu}$  synthesis.** The stoichiometric mixture of  $\text{BaCO}_3:\text{Eu}^{3+}$  and  $\text{NH}_4\text{I}$  powders was deposited in the agate mortar and transferred into a quartz crucible. Then it was placed into a quartz tube that was flushed afterwards with argon for 10 min. Keeping the stable argon flow the quartz tube was moved to a tube furnace preheated up to  $400^\circ\text{C}$  and held there for 30 min. After that samples were allowed to cool to the room temperature in a quartz tube under the argon flow. Obtained  $\text{BaI}_2:\text{Eu}$  powders of light-gray color were transferred into a container that was then tightly sealed. Short names of the samples corresponding to Eu-ions concentration are listed in Table 1.

### Characterization

X-ray diffraction patterns of the synthesized samples were collected on a «DRON – 3.0» X-ray diffractometer with  $\text{CoK}\alpha$  radiation in the  $2\theta$  range of  $15\text{--}65^\circ$ . Analysis of X-ray diffraction patterns and calculation of unit-cell parameters were conducted using

**Table 1**

Short names of the obtained samples depending on the amount of  $\text{Eu}^{3+}$  ions used in the synthesis.

Sample	1	2	3	4	5	6	7	8	9
$\text{Eu}^{3+}$ , at. %	0	0.1	0.5	1	1.5	2	3	4	5

WinPLOTR-2006 and DICVOL06 programs of the FullPROF pack.

The morphology and particle size of powders were evaluated by scanning electron microscopy (SEM) on a LEO–1420.

Room temperature optical absorption spectra were recorded using HR 2000 + spectrometer (Ocean Optics) equipped with Ocean Optics DH 2000 white light source. For collecting absorption spectra equal quantities of the samples were dispersed in immersion silicone oil. The thickness of the solution layer was the same for all measurements.

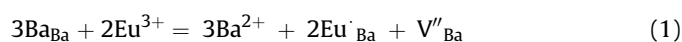
Room temperature photoluminescence measurements were conducted with Jobin Yvon Fluoromax 2 spectrofluorimeter. The photoluminescence (PL) and photoluminescence excitation (PLE) spectra were collected from  $\sim 1$  mm-thick layers of powder placed onto a quartz plate. The approximate contribution of the bands peaking at 490 nm to the total photoluminescence intensity in PL spectra were calculated with standard Integration function of Origin 8.1 program. The integral intensity values of the bands were measured within 460–600 nm range, while the total integral intensity of the luminescence within 350–600 nm range.

EPR measurements were carried out in the X-band (9.3–9.5 GHz) with a commercial Bruker X/Q-band E580 FT/CW ELEXSYS spectrometer within the 3.6–296 K temperature range using an Oxford Instruments ESR900 continuous flow cryostat. UV irradiation (330 nm) was performed using a mercury high-pressure arc lamp.

## 3. Results and discussion

In all cases XRD patterns on example of the 1, 4 and 9 samples presented in Fig. 1 exhibit reflections attributable to  $\text{BaI}_2 \cdot 2\text{H}_2\text{O}$  [Powder Diffraction File № 31–0145].

Domination of the reflections typical for  $\text{BaI}_2 \cdot 2\text{H}_2\text{O}$  in XRD patterns may be explained by the absorption of water from the atmosphere during the synthesis or during the transfer of as-prepared  $\text{BaI}_2:\text{Eu}$  samples into a container. It was impossible to come upon the synthesis steps when the hydration occurred and how strong impact it had on the initial anhydrous  $\text{BaI}_2$ . Therefore, further in the text no accent is put on whether the  $\text{BaI}_2$  or  $\text{BaI}_2 \cdot 2\text{H}_2\text{O}$  is the subject of the discussion. For simplification the “barium iodide” or  $\text{BaI}_2$  are used. It should be noted that upon the increase of Eu-ions concentration one can also notice the increase in the intensity of XRD-reflections of the admixture phase corresponding to  $\text{EuI}_2$  [PDF 77–0408]. On the one hand the presence of the XRD-reflections typical for the  $\text{EuI}_2$  indicates the transformation of  $\text{Eu}^{3+}$  into  $\text{Eu}^{2+}$  during the synthesis, while on the other – points out the incomplete incorporation of the Eu-ions into the  $\text{BaI}_2$  matrix. The  $\text{Eu}^{3+} \rightarrow \text{Eu}^{2+}$  transformation is well known to occur due to several reasons. In the present case it is, most likely, due to the decomposition involved by the  $\text{EuI}_3 \rightarrow \text{EuI}_2 + \text{I}_2$  ( $T > 200^\circ\text{C}$ ) reaction. Another option may be the interaction of the  $\text{Eu}^{3+}$  ions with defects in the  $\text{BaI}_2$  crystalline lattice. An illustrative examples are the  $\text{SiO}_2\text{--Al}_2\text{O}_3\text{--SrF}_2\text{--NaF--EuF}_3$  and  $\text{ZnO--B}_2\text{O}_3\text{--P}_2\text{O}_5\text{--Eu}_2\text{O}_3$  systems [23,24]. Similarly to them, the interaction of the  $\text{Eu}^{3+}$  ions with defects can be described in the way:



Calculated cell parameters ( $a$ ,  $b$ ,  $c$  and  $\beta$ ) and cell volumes for the 1, 4 and 9 samples are listed in Table 2.

Download English Version:

<https://daneshyari.com/en/article/7907396>

Download Persian Version:

<https://daneshyari.com/article/7907396>

[Daneshyari.com](https://daneshyari.com)