Optical Materials 79 (2018) 84–89

Contents lists available at ScienceDirect

Optical Materials

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

Luminescence of BaBrI and SrBrI single crystals doped with Eu^{2+}

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ARTICLE INFO

Article history:
Received 28 December 2017
Received in revised form
9 February 2018
Accepted 8 March 2018

Keywords:
Alkali earth halides
Europium
Luminescence
Optical spectroscopy
Ab initio calculation
Scintillators
BaBrI and SrBrI

ABSTRACT

The crystal growth procedure and luminescence properties of pure and Eu^{2+}-doped BaBrI and SrBrI crystals are reported. Emission and excitation spectra were recorded under ultraviolet and vacuum ultraviolet excitations. The energy of the first Eu^{2+} 4f-5d transition and SrBrI band gap are obtained. The electronic structure calculations were performed within GW approximation as implemented in the Vienna Ab Initio Simulation Package. The energy between lowest Eu^{2+} 5d state and the bottom of conduction band are found based on luminescence quenching parameters. The vacuum referred binding energy diagram of lanthanide levels was constructed using the chemical shift model.

1. Introduction

For many applications that use inorganic scintillators (such as high energy physics, positron emission tomography, and γ-ray detection), a high light yield is important along with good energy resolution, and fast response time. However, the search for new scintillators has now slowed down. Therefore, the attention again turned to materials that were previously considered to be luminophores. Moreover, it appears that scintillators based on binary systems have a higher light output than the original matrices. The light output for BaBrI:Eu^{2+} crystals was estimated as 90000 photons/MeV [1], whereas in $BaBr_2$ and BaI_2 it is only 58000 and 22000 photons/MeV, respectively [2]. Light output of SrBrI single crystal doped with Eu^{2+} was estimated about 47000 photons/MeV [1]. However, optical properties of these crystals has not been investigated well. In a previous article we have studied optical properties of BaBrI and BaClI crystals. The exciton creation energy, band gap and the energy of the lowest 4f-5d transition were estimated and VRBE diagram were constructed [3].

In this article, we present study of the optical properties of pure and Eu-doped SrBrI as well as BaBrI crystals. The optical properties of oxygen centers in BaBrI and SrBrI crystals are also reported. The band gap of SrBrI crystal is estimated. Thermal quenching of Eu^{2+} luminescence is studied. The vacuum referred binding energy (VRBE) diagram for SrBrI crystal is constructed based on experimental data and GGA-PBE calculations.

2. Methodology

2.1. Crystal growth

The compounds of alkaline earth halides are hygroscopic. Therefore, much attention is paid to drying raw materials before crystal growth. The thermogravimetric method (TG) and differential scanning calorimetry (DSC) were used to determine the melting points, the level of hydration and the possible dehydration temperature of the charge materials. The analysis of the charge was carried out using a synchronous thermal analyzer STA 449 Jupiter (NETZSCH). The starting materials were the anhydrous compounds

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https://doi.org/10.1016/j.optmat.2018.03.017
0925-3467/

of $BaBr_2$, BaI_2, $SrBr_2$ and SrI_2 (purity 99.9%, Lanhit, LTD). The stoichiometric mixtures of $BaBr_2$+BaI_2 and $SrBr_2$+SrI_2 were employed. The $EuBr_3$ was used for doping the mixtures. Eu^{2+} concentration employed is 0.05 mol.%. The melting points for BaBrI and SrBrI are 783 °C and 507 °C, respectively.

Quartz ampoules with special design of 20–30 mm in diameter were developed for bromide mixture drying and melt filtration. This procedure significantly improves the optical quality and scintillation characteristics of the crystals. Quartz ampoule consisted of two sections separated by quartz filter.

The thermal unit with controlled heating was used to dry the batch in the first section of quartz tube under vacuum. The drying process for raw materials was performed taking into account the TG and DSC data. As a next step, the charge was melted after thorough drying.

The molten compounds were filtered through a quartz filter. The filtered melt was collected in the second section of the ampoule. This section was sealed off under vacuum after filtration and cooling of the melt. The synthesized compound into this quartz ampoule was used to grow a single crystal. A vertical 20-zone furnace was used to grow BaBrI:Eu and SrBrI:Eu single crystals via the Bridgman method. The temperature gradient was 10–15 °C/cm. The rate of the crystal growth was 1 mm/h. The cooling rate of grown crystals was 10 °C/h. After that the growth procedure, the crystals were stored in mineral oil to protect from the atmosphere contamination.

Irregularly shaped 1–1.5 mm thick and 10–15 mm diameter crystal pieces were cleaved from the original boules for further studies. The plates were polished in glove box for the spectroscopic measurements.

2.2. Luminescence measurements

Photoluminescence (PL) was measured in vacuum cold-finger cryostat. The spectra were recorded with a MDR2 and SDL1 (LOMO) grating monochromator, a photomodule Hamamatsu H6780-04 (185–850 nm), and a photon-counter unit. The luminescence spectra were corrected for spectral response of detection channel. The photoluminescence excitation (PLE) spectra were measured with a grating monochromators MDR2 and 200 W xenon arc lamp for direct 4f-5d excitation and vacuum monochromator VM-2 (LOMO) and Hamamatsu deuterium lamp L7292 for measurements in VUV spectral region. The PLE spectra were corrected for the varying intensity of exciting light due. The X-ray excited luminescence was performed using an X-ray tube operating at 50 kV and 1 mA. Temperature dependences of luminescence were recorded in vacuum cryostat at linear heating. The heating rate was about 10 K/min.

2.3. Calculation details

Ab Initio calculations of BaBrI and SrBrI doped with Eu^{2+} were carried out within density functional theory (DFT) using VASP (Vienna *Ab Initio* Simulation Package) code [4]. The $2 \times 2 \times 1$ (48 atoms) supercell was constructed, in which one of Ba^{2+} or Sr^{2+} ions was replaced by Eu^{2+}.

Integration within the Brillouin zone was performed on a Γ-centered grid of 8 irreducible *k* points. Geometry optimization was performed with fixed cell dimensions. The convergence was achieved if the difference in total energy between the two last iterations was less than 10^{-6} eV.

3. Results and discussion

3.1. Exciton emission

The wide emission band at about 3.7 eV was observed at 78 K in undoped SrBrI crystals when excitation was performed into 5–10 eV region. The excitation peak (Fig. 1, curve 1) was located at about 5.6 eV. At 5.7 eV a small dip was monitored in excitation spectrum. Intensity of this band decreased in the doped crystals.

In BaBrI crystals the wide band luminescence peaked at 3.9 eV was observed. The excitation peak is located at about 5.3 eV. The wide peaks were found in excitation spectra in 5.5–10 eV range. This luminescence were attributed to self-trapped exciton luminescence [3]. The same luminescence were observed in the crystals under x-ray excitation.

In SrBrI the most efficient photoluminescence is excited within interband absorption, but excitation peak is located in a higher energy in comparison with BaBrI whereas emission band is shifted to lower energy. This behavior is typical for self-trapped exciton (STE). Similar to other alkali-earth halides [5–7], the STE in SrBrI can consist of molecular ion similar to H-center (hole on interstitial bromine or iodine ion) and an F-center-like part (electron trapped by iodine or bromine vacancy). Due to presence of different non-equivalent positions it is possible to observe several types of STE. However, in the present article no attention was paid to this question.

Early we estimated band gap of BaBrI and SrBrI crystals using position of exciton peak. Energy of exciton peak in SrBrI is about 5.7 eV Assuming binding energies of excitons in SrBrI and BaBrI are close, we can estimate band gap of SrBrI crystal following the procedure proposed in Ref. [3]. Exciton creation energy (E_x) in SrBrI is obtained at about 5.7 eV. Therefore, band gap is estimated about 6.0 eV.

3.2. Eu^{2+}-luminescence

The Eu doping leads to appearance of intense luminescence band peaked at about 2.94 eV. This emission spectrum results from 5d-4f transitions in Eu^{2+} ions. The emission peak is slightly shifted

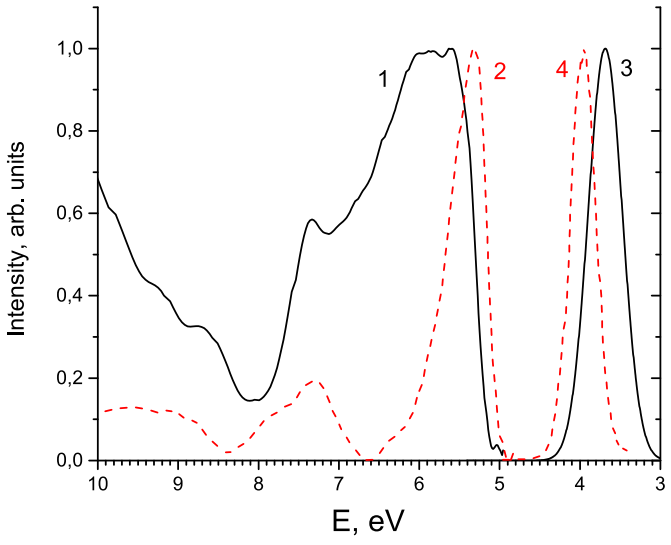

Fig. 1. Excitation and emission spectra of self-trapped exciton in BaBrI and SrBrI at 78 K. Excitation spectra of SrBrI (solid, curve 1) and BaBrI (dashed, curve 2) crystals monitored at 3.65 eV and 3.95 eV, respectively. Emission spectra were excited at 5.6 eV in SrBrI (curve 3) and 5.3 eV in BaBrI (curve 4) crystals.