Luminescence of divalent lanthanide doped BaBrI single crystal under synchrotron radiation excitations

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A B S T R A C T

Luminescence excitation spectra of BaBrI single crystals doped by divalent lanthanide ions are studied using synchrotron radiation excitations from the MAX IV 1.5 GeV storage ring. The energy of the edge and the formation of core cation exciton as well as the energy threshold of the multiplications of electronic excitations is found. It was clearly established the energy transfer from intrinsic luminescence centers to Sm$^{2+}$ and Eu$^{2+}$ ions.

1. Introduction

Past 20 years the scintillator studies has been mostly focused on the investigations of Ce$^{3+}$ and Eu$^{2+}$ doped halides (chloride, bromide, and iodide) [1,2]. The LaBr$_3$-Ce, Sr, SrI$_2$-Eu, BaBr$_3$-Eu and BaBrCl-Eu halide compounds have the parameters close to the theoretical limit on light output. All of these materials have been developed for ultraviolet spectral region, which is appropriated for PMT detectors.

However, new photodetectors based on avalanche photodiodes require a new class of scintillation materials having emission wavelength in the red or near infrared (NIR) spectral range. Successful attempts to obtain efficient red emitting scintillators and storages phosphors have been made before with alkali-earth halides doped by Sm$^{2+}$ ions [3]. Based on our preliminary estimations, we can expect that the alkaline-earth halide crystals (SrBrI and BaBrI) co-doped by Sm$^{2+}$ can also be successful red-NIR scintillators [4,5].

The study of lanthanide doped alkali-earth halides showed that excitonic transitions are involved in energy transfer process [6–8]. Therefore, the study of excitons and excitonic processes in these materials is necessary. The mixed alkaline-earth halides are moderately hygroscopic crystals. Taking into account that samples’ surface mostly suffers from water contaminations as well as that VUV excitations are absorbed in thin layer close to the crystal’s surface the surface quality is crucial for the VUV spectroscopic measurements. This fact induced practical difficulties in the study of hygroscopic samples under VUV synchrotron radiations before [9].

Detailed study of cation exciton and multiplications of electronic excitations in mixed alkali-earth systems (BaF$_2$-BaBr$_2$) was done by Mikhailin et al. [10]. That system is not hygroscopic. However, the study of more hygroscopic samples is performed for the first time. Therefore, our study may be useful for the design and performance of novel alkali-earth halide scintillators. In this paper, we are discussing some aspects of the growing process of BaBrI crystals doped by Eu$^{2+}$ and Sm$^{2+}$ ions and the results of the study of luminescence properties of these crystals under synchrotron radiation excitation.

2. Methodology

2.1. Crystal growth

The Eu$^{2+}$ and Sm$^{2+}$ doped BaBrI crystals were grown from the melt by the vertical Bridgman technique in an evacuated sealed quartz ampoule. These compounds of are hygroscopic. Therefore, before crystal growing the stoichiometric mixtures of BaBr$_2$ and BaI$_2$ thoroughly were dried in quartz ampoule under vacuum. The SmI$_2$ or EuBr$_3$ compound was introduced as an dopant directly into the raw before the drying in the concentration range from 0.01% to 5%.

The melting temperature for BaBrI was about 780 °C. The temperature gradient during the crystal growth did not exceed 5 °C/cm. The low gradient helps to avoid thermoelastic stresses that stimulates defects formation in the crystal. The ampoule was slowly cooled down at a rate of 5–10 °C/h after crystallization of the melt. The slow cooling
process prevents cracking and stress accumulations in the crystal. Due to the hygroscopic nature of the halogen materials, the extraction and processing of crystals was carried out in a dry glove box. More details of the crystal growth process of BaBrI single crystals were described elsewhere [11,12].

2.2. Luminescence measurements

The luminescence experiments were performed on the photoluminescence endstation of FinEstBeAMS beamline at MAX IV synchrotron facility, Lund, Sweden [13,14]. The luminescence experiments under synchrotron radiation excitations is a powerful method for wide band gap materials [15–19] as well as semiconductors [20–22]. The luminescence endstation was equipped by a close-cycle helium cryosystem (6–400 K). An external Andor Shamrock (303i) 0.3-m UV/visible spectrometer equipped by the CCD detector (Newton DU970P-BVF model from Andor) and the Hamamatsu photon counting head visible spectrometer equipped by the CCD detector (Newton DU970P-BVF model from Andor) was utilized for the luminescence detection. To suppress high orders of excitation at FinEstBeAMS beamline, a set of filters is used. Fused silica and MgF2 are chosen for the low energy region. At higher energies, thin films of Sn (4d BE 23.9 eV), Mg (2p BE 49.6 eV), Al (2p BE 72.5 eV) are applied.

2.3. Calculation details

To estimate absorption spectra in fundamental absorption region and band structure of BaBrI we performed ab initio calculation. Density of States (DOS) and optical absorption spectra in BaBrI were calculated within density functional theory with PBEsol [23] exchange-correlation functional according to procedures implemented in the VASP [24] code.

First, we relaxed lattice vectors and atomic positions within BaBrI unit cell using density functional. The thresholds for energy and forces during geometry optimization were $10^{-7}$ eV and 0.01 eV/Å, respectively. A good agreement between calculated (429.77 Å$^3$) and experimental (438.71 Å$^3$) volume was obtained (with 2% error). Then, we performed a GW0 calculation to obtain accurate electronic structure and Density of States. The GW0 approach allows to calculate electronic energies based on many-body self-energy $\Sigma$, instead of using DFT with exchange-correlation potential. This often yields very accurate results for electronic energies [26,27]. The calculated band gap was 5.33 eV, which is 0.25 eV smaller than the experimental value [4]. Then, frequency dependent dielectric function was calculated in BSE [28,29] procedure based on GW0 quasiparticle energies and DFT wavefunctions.

3. Results and discussion

3.1. Theoretical calculations

The density of electronic states DOS plotted in Fig. 1 is defined as number of electronic states with energies from $E$ to $E + \Delta E$ normalized by volume. The top of the valence band (shifted to zero eV in Fig. 1) is formed by bromine 4p and iodine 5p states, while 4.5s states of anions together with barium 5p states are located deeper and form three distinct bands between $-14$ and $-10$ eV. The very deep 5s states of Ba are located near $-25$ eV. The bottom of conduction band is formed by broad band of Ba 5d states extended from six to ten eV. The DOS can be used to qualitatively predict the energies and intensities of interband electronic transitions as described below.

The frequency dependent optical absorption coefficient was obtained from BSE calculated dielectric function and is plotted in Fig. 2 (dashed curves). Combined with the DOS results, the broad absorption band from 5.5 to 12 eV can be ascribed to transitions from anion $p$ to barium $d$ states. The calculations were performed without spin-orbit correction, therefore spin-orbit splitting of the valence band formed in the ground $5p$ state of $I^-$ could not be reproduced. Then, there is a gap in absorption near 15 eV due to absence of electronic states between $-10$ and $-3$ eV. This gap is followed by strong absorption in the range from 16 to 23 eV due to transitions from occupied 4.5s states of anions and $5p$ states of Ba. The high energy transitions from Ba 5s to Ba 5d were not reproduced due to limited number of bands involved in calculation.

3.2. Luminescence excitation spectra

Fig. 2 demonstrates the excitation spectra of Eu$^{2+}$ emission in BaBrI single crystal in wide spectral range. These spectra were measured for the 415 nm (2.99 eV) luminescence band attributed to 5d-4f transition in Eu$^{2+}$ ions [30,4]. A high intensity in the spectra onset (Fig. 2 a) is assigned to the intracenter excitation to the 5d states of Eu$^{2+}$ ion. The strong excitation band in fundamental absorption region of BaBrI ($E_g = 5.6$ eV) is caused the formation of $\Gamma$-exciton. The intensity dip in the luminescence excitation spectrum at 5.56 eV is due to the spin-orbit splitting of the valence band formed in the ground 5p state of $I^-$ (the so-called halogen doublets [31]).

The comparison of the excitation spectrum for BaBrI-Eu single crystal with the calculated absorption spectrum of BaBrI in the range of 7–12 eV shows that intensive absorption peaks are located where the luminescence is not excited. The luminescence attenuation at energy higher than the excitonic peak (Fig. 2 a) can be due to the decreasing light penetration depth into the crystal induced by a large absorption coefficient which is about $10^5$ cm$^{-1}$. This leads to efficient near-surface nonradiative recombination processes which are strong in this spectral region [10]. Absorption bands with energies higher than 22 eV were not reproduced because of limited number of electronic states used in calculations.

The calculated density of states diagram is given in Fig. 1. In accordance to the energy gap between core 5p- and free 5d-shells of Ba$^{2+}$ ion is about 19 eV. Therefore, the steplike buildup of the luminescence intensity at about 19 eV (Fig. 2 b) could be attributed to the creation threshold of the core-cation excitons in BaBrI. This type of excitons was found before in BaFBr [10], CsBr [32] and in other alkali halide [33,34].

There is also another explanation of the luminescence intensity buildup at about 20 eV. It can be due to multiplication of electronic excitation (MEE) process. Using a simplified theory, the threshold energy for MEE processes in ionic crystals can be estimated from: [34]:

$$E_t = E_q + E_e (1 + m_u/m_d),$$

(1)
where $E_g$ is band gap, $m_e$ and $m_h$ – effective masses of an electron and a hole, $E_a = E_g - E_x$ – energy of anionic exciton formation. In accordance to our estimations $m_e/m_h = 1.7$ and $E_a = 0.29$ eV [4]. Therefore, $E_t$ is about $3.5 - 5$ eV. The emission intensity of Eu$^{2+}$ increases at $h\nu > 20$ eV. Therefore, we suggest that the so-called effect of MEE is observed in BaBrI-Eu$^{2+}$ [10].

The general behavior of excitation spectrum is similar to the excitation spectra observed before in other systems, where excitonic mechanism of energy transfer from host-lattice to the impurity ions takes place [35,36]. On the other hand, the low energy excitation peak in Fig. 2 lies in the spectral region of excitation of self-trapped exciton (STE). This fact also indicates that STE participates in the transfer of excitation to europium ions confirming the resonant mechanism of energy transfer recently reported in [6].

The luminescence spectrum excited under 5.05 eV is given in the inset of Fig. 3. In the luminescence spectra at low temperatures several sharp lines attributed to 4f-4f transitions are observed. At room temperature wide 5d-4f luminescence band is also found [37]. The excitation spectrum of Sm$^{2+}$ luminescence attributed to $5D_0-7F_0$ transition at 687 nm (1.80 eV) to is depicted in Fig. 3. In the energy range 10–50 eV (Fig. 3, b) the excitation spectrum is similar to the corresponding spectrum of Eu$^{2+}$. However, the spectra are different in the energy range 4–8 eV. Low energy excitation peak of Eu$^{2+}$ luminescence is located in the region of STE excitation peak, whereas Sm$^{2+}$ excitation peak is shifted to lower energy. However, the excitation peak of Sm$^{2+}$ is similar to the excitation peak of intrinsic luminescence peaked at 495 nm (2.5 eV) observed in undoped BaBrI crystals. The origin of this intrinsic luminescence is unclear. It could be attributed to the impurity trapped exciton near oxygen centers [5,38] or recombination luminescence between $V_k$ and F centers [6]. The coincidence in excitation spectra of intrinsic 495 nm (2.5 eV) luminescence and Sm$^{2+}$ luminescence allows us to conclude that energy transfer from 495 nm (2.5 eV) luminescence to Sm$^{2+}$ center takes place.

4. Conclusion

Based on the UV-VUV excitation spectroscopy results as well as first principle calculations energy transfer processes from host lattice of BaBrI to Sm$^{3+}$ or Eu$^{2+}$ ions have been studied. It was confirmed that energy transfer from STE to Eu$^{2+}$ ion takes place. On the other hand, the energy transfer to Sm$^{2+}$ occurs via some intrinsic center distinguished from STE. Some peculiarities of the excitation spectra in VUV range of Eu$^{2+}$ emission are explained in terms of multiplication of electronic excitations or excitations of cation exciton.
Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References


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