



EPR and luminescence studies of the radiation induced Eu^{2+} centers in the $\text{EuAl}_3(\text{BO}_3)_4$ single crystals



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ARTICLE INFO

Article history:

Received 27 December 2016

Received in revised form

23 February 2017

Accepted 26 February 2017

Keywords:

EPR spectra

Multiferroics

Rare-earth

Luminescence

Aluminum borates

X-ray irradiation

Spin Hamiltonian parameters

Superposition model

Low-spin state

ABSTRACT

We have studied the X-ray irradiated $\text{EuAl}_3(\text{BO}_3)_4$ single crystals by means of luminescence and electron paramagnetic resonance (EPR) spectroscopy. It was found that the X-ray irradiation modifies the color of the $\text{EuAl}_3(\text{BO}_3)_4$ crystal and leads to the formation of a stable Eu^{2+} centers from the Eu^{3+} centers located in a host matrix. Annealing of the crystal at 600 °C leads to the restoration of the original color and the disappearance of Eu^{2+} centers. The EPR and luminescence spectra of the Eu^{2+} ion were studied in a wide temperature range. The angular dependence of Eu^{2+} EPR spectra is described by an axial spin Hamiltonian characterized by the spin of $S = 7/2$ with the following parameters: $g_z = g_x = 1.991$ (1); $b_2^0 = -267,86$ (16) $\cdot 10^{-4} \text{cm}^{-1}$; $b_4^0 = -4,20$ (8) $\cdot 10^{-4} \text{cm}^{-1}$; $b_6^0 = 0,37$ (13) $\cdot 10^{-4} \text{cm}^{-1}$; $A(151) = 31,4$ (3) $\cdot 10^{-4} \text{cm}^{-1}$; $A(153) = 13,9$ (3) $\cdot 10^{-4} \text{cm}^{-1}$. Based on the comparison of spin Hamiltonian parameters of Eu^{2+} and Gd^{3+} ions, it was concluded that Eu^{2+} ion located at the Eu^{3+} site in the $\text{EuAl}_3(\text{BO}_3)_4$ crystal lattice. Within the framework of the superposition model, the distortions introduced to the local environment by the Eu^{2+} and Gd^{3+} ions were analyzed. In the luminescence spectra, the bands associated with the Eu^{2+} and Eu^{3+} ions are detected. The photoluminescence decay kinetics of Eu^{3+} -related emission (614 nm) has a single-exponential character, whereas the Eu^{2+} -related band (323 nm) possess more complicated decay kinetics behavior that may point to the Eu^{2+} excited state ionization and its delayed recombination.

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1. Introduction

The borates $\text{ReM}_3(\text{BO}_3)_4$ (Re is a rare-earth ion or yttrium and M is Al, Fe, Ga, Cr) possess a number of unique properties that make them attractive for the study and application. They are characterized by good luminescent and non-linear features. At high level of doping, the concentration quenching in the alumoborates is absent and combined with excellent physical and chemical properties it makes these crystals promising as a media for the solid-state lasers. The single crystals of rare-earth borates can be used for effective frequency transformation of laser irradiation that exceeds by far the analogous parameters of the known media. Ytterbium-doped borate crystals allow obtaining the laser pulses of femtosecond duration. The activation of the crystals of borates family with

erbium generates the laser irradiation characterized by the wavelength of 1.5 μm , which finds the medical application and demonstrates low air propagation losses [1–6].

The possibility of doping with both rare-earth ions and the ions of iron group makes the alumoborates crystals attractive with respect to the magnetism since the interaction of two magnetic subsystems produces a number of specific features. For instance, the interaction between the iron ions in quasi-one-dimensional chains of $\text{GdFe}_3(\text{BO}_3)_4$ results in antiferromagnetic ordering at 37 K and the interaction with the rare-earth subsystem initiates a spin-reorientation transition at 10 K [7]. In some crystals, a magnetoelectric effect was found, so they can be classified as multiferroics [8–10].

It is known that the properties of the crystals doped intentionally or accidentally are substantially determined by the impurities and their energy states, location, and the corresponding lattice distortions are still the subjects of intensive research [11,12].

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In this connection, the alumoborate crystals are of particular interest as they contain both rare-earth ions and the ions with 3d and 4d shells.

The electron paramagnetic resonance (EPR) is an informative method that allows establishing the symmetry of the paramagnetic center, the charge state, and the directions of the magnetic axes. In particular, if the impurity charge does not coincide with the charge of the substituted lattice ion, it is possible to define the position of the compensator. A number of papers report EPR studies of Cr^{3+} [13–16], Mn^{2+} [17,18], Ti^{3+} [19] ions in alumoborates. In the rare-earth doped alumoborates, the EPR spectra were observed for Ce^{3+} and Yb^{3+} [20], Er^{3+} and Nd^{3+} [21], Gd^{3+} [22–24], Dy^{3+} [25] ions.

In the present work, by means of X-ray irradiation of the $\text{EuAl}_3(\text{BO}_3)_4$ crystal, a paramagnetic center of bivalent europium was formed. The EPR and luminescence methods were applied in a wide temperature range. Since the observed Eu^{2+} ion has the same configuration $4f^7$ as the Gd^{3+} ion reported before [23], the characteristics of these ions located at analogous lattice sites in the alumoborate crystal lattice has been compared.

2. Crystal structure and experimental procedure

The crystals of the borate family $\text{ReM}_3(\text{BO}_3)_4$ (R is a rare-earth metal or yttrium and M is a trivalent ion of Al, Ga, Fe, Sc, Cr) are crystallized in the huntite structure of $\text{CaMg}_3(\text{BO}_3)_4$ with the space group of R32 [23,25].

The $\text{EuAl}_3(\text{BO}_3)_4$ crystals were obtained as a result of spontaneous melt-solution crystallization. As a solvent medium, the potassium molybdate ($\text{K}_2\text{Mo}_3\text{O}_{10}$) was used. Pre-synthesized aluminum borate was added to the solvent. Besides, the mixture was supplemented with overdose of 10% B_2O_3 and the related additive of Gd_2O_3 [26]. The growth was performed by the solution cooling from 1150 °C down to 900 °C at the rate of 2 deg/hour. The obtained products were transparent, well-faceted crystals of 2–3 mm in size. The obtained $\text{EuAl}_3(\text{BO}_3)_4$ crystals have the form of prisms elongated along the C_3 axis, which facilitates their orientation in the measurements.

The parameters of trigonal cell for $\text{EuAl}_3(\text{BO}_3)_4$ are: $a = b = 9.312$, $c = 7.275$ [15]. Fig. 1 shows the crystal structure of $\text{EuAl}_3(\text{BO}_3)_4$ in a plane perpendicular to the C_3 -axis, the nearest environment of the rare-earth ion is marked off with the solid lines. Fig. 2 provides a more detailed view.

A unit cell of $\text{ReAl}_3(\text{BO}_3)_4$ contains $Z = 3$ formula units. The coordination polyhedrons of Re^{3+} , Al^{3+} and B^{3+} are trigonal prisms, octahedrons and triangles formed by the oxygen ions, respectively. The rare-earth ions are located at the rotary axes C_3 in slightly

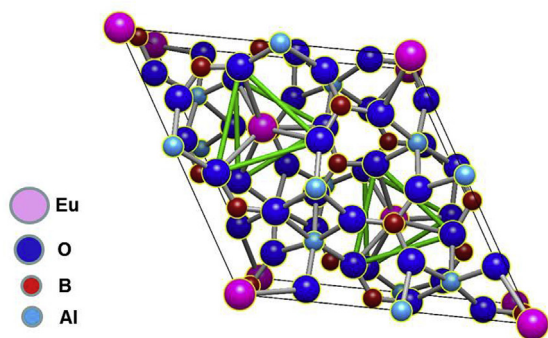


Fig. 1. Crystal structure of the $\text{EuAl}_3(\text{BO}_3)_4$ crystal. The C_3 -axis is perpendicular to the plane of the figure.

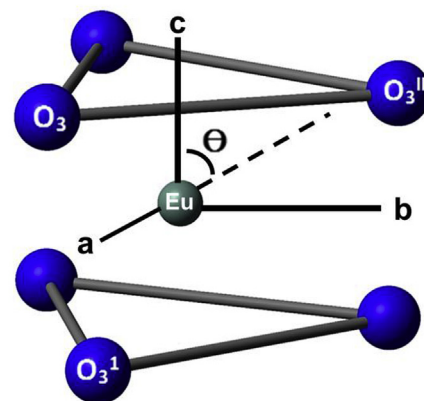


Fig. 2. Nearest environment of rare earth ion Eu in the lattice of $\text{EuAl}_3(\text{BO}_3)_4$ aluminum borates consisting of oxygen ions. R - O distance is the same for all oxygen ions.

distorted prisms where the upper and the lower triangles are rotated through a small angle.

The Al^{3+} ions are positioned in oxygen octahedrons. The edge-linked octahedrons form the twisted columns aligned with C-axis. The B_1 and B_2 atoms are located in oxygen triangles of two types: B_1 are positioned in triangles normal to the three-fold axes and alternating with Eu-prisms; B_2 are located in triangles rotated through the 3_1 axis and binding the twisted columns of Al-octahedrons.

The $\text{EuAl}_3(\text{BO}_3)_4$ sample was immersed into the bath of liquid nitrogen where it was X-ray irradiated for 20 min using an X-ray tube with 55 kV voltage and 30 mA current applied. The source of X-ray irradiation was highly stabilized by X-Ray equipment ISO-DEBYEFLEX 3003 for structure analysis. After the action of the X-ray irradiation, the sample obtained a dark tint and the characteristic photoluminescence and EPR spectra of Eu^{2+} ion were detected. The Eu^{2+} ions demonstrate uncommonly high stability, withstanding at room temperature (RT) for weeks. The annealing at 600 °C during 10 h brings the crystal back to the initial state, the color vanishes and the Eu^{2+} ions are not observed anymore in EPR and luminescence spectra.

Room temperature luminescence measurements in the 200–800 nm wavelength range were performed by a modified spectrofluorometer (custom made 5000 M model, Horiba JobinYvon) equipped with TBX-04 photon counting detector (IBH Scotland). A deuterium steady-state lamp was used for the excitation and emission spectra measurements. An X-ray tube operating at a voltage of 40 kV and 15 mA current (Seifert GmbH) was used as an excitation source for the radioluminescence measurements. All the spectra were corrected for experimental distortions. The xenon microsecond flashlamp was used for the luminescence decay measurements. Exponential fits of the decays were obtained by performing the convolution of the considered function with the instrumental response and a least-square sum fitting procedure (SpectraSolve software, Ames Photonics Inc.).

The EPR spectra measurements have been carried out with a Bruker ELEXSYS E580 spectrometer at X-band in the temperature range of 4–300 K.

3. Experimental results

3.1. Fine and hyperfine structure of EPR spectrum

An ion of bivalent europium (Eu^{2+}) is characterized by a partially filled shell of $4f^7$ configuration. The ground multiplet $^8S_{7/2}$ is associated with zero orbital moment $L = 0$, and the spin moment is

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