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Pair luminescence in Cr^{3+} -doped $Ba_2Mg(BO_3)_2$

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ABSTRACT

Cr^{3+} ions were introduced to the $Ba_2Mg(BO_3)_2$ host to provide information about the site occupation, crystal field strength, and the site symmetry. The samples were synthesized by solid-state reaction. Emission observed under 440 nm excitation was characteristic for Cr^{3+} ions in strong octahedral ligand field with Dq/B parameter ratio 2.74 and sharp R line at 698 nm. The charge mismatch between Cr^{3+} dopant and Mg^{2+} host ion is compensated by the creation of Cr^{3+} pair in the vicinity of Ba or Mg vacancy. The emission decay curve is bi-exponential with decay times 1.2 and 13.3 ms.

1. Introduction

Borate materials have been an object of interest as phosphors due to their high UV transparency, a variety of crystal structures (36% of them have no inversion center) [1] and low temperatures of synthesis compared to aluminates and silicates. The structure formed by borate groups can determine the optical properties of the material [2].

$Ba_2Mg(BO_3)_2$ (BaMBO) has a trigonal structure with space group R-3m, where Ba^{2+} cations occupy sites with C_{3v} point group symmetry and Mg^{2+} cations occupy sites with D_{3d} point group symmetry [3]. This borate belongs to so-called “simple” borates, i.e., borates, where borate groups (BO_3 or BO_4) do not share oxygen atoms in polyhedral to create chains, rings, and networks. The structure consists of alternate layers of BaO_9 and MgO_6 polyhedra separated by BO_3 groups (see Fig. 1.)

Research on BaMBO as a host material for white LED application has been conducted with Eu^{2+} - doped [3–6], Eu^{3+} [7,8] and Mn^{2+}, Eu^{2+} - co-doped BaMBO [9]. Eu^{2+} enter both Ba^{2+} and Mg^{2+} sites, which does not require any charge compensation and result in highly efficient red-orange luminescence under 350–400 nm excitation.

Cr^{3+} can serve as an optical probe, when incorporated into the host and provide information about the number of available sites, their symmetry, and crystal field strength [10]. Cr^{3+} ions, unlike Eu^{3+} optical probe ions, occupy octahedral sites only, which allows them to substitute the selected ions in the host. In a strong ligand field, the emission spectrum of Cr^{3+} ions is usually complex and provides information about vibronic energies and the presence of Cr pairs in the studied host [11,12].

For our best knowledge, this is the first report on Cr – doped BaMBO and its luminescent properties.

2. Experimental

The samples were synthesized by the conventional solid-state method. $Ba(NO_3)_2$, $Mg(NO_3)_2$*$6H_2O$, $Cr(NO_3)_3$*$9H_2O$ and H_3BO_3 were used as precursors, ground in a mortar under n-hexane and annealed at 900 °C for 16 h.

The phase purity and crystal structure were studied by X-Ray diffraction method (XRD) using the X'Pert PRO powder diffractometer (PANalytical) with a linear PIXcel detector and Cu Kα radiation ($\lambda = 1.54056$ Å).

Emission spectra at 300 and 77 K were recorded using Hamamatsu PMA-12 spectrophotometer, Nd: YAG - pumped Ti-Sapphire laser and Dewar flask. The excitation spectra and decay curves at 77 K were recorded using McPherson spectrometer, Hamamatsu R928 photomultiplier, and Tektronix MDO3052 digital oscilloscope.

Emission spectra and decay curves at 10 K were measured using Jobin-Yvon measurement system equipped with closed cycle helium cryostat and Nd: YAG – pumped Ti-Sapphire laser. Decay profiles were recorded with LeCroy digital oscilloscope.

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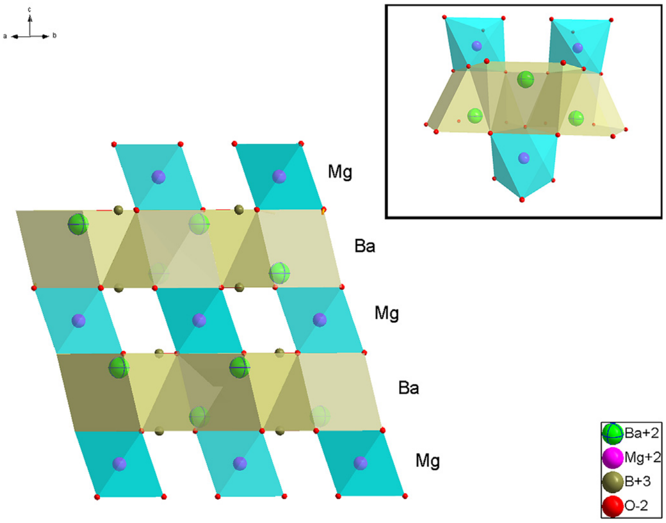

Fig. 1. Crystal structure of BaMBO. Inset: The location of Cr^{3+} pair in the vicinity of Ba^{2+} vacancy, where Cr^{3+} ions are in the opposite layers.

3. Results and discussion

3.1. Structural studies

$Ba_2Mg(BO_3)_2$ crystal structure is trigonal and characterized by R-3m space group [3]. There are one Ba^{2+} 9-coordinate site and one Mg^{2+} 6-coordinate site available for dopant ions, the former with the C_{3v} and latter with the D_{3d} point symmetry. The structure consists of two types of layers built up by MgO_6 octahedra and BaO_9 polyhedra (see Fig. 1.)

Cr^{3+} ions, due to large crystal field stabilization energy (CFSE) of octahedral (224.5 kJ/mol) [13] and the difference in ion sizes make the location of Cr^{3+} in the 9-coordinate Ba^{2+} sites and 3-coordinate B^{3+} sites highly improbable, and therefore negligible. The only remaining possible location of the dopant is quasi-octahedral 6-coordinated Mg^{2+} sites.

XRD results confirm the phase purity of BaMBO: Cr^{3+}, when Cr^{3+} concentration exceeds 1%. For Cr^{3+} concentration under 1%, additional peaks from BaO and B_2O_3 are present (see Fig 2.)

The disappearance of BaO and B_2O_3 phase for samples with larger Cr^{3+} concentration may result from the stabilization of BaMBO: Cr structure by Cr pair creation. The single Cr^{3+} ions at octahedral Mg^{2+} sites carry an additional charge, that must be compensated [14]. For low Cr^{3+} concentration, the probability of one Cr^{3+} ion's location in the vicinity of other Cr^{3+} ion is low. Therefore the structure remains unstable and prone to phases separation. The additional phases are unlikely to serve as a host to Cr^{3+} ions: B_2O_3, due to the lack of 6-coordinated sites and BaO, due to the significant difference in ionic radii (149 p.m. for Ba^{2+} and 75.5 p.m. for Cr^{3+} [15]).

3.2. Emission and excitation spectra

BaMBO: Cr^{3+} exhibits two broad bands in the excitation spectrum with maxima at 450 and 610 nm. They result from the $4A_{2g} \rightarrow 4T_{1g}$ and $4A_{2g} \rightarrow 4T_{2g}$ transitions, respectively (see Fig. 3). Applying O_h symmetry notation, sharp lines in the emission spectrum can be ascribed to the 2 Eg → $4A_{2g}$ spin forbidden transition (the R line) and the lines associated with pair luminescence. Maxima of excitation and emission bands, taken from deconvoluted excitation and emission spectra were used to calculate the crystal field strength (Dq) and the Racah parameters B and C. The following equation set

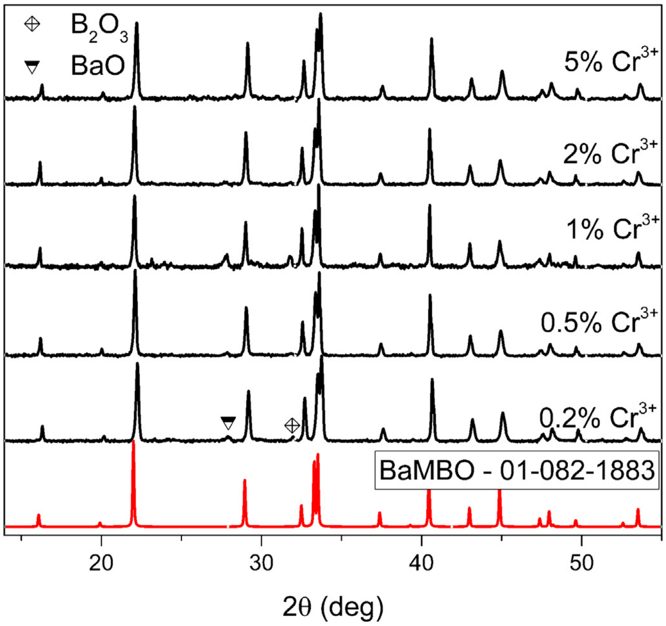

Fig. 2. XRD results for BaMBO: Cr^{3+} samples with relevant pattern.

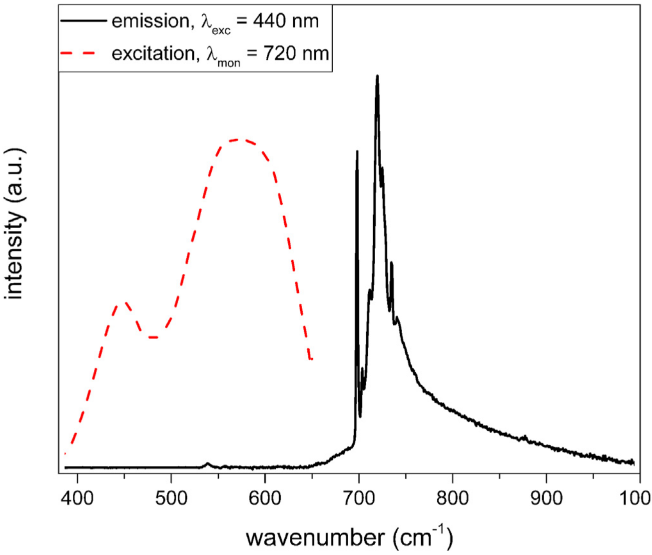

Fig. 3. The 77 K excitation and emission spectra of BaMBO: 2% Cr^{3+}.

(1) has been solved for this purpose [10]:

$$
\begin{aligned}
&E(^4A_{2g} \rightarrow {}^4T_{2g}) = 10\,Dq,\\
&x = [E(^4A_{2g} \rightarrow {}^4T_{2g}) - E(^4A_{2g} \rightarrow {}^4T_{1g})]/Dq,\\
&Dq/B = 15(x - 8)/(x^2 - 10\,x),\\
&E(^4A_{2g} \rightarrow {}^2E_g) = 3.05C + 7.09B - 1.8B^2/Dq,
\end{aligned}
\tag{1}
$$

where $E(^4A_{2g} \rightarrow EX)$ are energy difference between the ground level and the excited EX level. Calculated Dq/B parameter ratio is equal to 2.74, with B = 718 cm-1 and C = 2756 cm-1. The emission spectrum is characteristic for Cr^{3+} ions in a strong O_h crystal field [10].

The R line, observed at 698 nm (see Fig. 4), is asymmetrical,