

Distribution of the Eu^{3+} dopant ions over cation positions and luminescent properties in novel $M_3\text{Bi}_2(\text{BO}_3)_4:\text{Eu}^{3+}$ ($M = \text{Sr}, \text{Ba}$) red phosphors

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Here we represent the results of investigation of structural and optical properties of novel $M_3\text{Bi}_2(\text{BO}_3)_4:\text{Eu}^{3+}$ ($M = \text{Sr}, \text{Ba}$) red-emitting phosphors. These borates crystallize in $Pnma$ space group and are related to $A_3\text{REE}_2(\text{BO}_3)_4$ family, $A = \text{Ca}, \text{Sr}, \text{Ba}$ [Khamaganova, 2017]. Crystal structure is consisted of the isolated BO_3 triangles and three independent $M1$, $M2$ and $M3$ sites. The MO -polyhedra are connected by corners and edges forming the framework.

Series of the $M_3\text{Bi}_2(\text{BO}_3)_4:\text{Eu}^{3+}$ ($M = \text{Sr}, \text{Ba}$) were prepared using crystallization from a melt. X-ray powder diffraction data confirmed that samples were single-phased. There is an expectable decrease of the unit cell parameters and volume in these series along with the substitution of the larger Bi^{3+} ion ($R_{\text{CN}8} = 1.31 \text{ \AA}$) by the smaller Eu^{3+} ion ($R_{\text{CN}8} = 1.206 \text{ \AA}$). $M_3\text{Bi}_2(\text{BO}_3)_4$ ($M = \text{Sr}, \text{Ba}$) solutions have positionally-disordered structures; in $\text{Ba}_3\text{Bi}_2(\text{BO}_3)_4$ end-member the $M1$ – $M3$ sites are additionally splitted [Volkov *et al.*, 2013]. It can be assumed that as the amount of the europium increases, the Eu^{3+} ions can replace the Bi^{3+} ions in different M sites. A few small single crystals were obtained and distribution of the Eu^{3+} ions over three cation sites was refined for $\text{Sr}_3(\text{Bi}_{1-x}\text{Eu}_x)_2(\text{BO}_3)_4$ ($x_{\text{Eu}} = 0, 0.17$) [Shablinskii *et al.*, 2017], $\text{Ba}_3(\text{Bi}_{1-x}\text{Eu}_x)_2(\text{BO}_3)_4$ [Volkov *et al.*, 2013] and $\text{Ba}_3(\text{Bi}_{1-x}\text{Eu}_x)_2(\text{BO}_3)_4$ solid solutions ($x_{\text{Eu}} = 0.05, 0.35$ and 0.8) from single-crystal XRD data. The Ba, Bi and Eu atoms are disordered over these sites with the preferential occupation but with no complete ordering. Therefore, we refined the Ba/Bi/Eu occupations over the sites: the Eu^{3+} ions occupied the $M2$ site in $\text{Ba}_3\text{Bi}_{1.9}\text{Eu}_{0.1}(\text{BO}_3)_4$ and $\text{Ba}_3\text{Bi}_{1.3}\text{Eu}_{0.7}(\text{BO}_3)_4$, whilst the Eu^{3+} ions were distributed over all the cation sites in the $\text{Ba}_3\text{Bi}_{0.4}\text{Eu}_{1.6}(\text{BO}_3)_4$ crystal structure.

Luminescent properties of the $M_3\text{Bi}_2(\text{BO}_3)_4:\text{Eu}^{3+}$ phosphors were investigated: the optimum concentration was found to be at 50 at. % for $\text{Ba}_3\text{Bi}_2(\text{BO}_3)_4:\text{Eu}^{3+}$ ($\lambda_{\text{ex}} = 393 \text{ nm}$) while for the structurally similar $\text{Sr}_3\text{Y}_2(\text{BO}_3)_4$ [Zhang, Li, 2004] and $\text{Sr}_3\text{Bi}_2(\text{BO}_3)_4$ [Shablinskii *et al.*, 2017] borates it was determined as 10 and 15 at. % ($\lambda_{\text{ex}} = 393 \text{ nm}$). Hence a feature of the $\text{Ba}_3\text{Bi}_2(\text{BO}_3)_4:\text{Eu}^{3+}$ crystal structure is the high optimum concentration of the Eu^{3+} dopant in this phosphor matrix in comparison to the other borates of this family. The integral luminescence intensity of $^5\text{D}_0$ – $^7\text{F}_2$ transition increases when the largest amount of the Eu^{3+} ions occupies the $M2$ site. The concentration quenching occurs when the Eu^{3+} ions start to distribute over all three cation sites in the $\text{Ba}_3\text{Bi}_2(\text{BO}_3)_4:\text{Eu}^{3+}$ phosphor. The influence of the Eu^{3+} ions distribution and splitting positions in the crystal structures of the $M_3\text{Bi}_2(\text{BO}_3)_4:\text{Eu}^{3+}$ is discussed. The results show that the $\text{Ba}_3\text{Bi}_2(\text{BO}_3)_4:\text{Eu}^{3+}$ phosphors are promising candidates for solid state lighting application.

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