Materials Chemistry and Physics 207 (2018) 479–488

Contents lists available at ScienceDirect

Materials Chemistry and Physics

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

Emission tuning studies in $BaMgSiO_4$:RE (RE = Eu^{2+}, Sr^{2+}) for white LEDs

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HIGHLIGHTS

- The emission of Eu^{2+} in $BaMgSiO_4:Eu^{2+}$ shifts to the green region by increasing Eu concentration.
- The emission of Eu^{2+} in $BaMgSiO_4:Eu^{2+}$, ySr^{2+} shifts to the blue region by substitution Ba^{2+} by Sr^{2+}.
- The energy migrants from the $Eu_{(I,II)}$ O_9 to the $Eu_{III}O_6$ polyhedron efficiently.

ARTICLE INFO

Article history:
Available online 4 January 2018

Keywords:
Photoluminescence
Tunable emission
White LEDs

ABSTRACT

Color tuning is a challenge for improving white light LEDs. In this paper, the color tuning in $Ba_{1-x}MgSiO_4$:xEu^{2+} ($0 \leq x \leq 0.07$) and $Ba_{0.993-y}MgSiO_4$:$0.007Eu^{2+}$, ySr^{2+} ($0 \leq y \leq 0.07$) are investigated. The emission can be tuned by increasing Eu^{2+} concentration and substitution of the host lattice cation Ba^{2+} by Sr^{2+}. The emission shows a red shift in $Ba_{1-x}MgSiO_4$:xEu^{2+} with the increase of Eu^{2+} concentration. The red shift results from the preferential occupation of Eu^{2+}. On the contrary, the emission of $Ba_{0.993-y}MgSiO_4$:$0.007Eu^{2+}$, ySr^{2+} shows a blue shift when partial substitution of Ba^{2+} by Sr^{2+}. The blue shift is explained by the preferential occupation of Sr^{2+}, crystal field splitting of Eu^{2+} and the electron binding energy of Eu-O.

1. Introduction

White light-emitting diodes (LEDs) is a new generation of illumination as substitutes for conventional fluorescent lamps owing to the long lifetime, low energy consumption, and environmentally friendly characteristics [1–3]. Nowadays, white LEDs are mainly composed by the InGaN blue chip coated on the yellow phosphor $Y_3Al_5O_{12}:Ce^{3+}$ (YAG:Ce^{3+}) [4]. This technology has several drawbacks including the low color-rendering index (CRI) and the high color temperature (CCT) [5,6]. To overcome these problems, ultraviolet (NV) or near ultraviolet (NUV) LED red-blue-green (RBG) white LEDs have been suggested for the general illumination. Using the RBG phosphor can provide a higher CRI with good quality white light than the blue chip and YAG:Ce^{3+} method. Moreover, the ability to tune the emission color of a luminescent material is of great importance for practical applications.

$BaMgSiO_4:Eu^{2+}$ is a potential white LED phosphor for it can be efficiently excited by the photon of UV and NUV and emits the photon of blue and green [7–9]. Eu^{2+} and Mn^{2+} co-doped $BaMgSiO_4$ shows the white light [10]. $BaMgSiO_4:Eu^{2+}$ attracts our attention mainly because of the special crystal structure of $BaMgSiO_4$ host. The Ba ions in $BaMgSiO_4$ occupy both the 9-coordinated (Ba_I and Ba_{II}) and 6-coordinated (Ba_{III}) polyhedron [11]. The multi-Ba sites properties in $BaMgSiO_4$ lead to the different crystalline field intensity of BaO_n polyhedron. The energy level splitting of 5d orbit would be different when Eu^{2+} (outer electron configuration:$4f^7$) replace the different Ba sites, thus the Eu^{2+} in $BaMgSiO_4:Eu^{2+}$ shows the multi-colored emission. But there is a problem that how to control the doped ions to substitute the appointed Ba sites and obtain the expected emission color.

In this work, we main discussed the color tuning and the energy transfer of the Eu^{2+} and Sr^{2+} doping ions in $BaMgSiO_4$ in combining with the photoluminescence spectra of $BaMgSiO_4$:RE (RE = Eu^{2+}, Sr^{2+}) under the NUV excitation.

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https://doi.org/10.1016/j.matchemphys.2017.12.070
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2. Experimental section

$BaCO_3$ (99.50%), $(MgCO_3)_4\cdot Mg(OH)_2\cdot 5H_2O$ (99.50%), SiO_2(99.50%), Eu_2O_3 (99.99%) and $SrCO_3$ (99.90%) are used as the starting materials. First, the starting materials are mixed together in stoichiometric amounts. After intimately mixing the starting materials with ethanol, the obtained mixture are fired at 1300 °C for 8 h under a reducing atmosphere (H_2:N_2 = 5%:95%), and then cooled to the room temperature.

All the samples are checked by X-ray diffraction (XRD) using Rigaku diffractometer with Ni-filtered CuKα radiation. The UV and NUV excitation and emission spectra are measured by a Xe lamp (FLS-920T). Time-resolved fluorescence measurements were performed by time correlated single-photon counting on FLS-920T fluorescence spectrometer (Edinburgh Instruments) equipped with a pulsed hydrogen lamp. All the measurements are performed at room temperature.

3. Results and discussion

3.1. XRD analysis

The XRD patterns of $Ba_{1\text{-}x}MgSiO_4$:$x$$Eu^{2+}$ ($0 \le x \le 0.07$) and $Ba_{0.993\text{-}y}MgSiO_4$:$0.007Eu^{2+}$, ySr^{2+} ($0 \le y \le 0.07$) are respectively shown in the Fig. 1(a) and (b), together with the standard card No.81-2317, the insert is the enlarged image in the region of 27°−29.5°. From Fig. 1(a) and (b), it is observed that the obtained reflection peaks are matched well with the reported hexagonal phase $BaMgSiO_4$, except for a weak impurity peak at 32.1° which belongs to the $Ba_2MgSi_2O_7$ phase. The diffraction peaks of $Ba_{1\text{-}x}MgSiO_4$:$x$$Eu^{2+}$ ($0 \le x \le 0.07$) slightly shift to the large angle region with increasing the Eu concentration, which is shown in the enlarged image in the Fig. 1 (a). Based on ref. [11], the Ba^{2+} ions in $BaMgSiO_4$ occupy three sites with the coordination number (CN) 6, 9 and 9. The effective ionic radius of Ba^{2+} is respectively 1.35 Å and 1.47 Å in the hexa- and nine-coordinated polyhedron according to Ref. [12], which is larger than that of Eu^{2+} (1.17 Å and 1.30 Å). Therefore, the doped Eu^{2+} ions to replace Ba^{2+} ions will result in the reduction of the unit cell, and then the diffraction peaks of $Ba_{1\text{-}x}MgSiO_4$:$x$$Eu^{2+}$ ($0 \le x \le 0.07$) shift to the large angle region. The similar phenomenon is also observed in the XRD patterns of $Ba_{0.993\text{-}y}MgSiO_4$:$0.007Eu^{2+}$, ySr^{2+} ($0 \le y \le 0.07$) in Fig. 1 (b). The reason of the diffraction peak shift in Fig. 1 (b) is same as that of $Ba_{1\text{-}x}MgSiO_4$:$x$$Eu^{2+}$ ($0 \le x \le 0.07$) and is the effective ionic radii of Ba^{2+} (1.35 Å and 1.47 Å) are bigger than that of Sr^{2+} (1.18 Å and 1.31 Å) [12]. This phenomenon is consistent with Vegard's law and

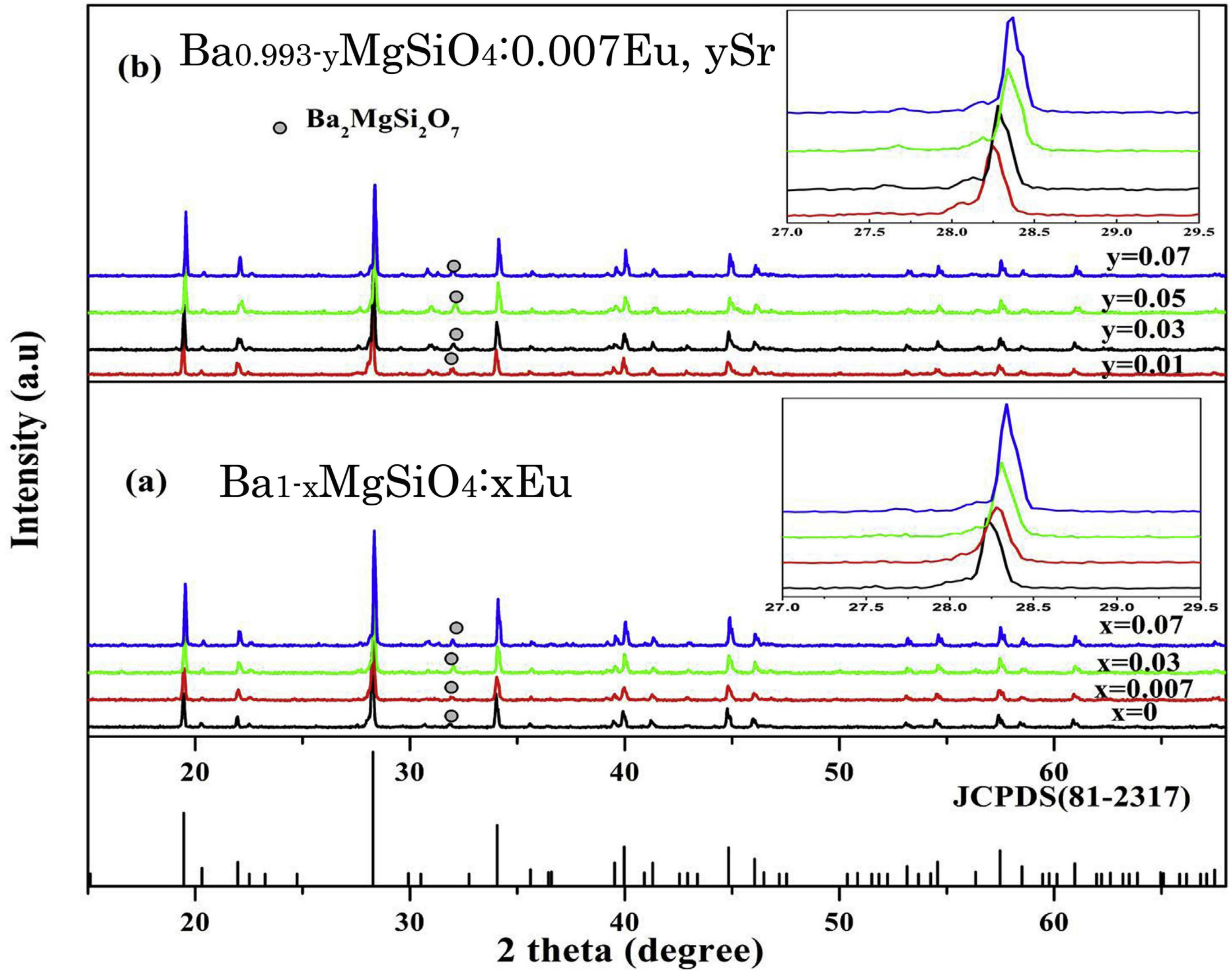

Fig. 1. XRD patterns of $Ba_{1\text{-}x}MgSiO_4$:$x$$Eu^{2+}$ ($0 \le x \le 0.07$) (a) and $Ba_{0.993\text{-}y}MgSiO_4$:$0.007Eu^{2+}$, ySr^{2+} ($0 \le y \le 0.07$) (b), together with the standard card No.81-2317.