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New insight into the structure evolution and site preferential occupancy of $Na_2Ba_6(Si_2O_7)(SiO_4)_2:Eu^{2+}$ phosphor by cation substitution effect

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ABSTRACT

A series of single-phased $Na_2Ba_{5.99-x}(Si_2O_7)(SiO_4)_2:0.01Eu^{2+}$, xMg^{2+} and $Na_2Ba_{5.99-y}(Si_2O_7)(SiO_4)_2:0.01Eu^{2+}$, yZn^{2+} phosphors have been successfully prepared *via* the solid-state reaction. Structural refinement, luminescence property, color tuning and thermally stability were systematically investigated. The as-prepared $Na_2Ba_6(Si_2O_7)(SiO_4)_2:0.01Eu^{2+}$ phosphor showed broad excitation bands from 250 nm to 450 nm and presented wide emission bands under 365 nm excitation, which could be decomposed by Gaussian fitting into three peaks corresponding to different Eu luminous centers named Eu1, Eu2 and Eu3. By substituting Mg^{2+} or Zn^{2+} for Ba^{2+}, the relative intensities of Eu1, Eu2 and Eu3 emission bands changed gradually. Combined with the variation tendencies of Ba–O bond lengths by Rietveld refinement, the possible mechanism of the luminescence transformation of Eu^{2+} ion was the preferential occupancy of Eu^{2+} at different crystallographic sites. In addition, the introduction of Mg^{2+} ion expressed more obvious improvement on the thermal quenching behaviors of Eu^{2+} than Zn^{2+} ion in this matrix. The emission intensities of Eu2 and Eu3 could be enhanced from 63.2% to 82.7% and 35.1%–46.8% at 373 K compared to the initial intensity when Mg^{2+} concentration was 0.10. Generally, this work sheds some new lights on the design and structure explanation of preferential occupancy at different crystallographic sites in phosphors.

1. Introduction

Owing to the excellent luminescence performances of rare earth ions activated phosphor materials, they can be widely applied in many technology areas such as solid-state lighting, WLEDs, flat panel displays, biological diagnostic and biomedical areas etc [1–4]. Given the widespread use of technologies that employed these materials, new and highly efficient phosphors are highly desirable and sought through several strategies, including single crystal growth method [5], cation/anion substitutions [6], single particle diagnosis approach [7], heuristics optimization based solid state combinatorial chemistry method [8], design of energy transfers at different sites [9] and so on. These processes generally regulated and controlled the coordination environment surrounding activators, especially Ce^{3+} and Eu^{2+} ions because their 5*d*-4*f* transitions are sensitive to the structural variations [10,11]. The excitation and emission spectra, even the thermal quenching behaviors of phosphors could be tuned efficiently by adjusting the material compositions and lattice structures [12]. In particular, multitudinous cation/anion substitutions have been widely investigated to design novel phosphor materials and optimize their luminescence properties. Meanwhile, lots of luminescent mechanisms related to cation/anion substitutions have been proposed to clarify the relationship between the structural changes and luminescence properties such as nephelauxetic effect and covalent bond theory [13], mixing of nanophases [14], crystal field effect [15,16], crystal-site engineering [17,18] and so on. However, these mechanisms could not explain all problems for one-time, and sometimes, certain phenomenon also needed to combine several theories and there were still some unclear underlying mechanisms that needed to be specified for further study. Among various luminescent mechanisms of cation/anion substitutions, crystal-site engineering mechanism has been well designed for finding novel and high efficient solid-state luminescence materials and considered recently [19]. In brief, the dopant ions could preferentially enter

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into a more appropriate site because of the possible size mismatch between the activator ion and the host cation at the specific site when there are several kinds of cation site in a host [20]. This method frequently formed solid solutions, and just adjusted the preferential occupancy of activators at different crystallographic sites with different coordination environments, leading to the control of the luminous properties of the phosphors [21–23]. Hence, the selection of host materials plays a crucial role in designing phosphor materials, it commonly requires host materials to contain more than one cation site for accommodating activator ions, and the local environment can be varied in a controllable way.

Due to the stable crystal structures, excellent physicochemical properties and flexible application spaces, alkaline earth silicate-based inorganic materials have drawn enormous attentions recently in many realms, such as advanced functional materials, ceramic industries and construction materials and so on. In particular, alkaline earth silicate-based phosphors such as $BaY_2Si_3O_{10}:Tm^{3+}$, Dy^{3+} [24], $Ca_2MgSi_2O_{7-x}N_x:Eu^{2+}$ [25], $CaY_4(SiO_4)_3O:Bi^{3+}$, Eu^{3+} [26], $Sr_3Gd_2(Si_3O_9)_2:Ce^{3+}$, Tb^{3+}/Mn^{2+} [27], $Ba_2Gd_2Si_4O_{13}:Ce^{3+}$ [28] have been studied and reported. Here, we choose $Na_2Ba_6(Si_2O_7)(SiO_4)_2$ (NBSS) as matrix. In this structure, it typically contains three kinds of Ba^{2+} sites, in which Ba1 and Ba2 are in nine-coordination environment 4*e* sites with tricapped trigonal prismatic geometry, while Ba3 occupies ten-coordinated O polyhedra 4*e* sites constructing bicapped square prism, and all sites are easily occupied by certain kinds of rare earth ions and transition metal ions [29]. Therefore, it could be simply believed that the Ba^{2+} sites would be accommodated by Eu^{2+} ions and lead to three different luminescent centers. Moreover, the coordination environment of 4*e* sites could be affected by the compositional substitution and structure variation, and then caused the modification and regulation of the luminescent properties of Eu^{2+} ions.

In the present study, the cation substitution strategy was applied to the mixed anion silicate structure NBSS host *via* solid state reaction. The doping concentration of Eu^{2+} was controlled at the level of 1.0 mol. % relative to Ba^{2+} in the NBSS host. The present work focused on analyzing the dependent of luminescent properties on the structural variations of NBSS:Eu^{2+} phosphors as gradually substituting Ba^{2+} by Mg^{2+} or Zn^{2+} ion. By changing the doping contents of Mg^{2+} or Zn^{2+} ions, the relative intensities of the three emission bands belonged to Eu1, Eu2 and Eu3 could be controlled and adjusted efficiently. Then the relationship between structural variations and the photoluminescence transformations was revealed and possible luminescence mechanisms were also proposed. Finally, the thermal quenching behaviors of $Na_2(Ba, Mg)_6(Si_2O_7)(SiO_4)_2:Eu^{2+}$ and $Na_2(Ba, Zn)_6(Si_2O_7)(SiO_4)_2:Eu^{2+}$ phosphors were also systematically investigated.

2. Experimental

2.1. Materials and synthesis

A series of polycrystalline $Na_2Ba_{5.99-x}(Si_2O_7)(SiO_4)_2:0.01Eu^{2+}$, xMg^{2+} (x = 0, 0.05, 0.10, 0.15, 0.20, 0.25, 0.30) (Mg^{2+} series) and $Na_2Ba_{5.99-y}(Si_2O_7)(SiO_4)_2:0.01Eu^{2+}$, yZn^{2+} (y = 0, 0.05, 0.10, 0.15, 0.20, 0.25) (Zn^{2+} series) (x, y represents mol. % in this article) powder samples were prepared *via* conventional high temperature solid state reaction process. On the basis of the similar effective ionic radius and valence of the cation, we suggested that Eu^{2+}, Mg^{2+} and Zn^{2+} ions prefer to occupy Ba^{2+} site in the host of NBSS. In order to facilitate the expressions, in the following sections, $Na_2Ba_{5.99-x}(Si_2O_7)(SiO_4)_2:0.01Eu^{2+}$, xMg^{2+} and $Na_2Ba_{5.99-y}(Si_2O_7)(SiO_4)_2:0.01Eu^{2+}$, yZn^{2+} were abbreviated as NBSS:Eu^{2+}, xMg^{2+} and NBSS:Eu^{2+}, yZn^{2+}. The starting materials, Na_2CO_3 (A.R.), $BaCO_3$ (A.R.), SiO_2 (A.R.), Eu_2O_3 (≥99.99%) $Mg(OH)_2\cdot4MgCO_3\cdot5H_2O$ (A.R.) and $5ZnO\cdot2ZnCO_3\cdot4H_2O$ (A.R.) were thoroughly ground and mixed for 30 min with stoichiometric molar ratios in an agate mortar to form a homogeneous mixture. Then the mixtures were transferred into alumina crucibles and sintered at 1000 °C for 8 h under a reducing atmosphere of 95% N_2-5% H_2 in a horizontal tube furnace. After slowly cooled down to room temperature, the products were ground into powders, washed in the beaker and dried in the air oven, then used for the subsequent texts.

2.2. Characterization

The phase purity of the as-prepared samples was characterized by X-ray powder diffractometer (XRD) (Bruker D8 Focus, Bruker, Kalsruhe, Germany) with Ni-filtered Cu-Kα (λ = 1.540598 Å) radiation at 40 kV tube voltage and 40 mA tube current. The XRD data were collected in a 2θ range from 5° to 70°, with the continuous scan mode at the speed of 0.05 s per step with step size of 0.01°. The measurements of photoluminescence emission and photoluminescence excitation spectra were performed by using fluorescence spectrometer (Fluoromax-4P, Horiba Jobin Yvon, New Jersey, USA) equipped with a 450 W xenon lamp as the excitation source and both excitation and emission spectra were set up to be 1.0 nm with the width of the mono-chromator slits adjusted as 0.50 nm.

3. Results and discussion

3.1. Phase identification, XRD refinement and crystal structure

The phase purity of the as-prepared samples was firstly identified by XRD. The XRD patterns of representative NBSS:Eu^{2+}, xMg^{2+} (x = 0, 0.10, 0.20, 0.30), NBSS:Eu^{2+}, yZn^{2+} (y = 0.05, 0.15, 0.25) as well as the standard reference of monoclinic NBSS (ICSD-62912) are given in Fig. 1. Although some Ba sites have be substituted by smaller Mg or Zn ions based on the charge balance and ion radii, all the diffraction peaks were well-indexed to the reported monoclinic NBSS phase and no other distinct impurities were observed, indicating that single-phase NBSS samples were obtained even introducing a small quantity of Mg or Zn ions. In addition, Fig. S1 depicts the partial powder XRD patterns between 30.7° and 31.8° of NBSS:Eu^{2+}, xMg^{2+} and NBSS:Eu^{2+}, yZn^{2+} samples with substitution concentrations of Mg^{2+} and Zn^{2+} range from 0 to 0.30 and 0 to 0.25. We could find that the 2θ of diffraction peaks shifted to higher value with the increasing of Mg^{2+} and Zn^{2+} ions. The phenomena were ascribed to the smaller Mg^{2+} and Zn^{2+} ions substituted for the larger Ba^{2+} ions. It also certified the successful incorporation of Mg^{2+} and Zn^{2+} into the lattice and the formation of solid solutions according to the Vegard rule [30]. Fig. 2 shows the Rietveld fitting of the XRD pattern of representative NBSS:Eu^{2+} sample upon the start structural model of NBSS (ICSD-62912). The Refined structure parameters, cell parameters and selected bond length of NBSS:Eu^{2+} sample, Mg^{2+}-substituted NBSS:Eu^{2+}, xMg^{2+} (x = 0.05, 0.10, 0.15, 0.20, 0.25, 0.30) and Zn^{2+}-substituted NBSS:Eu^{2+}, yZn^{2+} (y = 0.05, 0.10, 0.15, 0.20, 0.25) samples are listed in Tables 1 and 2 and Tables S1–S2. According to the refinement data, the NBSS:Eu^{2+} sample crystallized in monoclinic phase with space group of $P2_1/a$, a = 11.5378 Å, b = 9.5183 Å, c = 7.8565 Å, V = 822.045 Å^3 and Z = 2. All atom positions, fraction factors, and thermal vibration parameters were refined by convergence and satisfied well the reflection conditions, R_{wp} = 5.43%, R_p = 8.73% and χ^2 = 7.22. Moreover, we could find in Fig. 3(a) that cell parameters