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Intense emission of $Ba_2MgSi_2O_7:Eu^{2+}$ under X-ray excitation for potential detecting applications

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ABSTRACT

A series of $Ba_{2\text{-}x}Eu_xMgSi_2O_7$ phosphors was prepared by a solid-state reaction method at high temperature. The theoretical density of the optimal $Ba_{1.93}Eu_{0.07}MgSi_2O_7$ material was calculated from the Rietveld refinement result. Eu L_3-edge X-ray absorption near edge structure (XANES) spectrum was measured to confirm the valence of Eu ions in $Ba_2MgSi_2O_7$. The X-ray excited radioluminescence and the thermoluminescence after β-ray irradiation were investigated based on the VUV-vis photoluminescence. The light yield of the optimal $Ba_{1.93}Eu_{0.07}MgSi_2O_7$ sample under X-ray excitation was estimated to be $\sim 29{,}000 \pm 6000$ photons/M eV. So the temperature-dependent luminescence properties of this sample under X-ray and 344 nm excitation were further studied, and the charge traps in the scintillation process were discussed through thermoluminescence spectra. The high scintillation intensity together with an appropriate intrinsic decay time and its non-hygroscopicity endow the further optimized phosphor $Ba_{1.93}Eu_{0.07}MgSi_2O_7$ a promising scintillation material for X-ray detection.

1. Introduction

Nowadays, much attention is being addressed to f-d transitions of lanthanide ions in different hosts for applications in lighting and displays [1–3]. As important host compounds of luminescence of lanthanide or transition metal ions, silicates have attracted much attention due to their good chemical and thermal stabilities [4–8]. Eu^{2+} ions have $4f^7$ ground and $4f^65d$ excited states, the parity allowed $4f^65d \rightarrow 4f^7$ transitions exhibit broad emission bands with decay times typically about 500 ns to 1 μs [9]. Thus Eu^{2+} doped materials may also have potential applications as scintillators [9–11]. Although Ce^{3+} doped luminescent materials are applied as scintillators to detect X/γ rays or thermal neutrons due to the fast Ce^{3+} decay characteristic, Eu^{2+} doped luminescent materials are less frequently reported for scintillators application [9,10].

The synthesis and characterization of Eu^{2+} doped $Ba_2MgSi_2O_7$ phosphors have been reported, but most of the work just focused on the photoluminescence properties [4–7]. In this article, the luminescence properties of Eu^{2+} doped $Ba_2MgSi_2O_7$ under VUV – UV (vacuum ultraviolet – ultraviolet) and X-ray excitation were reported. We will address the high scintillation intensity of $Ba_{1.93}Eu_{0.07}MgSi_2O_7$ and the role of charge carrier traps in the scintillation process under X-ray excitation at different temperatures.

2. Experimental

The polycrystalline luminescent materials $Ba_{2\text{-}x}Eu_xMgSi_2O_7$ (x=0.01, 0.07, 0.10) were prepared by a high temperature solid state reaction method in a CO reducing ambient which was generated from the incomplete combustion of thermal carbon. The starting materials were $BaCO_3$ (analytical reagent, A.R.), MgO (A.R.), SiO_2 (A.R.) and Eu_2O_3 (99.99%). After these raw materials were weighed stoichiometrically and mixed thoroughly in an agate mortar, they were pre-fired at 1073 K for 2 h and then reground and sintered at 1543 K for 5 h to obtain final products.

The phase purity and structure of the final products were checked by X-ray powder diffraction (XRD) using a D8 ADVANCE diffractometer with CuKα radiation (λ=0.15418 nm) at room temperature (RT). The Eu L_3-edge XANES spectra were collected on Shanghai Synchrotron Radiation Facility (SSRF) in a transmission mode. All spectra were achieved on BL14W beam line of the storage ring operating at 3.5 G eV with an optimal current around

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220 mA at RT. A liquid-He-cooled Si(111) double crystal monochromator was used in measurement. The ionization chamber with constant temperature at 298 K contained argon and nitrogen. The luminescent spectra in the UV–vis range and the decay curves were recorded with an Edinburgh Instruments FLS 920 combined fluorescence lifetime and steady-state spectrometer which was equipped with a time-correlated single-photon counting (TCSPC) card. The instrument was equipped with a CTI-Cryogenics temperature control system. A 450 W xenon lamp was used as the excitation source for the UV–vis spectra recording, the excitation photons for the luminescence decay curves collecting were provided by a 150 W F900 flash lamp with a pulse width of 1 ns and pulse rate of 40–100 Hz at RT. The VUV excitation and corresponding emission spectra were measured at the VUV spectroscopy experimental station on beam line 4B8 of the Beijing Synchrotron Radiation Facility. The emission spectra under X-ray excitation at RT and different temperatures, and thermoluminescence spectra were recorded by facilities at Delft University of Technology, The Netherlands [11]. The measurement and estimation of the light yield under X-ray excitation have been described in detail in our previous work [12].

3. Results and discussion

$M_2MgSi_2O_7$ (M=Ca, Sr, Ba) compounds have been identified to crystalize in tetragonal and monoclinic systems, respectively [4–6,13–18]. For our synthesized samples, XRD patterns of $Ba_2MgSi_2O_7$:Eu^{2+} are consistent with the monoclinic $Ba_2MgSi_2O_7$ [7,8]. To calculate the theoretical density, which is one of the main parameters of scintillation materials, the Rietveld refinement was performed for $Ba_{1.93}Eu_{0.07}MgSi_2O_7$ sample using the C2/c structure model as shown in Fig. 1[19]. The as-obtained goodness of fit parameters R_{wp}=2.06% R_p=1.31%, and R_B=0.98% can confirm the structure of our synthesized samples belong to the monoclinic system. The final refined structural parameters for $Ba_{1.93}Eu_{0.07}MgSi_2O_7$ are summarized in Table 1 and the theoretical density is calculated to be about 4.36 g/cm^3 according to the refinement result. Furthermore, another important parameter of scintillation materials, the effective atomic number (Z_{eff}) of $Ba_2MgSi_2O_7$ is estimated to be ~45.5 [20].

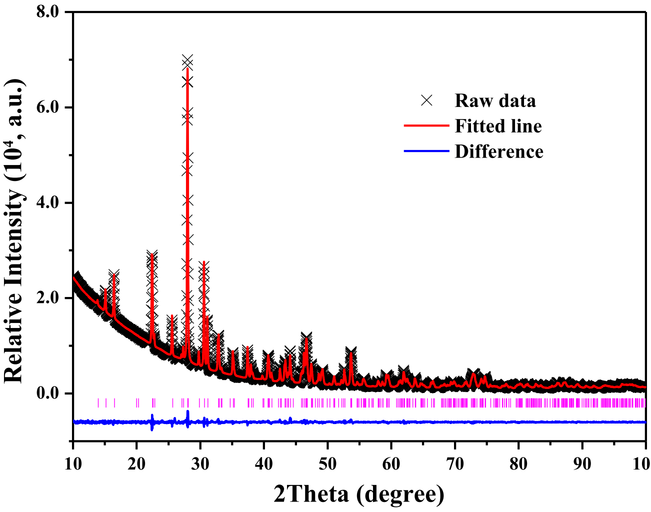

Fig. 1. The experimental (crosses) and calculated (red solid line) XRD patterns and their difference (blue solid line) of $Ba_{1.93}Eu_{0.07}MgSi_2O_7$. The pink ticks mark the Bragg reflection positions. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 1
Final refined structural parameters for $Ba_{1.93}Eu_{0.07}MgSi_2O_7$[a].

Atoms	Site	x	y	z	Occ.	B_{iso} (Å^2)
Ba1	8f	0.2727(1)	0.45580(9)	0.0250(1)	0.965	1.020(9)
Eu1	8f	0.2727(1)	0.45580(9)	0.0250(1)	0.035	1.020(9)
Mg1	4e	0	0.2576(7)	0.25	1	1.00(7)
Si1	8f	0.8867(7)	0.2816(3)	−0.1375(6)	1	1.19(6)
O1	4e	0	0.3343(9)	−0.25	1	1.16(7)
O2	8f	0.704(1)	0.3459(8)	−0.232(1)	1	1.16(7)
O3	8f	0.974(1)	0.3488(9)	0.041(1)	1	1.16(7)
O4	8f	0.900(1)	0.1354(6)	−0.133(1)	1	1.16(7)

[a] Symmetry, monoclinic; space group, C2/c; Z=4; a=8.4174(1) Å, b=10.7184(1) Å, c=8.4525(1) Å, β=110.7604(8) and V=713.08(2) Å^3; ρ=4.36 g/cm^{-3}. The occupancy factors for Ba/Eu were fixed as 0.965/0.035 according to the nominal composition in the refinement.

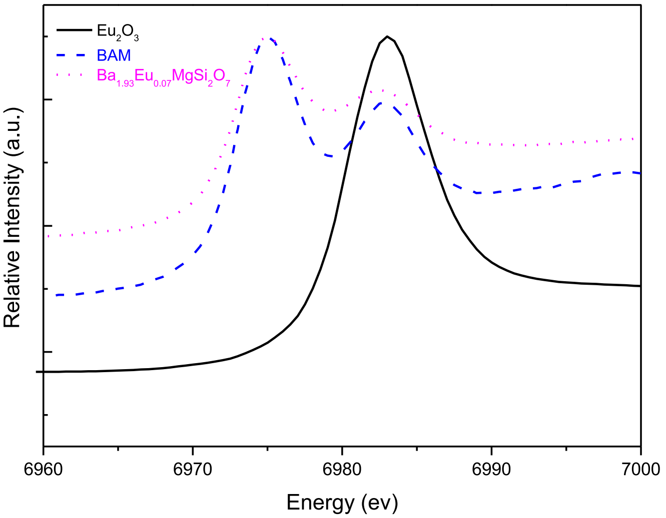

Fig. 2. The XANES spectra at Eu-L_3 edge of $Ba_{1.93}Eu_{0.07}MgSi_2O_7$, commercial $BaMgAl_{10}O_{17}$:Eu^{2+} (BAM) and Eu_2O_3 at RT.

To confirm the valence of Eu ions in $Ba_2MgSi_2O_7$, the Eu L_3 edge X-ray absorption near edge structure (XANES) spectrum of $Ba_{1.93}Eu_{0.07}MgSi_2O_7$ was measured and compared with that of commercial $BaMgAl_{10}O_{17}$:Eu^{2+} (BAM) and Eu_2O_3 at RT as shown in Fig. 2. The absorption peak at ~6983 eV in XANES spectrum of Eu_2O_3 (black solid curve) is due to so-called "white line" coupled to the absorption of L_3 edge of Eu^{3+}, and that at ~6975 eV in other two curves is due to the absorption of L_3 edge of Eu^{2+}[21]. The results indicate that Eu^{2+} occurs together with Eu^{3+} in $Ba_{1.93}Eu_{0.07}MgSi_2O_7$.

The photoluminescence, cathodoluminescence and electronic properties of $Ba_{2-x}Eu_xMgSi_2O_7$ have been reported in our previous work [7]. Fig. 3(a) shows the synchrotron radiation VUV-UV (black solid line) and lab UV–vis (red dash line) excitation spectra of $Ba_{1.9}Eu_{0.1}MgSi_2O_7$ by monitoring Eu^{2+} 501 nm emission at RT. The host excitonic absorption band can be observed below 200 nm with a maximum at about 180 nm. The broad band from 200 to 450 nm corresponds to the $4f^7 \rightarrow 4f^6 5d$ transitions of Eu^{2+} in $Ba_2MgSi_2O_7$. Two factors, the crystal field splitting of Eu^{2+} 5d state and the ^7F_J (J=0, …, 6) multiplets arising from the spin-orbit coupling of remaining $4f^6$ core in the excited state of Eu^{2+}, play a significant role in the shape of the f-d bands in excitation spectra. Since Eu^{2+} ions occupy Ba^{2+} sites with C_1 symmetry in the host compound, five f-d excitation bands would appear when we do not consider the coulomb interaction between $4f^6$ and 5d electrons to a first approximation, due to crystal field splitting of Eu^{2+} 5d state in this low symmetry site [22]. The unresolved bands in this range may first result from the overlapping of five f-d excitation bands. Furthermore, the fine ^7F_J (J=0, …, 6) structure may