

Dy³⁺-activated M₂SiO₄ (M = Ba, Mg, Sr)-type phosphors

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Abstract. The alkaline orthosilicates of M₂SiO₄ (M = Ba, Mg, Sr) activated with Dy³⁺ and co-doped with Ho³⁺ are prepared through conventional solid-state method, i.e., mixing and grinding of solid form precursors followed by high-temperature heat treatments of several hours in furnaces, generally under open atmosphere and investigated by X-ray diffraction (XRD) to get phase properties and photoluminescence (PL) analysis to get luminescence properties. The thermal behaviours of well-mixed samples were determined by differential thermal analysis (DTA)/thermogravimetry (TG). The PL spectra show that the 478 and 572 nm maximum emission bands are attributed, respectively, to ⁴F_{9/2} → ⁶H_{15/2} and ⁴F_{9/2} → ⁶H_{13/2} transitions of Dy³⁺ ions.

Keywords. Alkaline orthosilicate; solid-state reaction method; open atmosphere; luminescence; rare-earth ions.

1. Introduction

Silicates are classified as ortho or neo (1:4): isolated SiO₄ tetrahedra within the structure, i.e., absence of bridging oxygen atom between two silicon atoms, such as in olivine group, meta or cyclo (1:3) closed rings of linked Si–O tetrahedra sharing two oxygens like in beryl group and pyro or soro (2:7) having two linked Si–O tetrahedra sharing the oxygen depending upon Si:O ratio. They draw attention because of their potential applications in electronic packaging, photoluminescence (PL) and microwave communication areas due to their high efficiency, easy synthesis method and plenty of host materials [1–3]. Rare-earth-ion-activated inorganic lattices are a class of important functional luminescent materials being widely applied in varied fields, displays, solid-state lasers, lighting, medical treatment, etc. [4]. The trivalent Dy³⁺ ions exhibit 4f⁹ electronic configuration and two main emissions: the blue band (475–500 nm) due to the ⁴F_{9/2} → ⁶H_{15/2} transitions, and the yellow peak (570–600 nm) corresponding to the ⁴F_{9/2} → ⁶H_{13/2} transitions. They have been widely used in inorganic hosts as activators or co-dopants [5,6]. Therefore, Dy³⁺-activated phosphors can show blue, yellow and white emission on tuning the ratio of two dominant emission bands.

This work aimed to produce the alkaline orthosilicate of M₂SiO₄ (M = Ba, Mg, Sr) activated with Dy³⁺ and co-doped with Ho³⁺ by solid-state reaction method under open atmosphere.

2. Materials and methods

Stoichiometric amounts of high-purity raw materials 4MgCO₃·Mg(OH)₂·5H₂O (A.R.), BaCO₃ (99.9%), SrCO₃ (99.9%),

Dy₂O₃ (99.99%) and Ho₂O₃ (99.99% (Dy³⁺ and Ho³⁺ content of all samples was fixed to 0.2 and 0.1%, respectively, for the target composition M_{1.988}Dy_{0.008}Ho_{0.004}SiO₄ of M₂SiO₄ (M = Ba, Mg, Sr)) were mixed well and ground in an agate mortar. The powder forms of all three compositions were then pre-heated at 800°C for 2 h in a furnace. The pre-heated samples of three types of phosphor systems, which were Ba₂SiO₄:Dy, Ho, Mg₂SiO₄:Dy, Ho and Sr₂SiO₄:Dy, Ho, were sintered in pure alumina crucibles at 1300°C for 3 h, 1300°C for 6 h + 1320°C for 8 h and 1250°C for 6 h + 1270°C for 8 h under open atmosphere, respectively, and then cooled down to room temperature slowly. The synthesized phosphors were ground to powder form for the characterizations.

Simultaneous differential thermal analysis (DTA) and thermogravimetric (TG) analysis (Seiko Instruments Inc./Exstar TG/DTA 6200) at a heating rate of 10°C min⁻¹ from room temperature to 1300°C was employed to analyse the decomposition and the oxidation process of the mixed powders of phosphor systems. Then the heat treatments were applied, and a BRUKER AXS D8 ADVANCE model X-ray diffractometer, run at 40 kV and 30 mA (Cu-Kα radiation) in a step-scan mode (0.02°/2θ), was used to determine phases after sintering. Finally, the excitation and emission spectra of the synthesized phosphors were obtained using a photoluminescence spectrometer (Photon Technology International (PTI), QuantaMaster™ 30).

3. Results and discussion

3.1 Thermal analysis

To study the thermal behaviour of phosphor systems, mainly composed of 4MgCO₃·Mg(OH)₂·5H₂O, BaCO₃ and SrCO₃, DTA/TG was carried out between 50 and 1300°C (figures 1–3).

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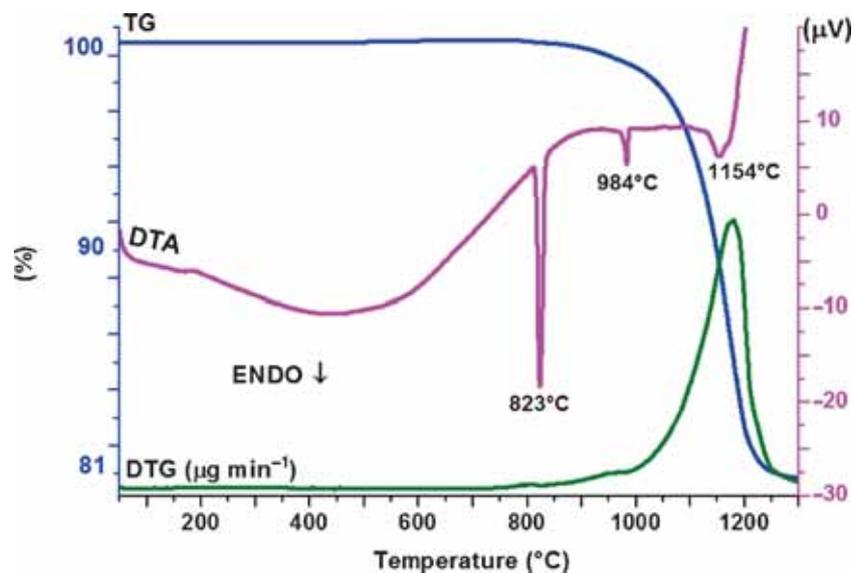


Figure 1. DTA/TG curves of $\text{Ba}_2\text{SiO}_4:\text{Dy}^{3+},\text{Ho}^{3+}$.

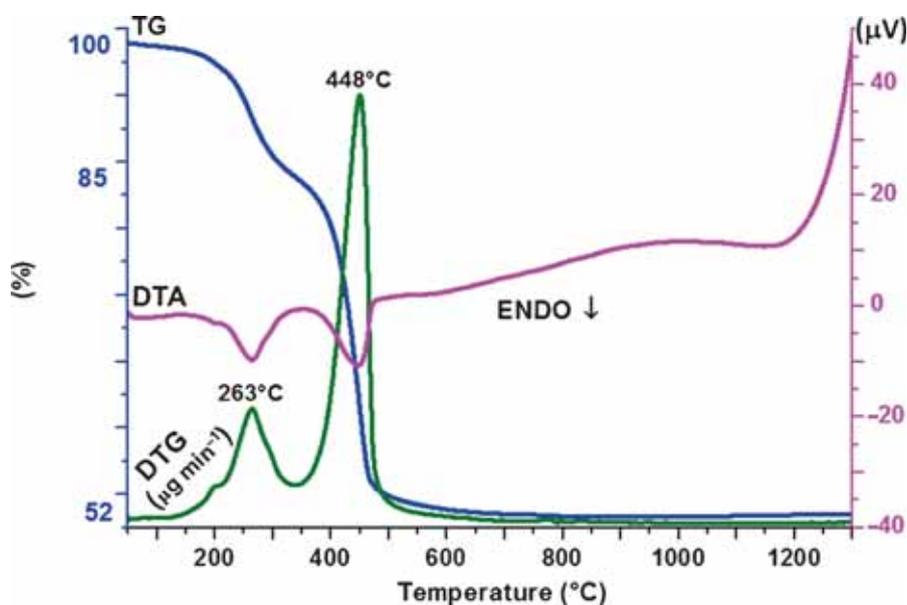


Figure 2. DTA/TG curves of $\text{Mg}_2\text{SiO}_4:\text{Dy}^{3+},\text{Ho}^{3+}$.

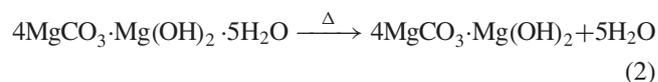
Figure 1 shows that the major weight loss between 900 and 1300°C is related to the decomposition of BaCO_3 and elimination of CO_2 in the system. The thermal behaviour of BaCO_3 decomposition reaction under heating is



With regard to the first endothermic peak attributed to the decomposition of BaCO_3 , which changes into BaO , from figure 1, an orthorhombic to rhombohedral transition at 823°C and a rhombohedral to cubic phase transition at 984°C take place. The TG curve exhibits a total mass loss equal to

19.1%, which is almost similar to the calculated mass loss (~19.2%).

As shown in figure 2, the dramatic weight losses starting from 200 to 350°C and a much larger decrease from 350 to 550°C are related to the decomposition of $4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$ in the system. The thermal behaviour of $4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$ reactions under heating could be summarized as follows:



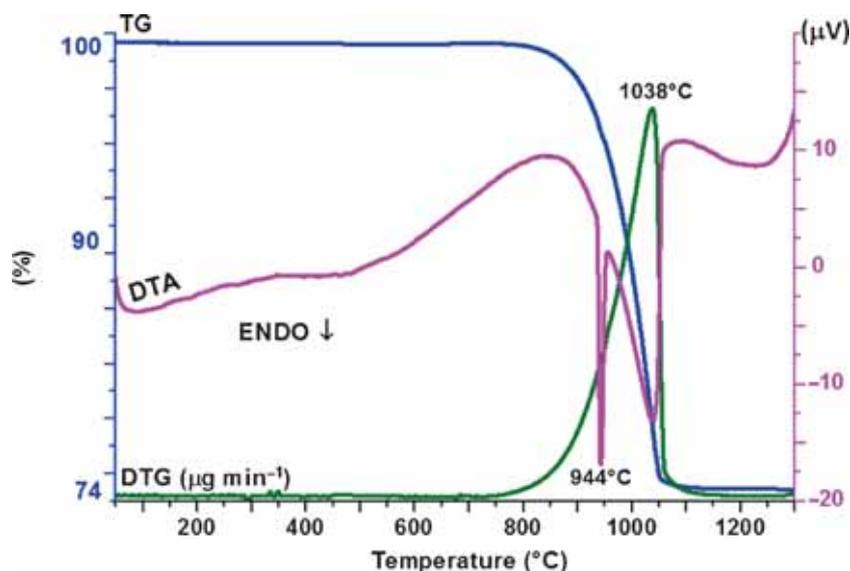
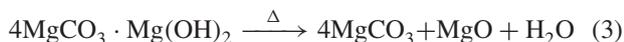


Figure 3. DTA/TG curves of Sr₂SiO₄:Dy³⁺,Ho³⁺.



The first endothermic peak is (at 263°C) attributed to the deviation of the hydroxyl group from Mg(OH)₂. The second endothermic peak shows (at 448°C) the decomposition of MgCO₃, which changes into MgO. The TG curve exhibits a total mass loss equal to 47.0%, which is almost similar to the calculated mass loss (~46.3%) attributed to the complete decomposition process of 4MgCO₃·Mg(OH)₂·5H₂O.

Figure 3 shows that there is a significant weight loss between 800 and 1150°C related to the decomposition of SrCO₃ and elimination of CO₂ in the system. The thermal behaviour of SrCO₃ decomposition reaction under heating is



With regard to the first endothermic peak attributed to the decomposition of SrCO₃, which changes into SrO, from figure 3, an orthorhombic to rhombohedral transition at 944°C takes place. The TG curve exhibits a total mass loss equal to 26.0%, which is almost similar to the calculated mass loss (~25.0%).

3.2 X-ray diffraction (XRD) analysis

The thermal analysis results helped determine the heat treatment temperatures for each sample. Thus, the first crystal formation temperature was more than about 800°C; hence the pre-sintering stage was applied at 800°C for 2 h and the basic sintering process was applied at 1300°C for 3 h, 1300°C for 6 h + 1320°C for 8 h and 1250°C for 6 h + 1270°C for 8 h for Ba₂SiO₄:Dy, Ho, Mg₂SiO₄:Dy, Ho and Sr₂SiO₄:Dy, Ho phosphors, respectively. XRD analysis was applied after the sinterings.

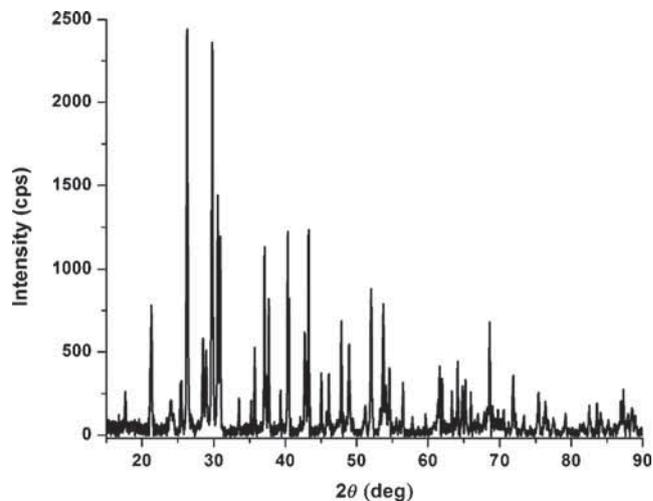


Figure 4. XRD pattern of Ba₂SiO₄:Dy³⁺, Ho³⁺ that was sintered at 1300°C for 3 h.

The XRD pattern of Ba₂SiO₄:Dy³⁺,Ho³⁺ is shown in figure 4. It matches well with the PDF 01-070-2113 Ba₂SiO₄ card [2] owing to optimum sintering conditions. All peaks show a single phase because no secondary phases are observed. The sample crystallizes in the orthorhombic structure with the lattice parameters $a = 5.805 \text{ \AA}$, $b = 10.2 \text{ \AA}$, $c = 7.499 \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 90^\circ$ and $\gamma = 90^\circ$.

The XRD pattern of Mg₂SiO₄:Dy³⁺,Ho³⁺ is presented in figure 5.

The determined diffraction patterns of Mg₂SiO₄:Dy³⁺, Ho³⁺, which was sintered at 1320°C for 8 h, can be well matched with the PDF 00-034-0189 card. The sample has an orthorhombic structure with the lattice parameters $a = 5.9817 \text{ \AA}$, $b = 10.1978 \text{ \AA}$, $c = 4.7553 \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 90^\circ$ and $\gamma = 90^\circ$. The important point here is that

the lower sintering temperature (1300°C for 6 h) is not sufficient for a single phase. It can be clearly seen from figure 6 that there are mainly MgO and SiO₂ secondary phases; hence increasing the sintering temperature causes elimination of SiO₂ and lowering of the MgO secondary phase.

Sr₂SiO₄:Dy³⁺, Ho³⁺ XRD pattern matches well with the PDF 00-039-1256 α -Sr₂SiO₄ card, thanks to optimum sintering conditions. The peaks show a single phase because of absence of secondary phases. The sample crystallizes in the orthorhombic structure with the lattice parameters $a = 7.079 \text{ \AA}$, $b = 5.672 \text{ \AA}$, $c = 9.743 \text{ \AA}$, (alpha) $\alpha = 90^\circ$, (beta) $\beta = 90^\circ$ and (gamma) $\gamma = 90^\circ$. The two main crystallographic modifications of strontium orthosilicate (Sr₂SiO₄), β -Sr₂SiO₄ (monoclinic) and α' -Sr₂SiO₄ (orthorhombic),

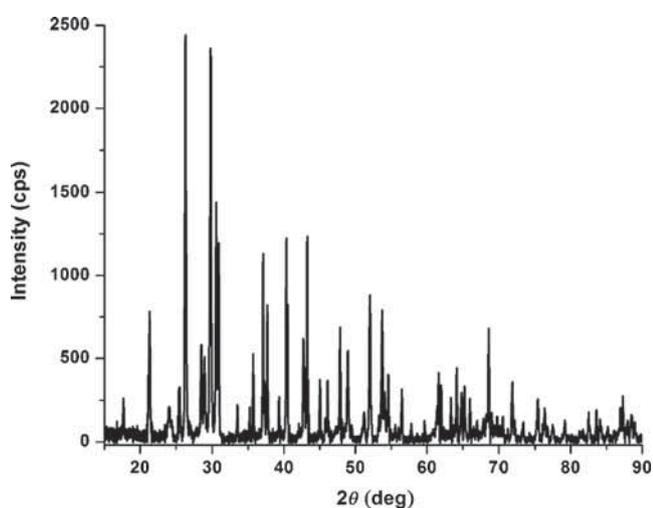


Figure 5. Comparative XRD patterns of Mg₂SiO₄:Dy³⁺,Ho³⁺ that was sintered at 1300°C for 6 h and 1320°C for 8 h.

have nearly related crystal structures that are made of SiO₄ tetrahedra. Despite this similarity, the difference is the small slope in the SiO₄ tetrahedra (Td) causing the lack of a mirror plane parallel to the (100) plane in the case of β -Sr₂SiO₄ [7]. Hence in the XRD spectra of the phosphor that was prepared, neither β -Sr₂SiO₄ phase nor secondary phase has been determined and this indicated that all prepared samples have a single phase, α' -Sr₂SiO₄.

3.3 Photoluminescence properties

All samples show good excitation and emission bands owing to activation by the rare earths, which are luminescence centres.

Figure 7 shows the PL spectra of Ba₂SiO₄:Dy³⁺,Ho³⁺ phosphor, which is excited at 386 nm in UV region and yields broad emission around 580 nm in green–yellow region.

The PL analysis of this system indicates 580 nm maximum narrow emission and another 482 nm emission band attributed to $^4F_{9/2} \rightarrow ^6H_{15/2}$ and $^4F_{9/2} \rightarrow ^6H_{13/2}$ transitions of Dy³⁺ ion, respectively [8–10]. The excitation band between 210 and 315 nm (292 nm) is attributed to charge transfer band (CTB) between the Dy³⁺ ion and the surrounding oxygen anions [8]. Furthermore, the 386 nm maximum excitation band and the other 321, 346, 421 and 446 nm excitation bands are attributed to $^6H_{15/2} \rightarrow ^4M_{17/2}$, $^5H_{15/2} \rightarrow ^4M_{15/2}$, $^6P_{7/2}$, $^6H_{15/2} \rightarrow ^4G_{11/2}$ and $^6H_{15/2} \rightarrow ^4I_{15/2}$ transitions of Dy³⁺ ion, respectively [8]. The strong excitation band located in the 350–410 nm wavelength range indicates that Dy³⁺ is significant for NUV white LEDs.

The PL spectra of Mg₂SiO₄:Dy³⁺,Ho³⁺ (in figure 8) phosphor under excitation at 352 nm in UV region showed maximum emission at 573 nm in yellow region.

The Mg₂SiO₄:Dy³⁺,Ho³⁺ phosphor shows a maximum narrow emission at 573 nm and another one at 482 nm, which are attributed to $^4F_{9/2} \rightarrow ^6H_{15/2}$ and $^4F_{9/2} \rightarrow ^6H_{13/2}$

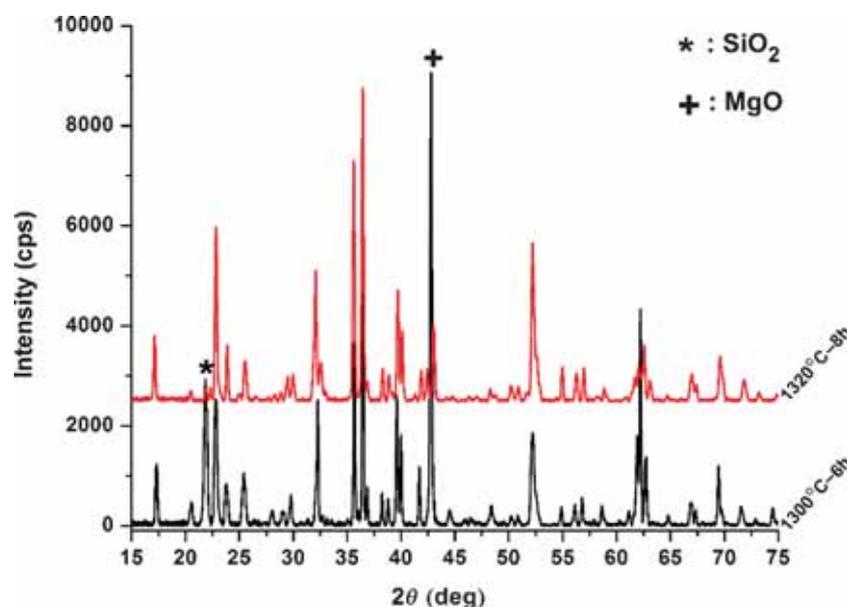


Figure 6. XRD pattern of Sr₂SiO₄:Dy³⁺,Ho³⁺ that was sintered at 1270°C for 8 h.

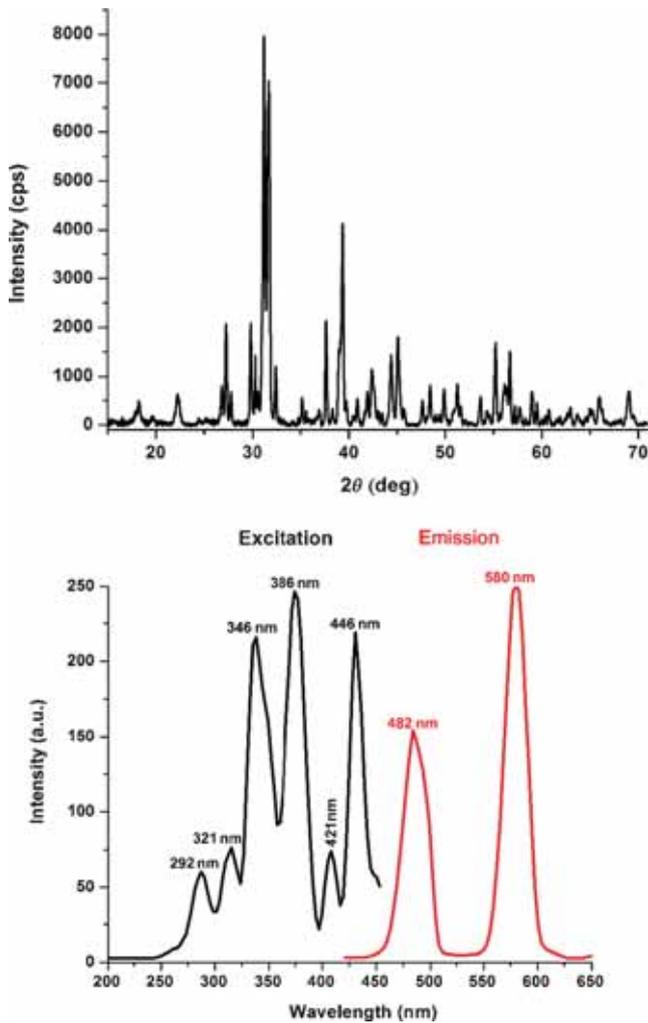


Figure 7. Photoluminescence spectra of Ba₂SiO₄:Dy³⁺,Ho³⁺.

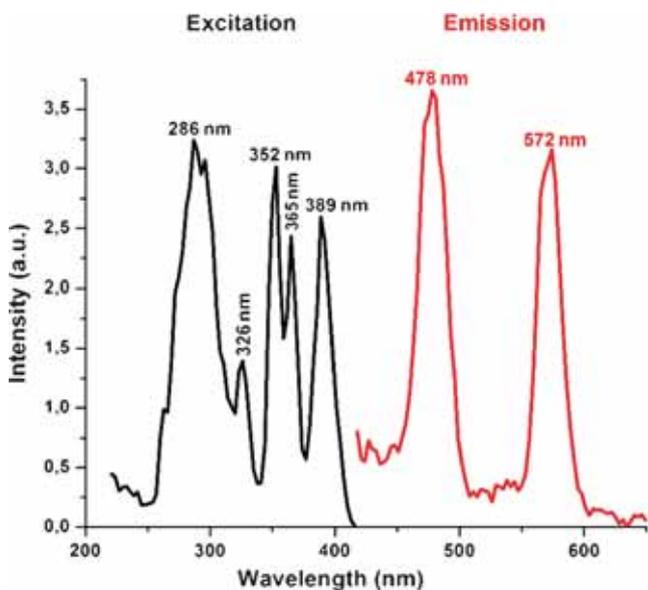


Figure 8. Photoluminescence spectra of Mg₂SiO₄:Dy³⁺,Ho³⁺ phosphor.

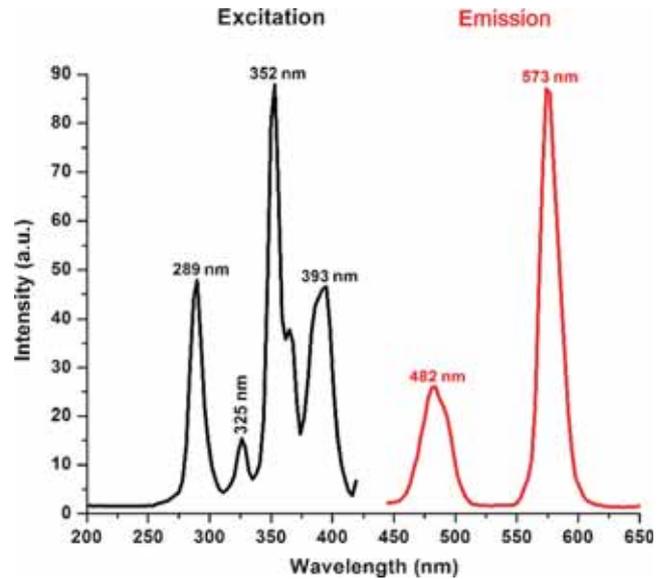


Figure 9. Photoluminescence spectra of Sr₂SiO₄:Dy³⁺,Ho³⁺ phosphor.

transitions of Dy³⁺ ion, similar to those in Dy³⁺-activated Ba₂SiO₄, respectively [8–10]. Also the similar excitation band at 289 nm is attributed to the CTB between the Dy³⁺ ion and the surrounding oxygen anions [8] and the other 326, 352 and 393 nm bands are attributed to ⁶H_{15/2} → ⁴M_{17/2}, ⁵H_{15/2} → ⁴M_{15/2}, ⁶P_{7/2} and ⁶H_{15/2} → ⁴I_{15/2}, ⁴F_{7/2} transitions of Dy³⁺ ion, respectively [8]. The strong excitation band located in the 350–410 nm wavelength range indicates that this phosphor is significant for NUV white LEDs, similar to the previous phosphor.

Figure 9 shows the PL spectra of Sr₂SiO₄:Dy³⁺,Ho³⁺ phosphor that was excited at 352 nm in UV region and yields two maximum narrow emissions at 478 nm in blue and 572 nm in yellow region.

The PL spectra show that the 478 and 572 nm maximum emission bands are attributed to ⁴F_{9/2} → ⁶H_{15/2} and ⁴F_{9/2} → ⁶H_{13/2} transitions of Dy³⁺ ion, similar to the previous two phosphors, respectively [8–10]. The excitation bands at 286, 326, 352, 365 and 389 nm are related to the CTB between the Dy³⁺ ion and the surrounding oxygen anions, ⁶H_{15/2} → ⁴M_{17/2}, ⁵H_{15/2} → ⁴M_{15/2}, ⁶P_{7/2}, ⁶H_{15/2} → ⁴I_{11/2}, ⁶H_{15/2} → ⁴G_{11/2} and ⁶H_{15/2} → ⁴I_{13/2}, ⁴F_{7/2} transitions of Dy³⁺ ion, respectively [8]. The strong excitation band located in the 350–410 nm wavelength range is like those of the previous phosphors and this phosphor can be significant for NUV white LEDs.

4. Conclusions

We aimed to synthesize and to characterize M₂SiO₄ (M = Ba, Mg, Sr) activated with Dy³⁺ and co-doped with Ho³⁺. Another important objective was to explore the PL properties of M₂SiO₄ (M = Ba, Mg, Sr) activated with Dy³⁺ and

co-doped with Ho^{3+} . It was proved that the host structures synthesized via the solid-state reaction method, M_2SiO_4 ($\text{M} = \text{Ba}, \text{Mg}, \text{Sr}$) activated with Dy^{3+} and co-doped with Ho^{3+} rare-earth ions, are good phosphors with intense emissions in blue and yellow regions, which correspond to the magnetic dipole transition (${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{15/2}$) and the hypersensitive electric dipole transition (${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{13/2}$), respectively, of Dy^{3+} . Hence the PL analysis showed that all the different activated hosts exhibit similar emissions due to the same emission centre, thanks to its two intense emission bands in the blue (470–500 nm) and yellow regions (560–600 nm). An important point to be noticed here in all the PL analysis results is that Dy^{3+} -doped and Ho^{3+} -co-doped Ba_2SiO_4 host structure has the maximum intensity compared with other hosts with the same rare-earth ions.

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