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Analysis of emission of Eu^{3+} and Dy^{3+} doped Magnesium Boro-Tellurite (MBT) ceramics

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Rare earth (RE) ions play an important role in the improvement of the optical properties of ceramics. Rare-earth ceramics are commonly used in display panels, fluorescent lamps and lasers. The luminescence properties of Magnesium Boro-Tellurite (MBT) Eu^{3+} and Dy^{3+} doped ceramics have not been reported before. Therefore, the aim of this paper is to determine the effect of different compositions on the luminescence properties of the MBT material. A series of $xTeO_2$–$(70-x)B_2O_3$–$30MgO$ ceramics with $10 \leqslant x \leqslant 40$ mol % doped with 1 mol % of Eu^{3+} and Dy^{3+} ions was prepared via the solid-state reaction method. The influence of various compositions on the crystalline phase and photoluminescence properties of the samples were investigated by X-ray diffraction (XRD) and luminescence spectroscopy. The crystalline phases obtained in this study are $Mg_3(BO_3)_2$, MgB_4O_7, $Mg_2B_2O_5$, $Mg(Te_2O_5)$ and $MgTe_3O_6$. It was stated that the crystalline phases have not changed as a result of doping with Eu^{3+} and Dy^{3+} ions. The emission spectra of Eu^{3+}: MBT ceramics showed strong red emission at 612 nm due to the transition of $^5D_0 \rightarrow {}^7F_2$ and meanwhile, the Dy^{3+}: MBT ceramics showed a blue emission at 480 nm due to $^4F_{9/2} \rightarrow {}^6H_{15/2}$ transition and yellow emission at 576 nm due to $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition. Both the rare-earth doped phosphors showed bright emission.

Keywords: *Magnesium Boro-Tellurite (MBT); luminescence; ceramics*

1. Introduction

Luminescence materials play an important role in the high-resolution display devices, such as cathode ray tubes (CRT), plasma display panels (PDP) and field emission displays (FED) [1, 2]. The rare earth-activated phosphor has shown to be a good luminescent material due to the improvement in lumen output, color rendering index, energy efficiency and radiation stability [3, 4]. In addition, Eu^{3+} and Dy^{3+} ions are important due to emission near-UV and visible light range. It is well known that Eu^{3+} ions show red color emission corresponding to the transition of $^5D_0$–$^7F_2$ at 611 nm [5–8]. On the other hand, Dy^{3+} ions exhibit two visible emission peaks including a blue emission at 480 nm, corresponding to the transition of $^4F_{9/2}$–$^6H_{15/2}$ and a yellow emission at 570 nm due to the $^4F_{9/2}$–$^6F_{13/2}$ transitions [9–13].

In recent years, there has been an increasing interest in rare-earth (RE) doped borate and tellurite due to their potential applications in glass. The research on boro-tellurite glasses doped with different rare earth ions have been reported by many researchers [14, 15]. However, the luminescence properties of Magnesium Boro-Tellurite (MBT) Eu^{3+} and Dy^{3+} doped ceramics have rarely been reported. Furthermore, there is no reliable evidence of the connection between luminescence properties and the host composition. Therefore, in this paper the influence of different TeO_2 concentrations on the luminescent properties of MBT Eu^{3+} and Dy^{3+} ions doped ceramic material were investigated.

2. Experimental

MBT: Eu^{3+} and MBT: Dy^{3+} ceramics samples were prepared by the conventional solid state method with the composition of

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$x\text{TeO}_2$–$(70-x)\text{B}_2\text{O}_3$–$30\text{MgO}$ with $10 \leqslant x \leqslant 40$ mol % doped with 1 mol % of Eu^{3+} and Dy^{3+} ions. H_3BO_3 (99.99 %), TeO_2 (99.99 %), MgO (99.99 %), Eu_2O_3 (99.99 %) and Dy_2O_3 (99.99 %) were used as raw materials. The starting materials were weighed according to the composition of the samples and thoroughly grounded in an agate mortar. Then, the homogeneous mixtures were sintered at 750 °C for 6 hours. Phase identification of the samples was carried out by X-ray diffractometer (XRD), Siemens Diffraction D500, with CuKα radiation. The emission spectra were obtained using Jasco fluorescence spectrophotometer, model FP8000. All the measurements were recorded at room temperature.

3. Results and discussion

3.1. XRD analysis

The X-ray diffraction patterns of MBT: Eu^{3+} and MBT: Dy^{3+} ceramics are shown in Fig. 1 and 2. The crystalline phase of $\text{Mg}_3(\text{BO}_3)_2$, MgB_4O_7, $\text{Mg}_2\text{B}_2\text{O}_5$, $\text{Mg}(\text{Te}_2\text{O}_5)$ and MgTe_3O_6 were identified by comparing with the standard JCPDS Card No. of 00-003-0823, 00-031-0787, 00-016-0168, 01-073-3922 and 00-022-0437), respectively. Meanwhile, in MBT: Dy^{3+} ceramics, six different crystalline phases were identified as $\text{Mg}_3(\text{BO}_3)_2$, MgB_4O_7, $\text{Mg}_2\text{B}_2\text{O}_5$, $\text{Mg}(\text{Te}_2\text{O}_5)$, $\text{MgTe}_6\text{O}_{13}$ and TeO_2 with the standard JCPDS Card No. 01-075-1807, 00-031-0787, 00-016-0168, 01-073-3922, 00-028-0634 and 01-074-0269, respectively. $\text{Mg}(\text{Te}_2\text{O}_5)$ phase is the majority phase. However, as the concentration of TeO_2 increases, the impurity phases of $\text{Mg}_3(\text{BO}_3)_2$, MgB_4O_7, and $\text{Mg}_2\text{B}_2\text{O}_5$ gradually disappear up to 40 mol % of TeO_2, and it can be seen that $\text{Mg}(\text{Te}_2\text{O}_5)$ and MgTe_3O_6 phases become then dominant. Moreover, the incorporation of Eu^{3+} and Dy^{3+} ions does not change the crystalline phase of the prepared samples due to the low dopant concentrations.

3.2. Luminescence spectra analysis

3.2.1. MBT: Eu^{3+} ceramics

The emission spectra of MBT: Eu^{3+} ceramics, recorded using 396 nm excitation, are shown in
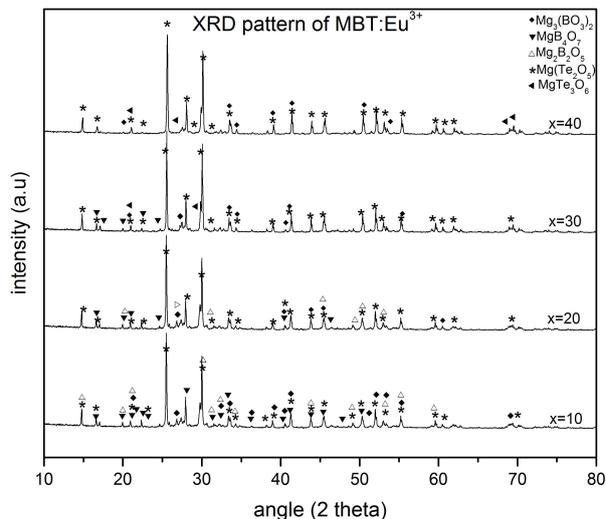

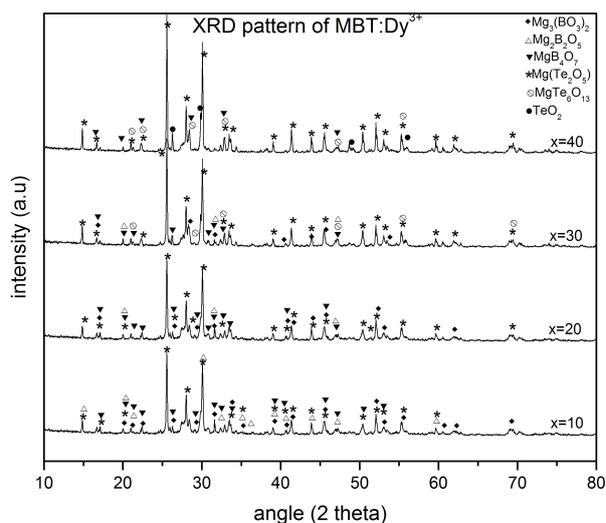Fig. 1. X-ray diffraction patterns of MBT: Eu^{3+} ceramics.

Fig. 2. X-ray diffraction patterns of MBT: Dy^{3+} ceramics.

Fig. 3. It can be seen that the emission spectra of the MBT: Eu^{3+} ceramics are composed of intense and sharp lines, in the wavelength range of 550 to 750 nm, which are attributed to the transition from the excited $^5\text{D}_0$ level to $^7\text{F}_J$ (J = 0 to 4) levels [16]. The strong emission peaks, observed at 591 nm and 612 nm, can be assigned to the transitions of $^5\text{D}_0$–$^7\text{F}_1$ and $^5\text{D}_0$–$^7\text{F}_2$, which corresponds to the orangish-red and red emission, respectively [17, 18]. The weak emission observed at 649 nm is due to the transition of $^5\text{D}_0$–$^7\text{F}_3$ and the

one at 701 nm is attributed to the $^5D_0$–$^7F_4$ transition. Among these peaks, the red emission peak at 612 nm is more dominant than the other peaks, and this peak originates from the electric dipole transitions of $^5D_0$–$^7F_2$, which indicates that Eu^{3+} occupies a non-centrosymmetric site [19].

The luminescence spectra show that the emission intensity of MBT: Eu^{3+} ceramics is enhanced with an increase of TeO_2 from 10 to 40 mol %, which results in enhancement of the red emission of the samples. From Fig. 3 it is apparent that the luminescent intensity reaches its maximum in MBT: Eu^{3+} (x = 30). Fig. 4 shows that the ratio of $^5D_0$–$^7F_1$/$^5D_0$–$^7F_2$ intensities increases with the increase in x value up to 30 mol %. This is because the $^5D_0$–$^7F_1$/$^5D_0$–$^7F_2$ ratio is related to the electronegativity of the next-neighbor element [20]. The Te atom has a higher electronegativity than the B atom and the substitution of B by Te has an influence on the property of ion bond in the host, which further affects the excitation energy of $xTeO_2$–$(70 - x)B_2O_3$–$30MgO$ group [20].

Fig. 4. $^5D_0$–$^7F_1$/$^5D_0$–$^7F_2$ intensity ratio of Eu^{3+} in MBT: Eu^{3+} ceramics (the line is shown for eyes guideline).

Fig. 5. Comparison of the room temperature PL spectra from MBT: Dy^{3+} ceramics.
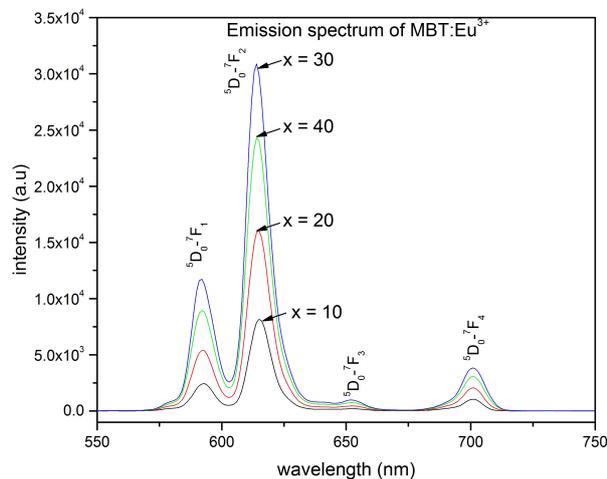

Fig. 3. Comparison of the room temperature PL spectra from MBT: Eu^{3+} ceramics.

3.2.2. MBT: Dy^{3+} ceramics

The emission spectra of MBT: Dy^{3+} ceramics at 350 nm excitation are shown in Fig. 5. All the spectra show the main characteristic emission lines of Dy^{3+}, which consist of ma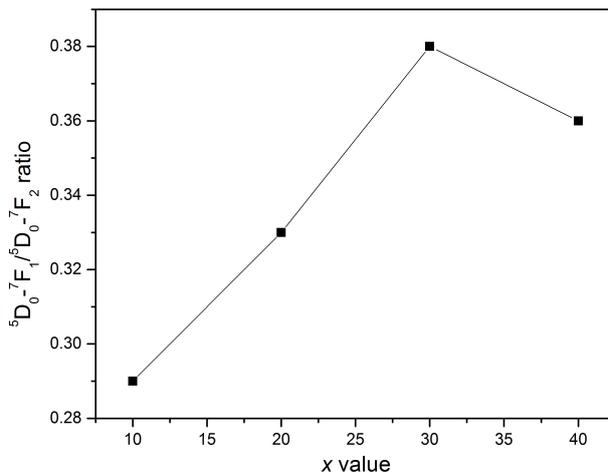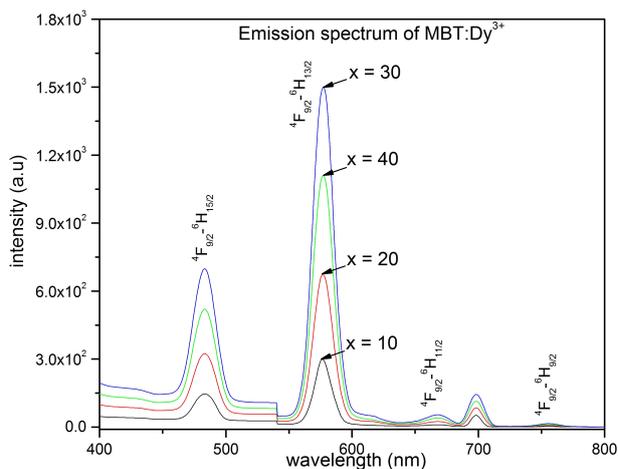gnetic dipole transition, $^4F_{9/2}$–$^6H_{15/2}$ at 483 nm (blue), and hypersensitive electric dipole transition, $^4F_{9/2}$–$^6H_{13/2}$ at 577 nm (yellow) [21]. Apart from these peaks, two weak emission peaks at 668 nm and 698 nm resulting from transition of $^4F_{9/2}$–$^6H_{11/2}$ and $^4F_{9/2}$–$^6H_{9/2}$ are observed. The luminescence spectra show that the emission intensity of MBT: Dy^{3+} ceramics has been enhanced with an increase of TeO_2 from 10 to 30 mol %. The emission at 577 nm is stronger compared to the other emissions and is dominant in the emission spectra.

4. Conclusion

In summary, the most obvious findings to emerge from this study are that the obtained ceramics exhibit a crystalline phase for both MBT: Eu^{3+} and MBT: Dy^{3+} compositions. The luminescence of the MBT: Eu^{3+} and MBT: Dy^{3+} ceramics shows that the maximum luminescent intensity is achieved at the TeO$_2$ concentration of 30 mol %. MBT: Eu^{3+} ceramics shows a strong red emission and MBT: Dy^{3+} ceramics exhibits an intense yellow emission. Meanwhile, photoluminescence results of MBT: Eu^{3+} and MBT: Dy^{3+} ceramics show that these ceramics are brightly luminescent and have a high potential application in solid-state lighting devices.

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