

Influence of Eu^{3+} , Dy^{3+} and Sm^{3+} on the Structural and Luminescence Properties of Magnesium Borophosphate Ceramic

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Abstract— A quaternary system of magnesium borophosphate (MBP) ceramic with nominal composition of $49\text{B}_2\text{O}_3\text{-}15\text{P}_2\text{O}_5\text{-}25\text{MgO}\text{-}10\text{TeO}_2\text{-}1\text{RE}$ (RE = Eu^{3+} , Dy^{3+} , Sm^{3+}) was successfully prepared using solid state reaction method sintered at 900 °C for 5 hours. Crystalline phases of all ceramic samples were characterized using an X-Ray Diffractometer. The samples were polycrystalline phase of $\text{B}(\text{PO}_4)$, $\text{Mg}(\text{PO}_3)_2$ and $\text{Mg}(\text{BO}_3)(\text{PO}_4)$. Infrared spectra displayed the presence of B-O-B, BO_3 , BO_4 and P-O stretching modes of P-O-P, P=O and PO_4 unit in the ceramic network. The emission spectra of ceramic samples revealed five prominent peaks centred at 588 nm, 593 nm, 613 nm, 657 nm and 700 nm which were assigned to the transition from $^5\text{D}_0\text{-}^7\text{F}_J$ ($J = 0, 1, 2, 3, 4$) states of Eu^{3+} ion and Sm^{3+} emission due to transition from $^4\text{G}_{5/2}\text{-}^6\text{H}_{J/2}$ ($J = 5, 7, 9, 11$) respectively. Meanwhile, Dy^{3+} emission is due to $^4\text{F}_{9/2}\text{-}^5\text{H}_{15/2}$ and $^4\text{F}_{9/2}\text{-}^6\text{H}_{13/2}$ transitions. Among all these rare-earth (RE) elements, Eu^{3+} showed the strongest luminescence intensity with dominated by the $^5\text{D}_0\text{-}^7\text{F}_1$ transition. The proposed ceramic compositions were demonstrated to be potential for solid-state lasers and development optical devices.

Index Terms— luminescence, rare-earths, borophosphate, ceramic

1 INTRODUCTION

Rare-earth ions (REIs) possess unique optical properties such as high efficiency and long decay time plus being one of the attractive materials in the development of phosphors [1]. RE oxides also is a promising material for the advancement of high-performance luminescent device due to its efficiency and narrow emission property in the visible region [2]. REIs too have great interest in its applications such as laser materials, phosphors and fluorescent tubes. Of all the RE oxide elements, Europium (Eu^{3+}), Dysprosium (Dy^{3+}) and Samarium (Sm^{3+}) are popular activators ions for various host lattices [3]. It is well known that Eu^{3+} is one of the most important activators because of its rich red emission light where it is widely use in field emission technology and Light Emitting Diodes (LEDs) [4]. Previous study reported that Lanthanum Aluminum Germanate ($\text{LaAlGe}_2\text{O}_7$) doped Eu^{3+} has been identified as another good material which displays an intense red emission under ultraviolet (UV) sources. Thus, $\text{LaAlGe}_2\text{O}_7$ doped Eu^{3+} is also a potential red-emitting phosphor due to this excellent luminescent property and was used as novel optical materials [5].

On the other hand, Dy^{3+} ions are also considered as an important activator ion since it is highly insoluble and thermally stable [6]. Martin *et al* claimed that Dy^{3+} is considered as an excellent commercial white light long lasting

phosphor. Hence, luminescence material doped with Dy^{3+} has drawn much interest in fabrication of White LEDs (WLEDs) and hold great potential in technological applications especially in optoelectronic materials [7]. Alternatively, Sm^{3+} offers a strong luminescence in the reddish orange spectral regions, strong intensity and long fluorescence lifetime. Moreover, Sm^{3+} ions have attracted much practical interest due to its potential application for high-density optical storage. Other than that, luminescence properties of Sm^{3+} have indicated that Sm^{3+} is suitable for solid state laser and LEDs [8]. Up till now, REIs doped luminescence material had become an interesting topic in luminescence material. Therefore, the purpose of this study is to identify the influence of Eu^{3+} , Dy^{3+} and Sm^{3+} on network structure and analyze the characteristic of luminescence of Eu^{3+} , Dy^{3+} and Sm^{3+} in MBP ceramic.

2 MATERIALS AND METHOD

Raw materials with high purity (Sigma Aldrich, 99.9%) such as phosphoric acid (H_3PO_4) orthoboric acid (H_3BO_3), magnesium oxides (MgO) and, tellurium dioxide (TeO_2) were weighed and mixed according to the composition respectively. A nominal composition of $49\text{B}_2\text{O}_3\text{-}15\text{P}_2\text{O}_5\text{-}25\text{MgO}\text{-}10\text{TeO}_2$ was doped with various RE such as Europium (III) oxide (Eu_2O_3 , 99.9%), Dysprosium Oxide (Dy_2O_3 , 99.9%) and, Samarium (III) oxide (Sm_2O_3 , 99.9%) which are 1 mol % in order to find the most suitable REIs for the MBP ceramic system. These mixtures were stirred using magnetic stirrer at 80 °C for 2 hours to ensure the homogeneity of the samples before being placed into alumina crucible. These samples were sintered for 5 hours in a furnace of 900 °C. Then, all samples were grinded into powder form for analysis. The phases of the obtained samples were identified by an X-ray Diffractometer using Siemens Diffractometer D5000 system operating at 40 kV, 30

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mA. Diffraction patterns were collected in the range of 2θ from 10° to 90° .

Structural features of samples were identified via infrared spectroscopy. Infrared spectra were examined using Perkin-Elmer Spectrum One Infrared Spectrometer. These infrared spectra were recorded in the range of 400 cm^{-1} to 4000 cm^{-1} wavenumber using 100 scans at 4 cm^{-1} resolutions. Luminescence spectra were recorded using Jasco Photoluminescence Spectroscopy. Samples were placed in a sample holder and were scanned for radiation spectral wavelength in the visible range of 200 nm to 900 nm with xenon lamp as an excitation source.

3 RESULTS AND DISCUSSIONS

XRD pattern is one of the most convenient and common method to determine the phase of sample. Fig. 1 shows the XRD pattern of MBP ceramic.

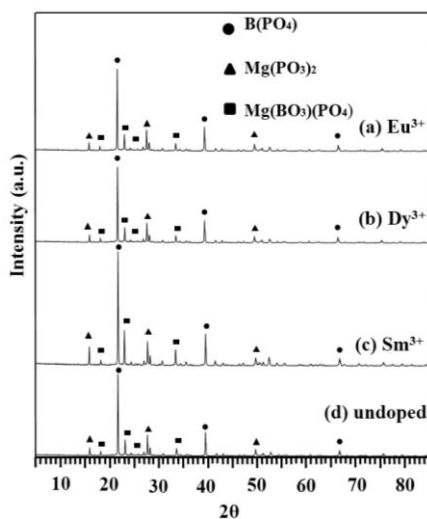


Fig. 1: XRD pattern of (a) Eu^{3+} (b) Dy^{3+} (c) Sm^{3+} doped MBP ceramic and (d) undoped sample as reference

From Fig.1, it can be seen that all major diffraction peaks are well-matched with the reference. This probably due to its very small concentration of those three REIs in the ceramic samples. Fig. 2 represents the IR spectra of MBP ceramic. Its discussion is presented using the absorption spectra obtained in the frequency ranging from 400 cm^{-1} to 4000 cm^{-1} for all ceramic samples.

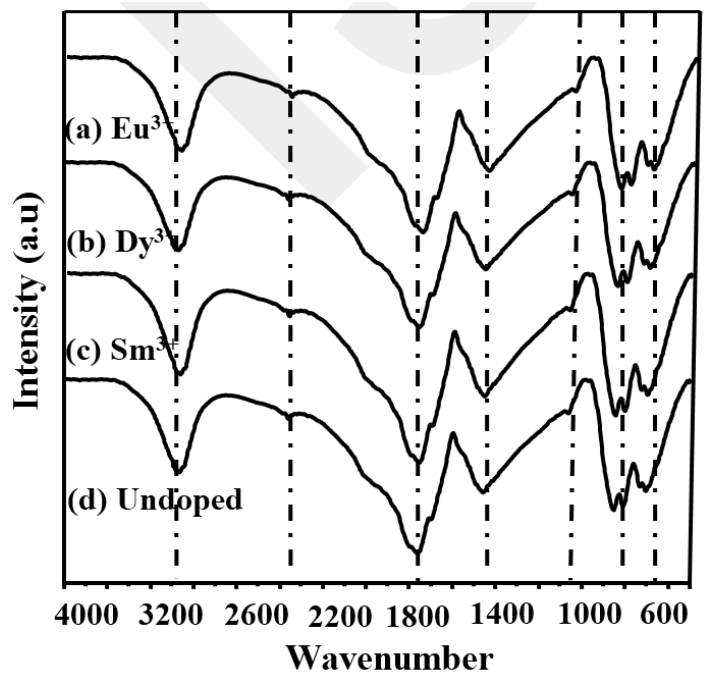


Fig. 2: IR spectra of (a) Eu^{3+} (b) Dy^{3+} (c) Sm^{3+} doped MBP ceramic and (d) undoped sample for comparison

Fig. 2 indicates that the addition of Eu^{3+} , Dy^{3+} and Sm^{3+} into the MBP ceramic did not show any changes to the IR spectra. The difference ionic radius of the dopant ions ($\text{Eu}^{3+} = 0.95\text{ \AA}$, $\text{Dy}^{3+} = 0.91\text{ \AA}$ and $\text{Sm}^{3+} = 0.96\text{ \AA}$) compared to Boron ($\text{B}^+ = 0.3\text{ \AA}$) and Phosphorus ($\text{P}^+ = 0.34\text{ \AA}$) [9,10] make them possible to grab an interstitial position in the network structure rather than replacing any B^+ and P^+ ions. Thus, it was clear that the introduction of an activator of Eu^{3+} , Dy^{3+} and Sm^{3+} ions do not offer any influence to the structure of MBP ceramic. This result is in good agreement with the previous report [11-14]. Table 1 summarizes the peak positions and its assignments of RE doped MPB ceramic.

TABLE 1
ASSIGNMENTS OF BANDS IN THE INFRARED SPECTRA
OF $\text{Eu}^{3+}/\text{Dy}^{3+}/\text{Sm}^{3+}$ DOPED MBP CERAMIC

Peak	Band Center (cm^{-1})	Assignments
1	600-800	B-O stretching vibrations from varied types of borate groups [11]
2	846-860	PO_2 stretching of the doubly bonded oxygen vibrations ($\text{P}=\text{O}$) [11]
3	905	Asymmetric stretching vibration of P-O-P groups [12]
4	1087	Asymmetric stretching of PO_3 groups [12]
5	860-1200	B-O bending vibrations in BO_4 unit [13]
6	1200-1600	B-O stretching vibration in BO_3 unit [13]
7	1634	Vibrations mode of OH bending [14]
8	3498	Fundamental stretching of O-H groups [14]

The emission spectra of MBP ceramic doped with 1 mol % of Eu^{3+} is shown in Fig. 3 (a). The sample was excited using a xenon lamp with an excitation of 390 nm. All peaks of Eu^{3+} were observed in the visible region spectral of 550 nm to 750 nm.

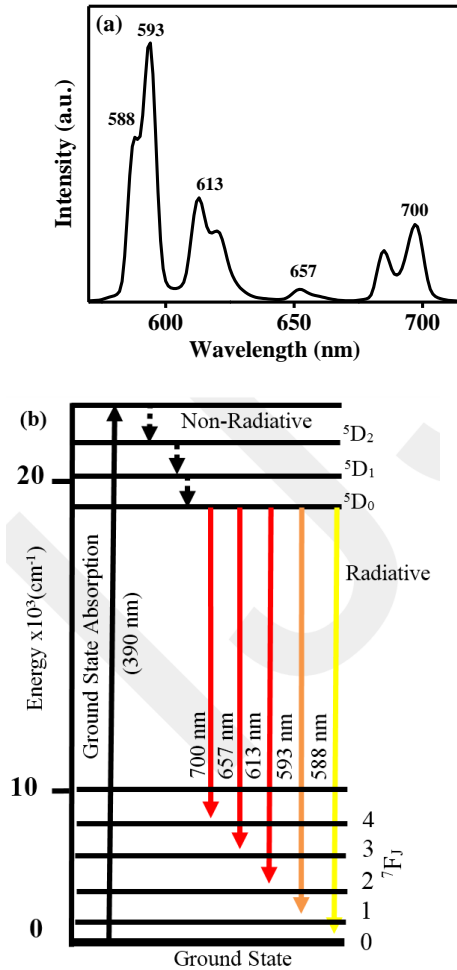


Fig. 3: (a) Luminescence spectra of Eu^{3+} doped MBP ceramic excited at 390 nm (b) Partial energy level diagram of Eu^{3+}

From Fig. 3 (a), it can be seen that the emission spectra consisted of a few intense emissions at 588 nm, 593 nm, 613 nm, 657 nm and 700 nm. These peaks were assigned to the ${}^5\text{D}_0$ - ${}^7\text{F}_j$ ($j = 0, 1, 2, 3, 4$) transition. The emission intensity peak at 593 nm was stronger than 613 nm which means that it was dominated by the ${}^5\text{D}_0$ - ${}^7\text{F}_1$ transition. It is well-known that this transition belongs to the magnetic dipole transition which scarcely changes the crystal field strength around the Eu^{3+} ions [15]. This indicates that Eu^{3+} occupies the inversion symmetry site in the lattice [16]. On the other hand, the electric dipole transition (${}^5\text{D}_0$ - ${}^7\text{F}_2$) was prominent in the emission spectra [17]. All transitions of emission spectra of Eu^{3+} can be corresponded to the energy level. Fig. 3 (b) describes the energy level for the emission process observed for Eu^{3+} ions doped MBP ceramic. Fig. 4 (a) shows the emission spectra of 1 mol % Dy^{3+} doped in MBP ceramic under the excitation of 350 nm. The sample was observed in the spectral range of 450 nm to 650 nm.

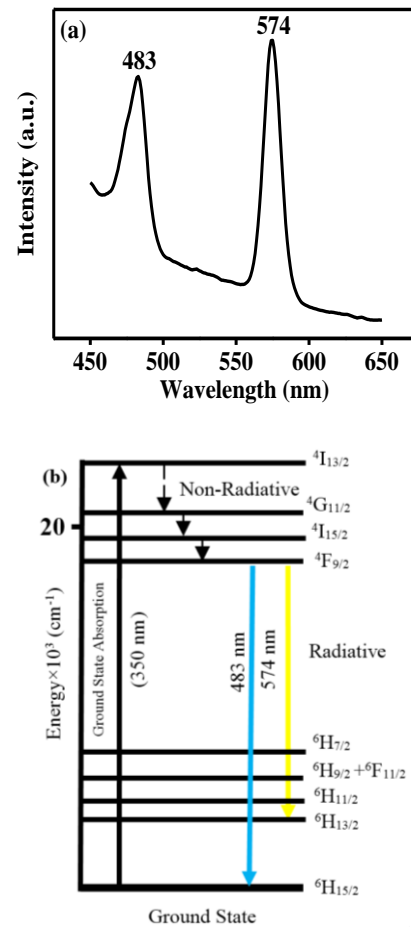


Fig. 4: (a) Luminescence spectra of Dy^{3+} doped MBP ceramic excited at 350 nm (b) Partial energy level diagram of Dy^{3+}

It is also observed that there were two intense emissions at 483 nm (blue) and 574 nm (yellow). Notice that luminescence spectra dominated by electric dipole transition (${}^4\text{F}_{9/2}$ - ${}^5\text{H}_{13/2}$) where a very hypersensitive transition occurs [18] and its intensity depends on the nature of the host. This result indicates that Dy^{3+} ions are located at low symmetry local site in the host lattice. On the contrary, 483 nm (${}^4\text{F}_{9/2}$ - ${}^5\text{H}_{15/2}$) is prominent in the emission spectra which is less sensitive to the host [19, 20]. All the transition emission spectra of Dy^{3+} are corresponded to energy level. Fig. 4 (b) describes the energy level for Dy^{3+} ions doped MBP ceramic. The emission spectra of MBP ceramic doped with 1 mol % of Sm^{3+} obtained in the region of 550 nm to 750 nm under excitation 404 nm are shown in Fig. 5 (a).

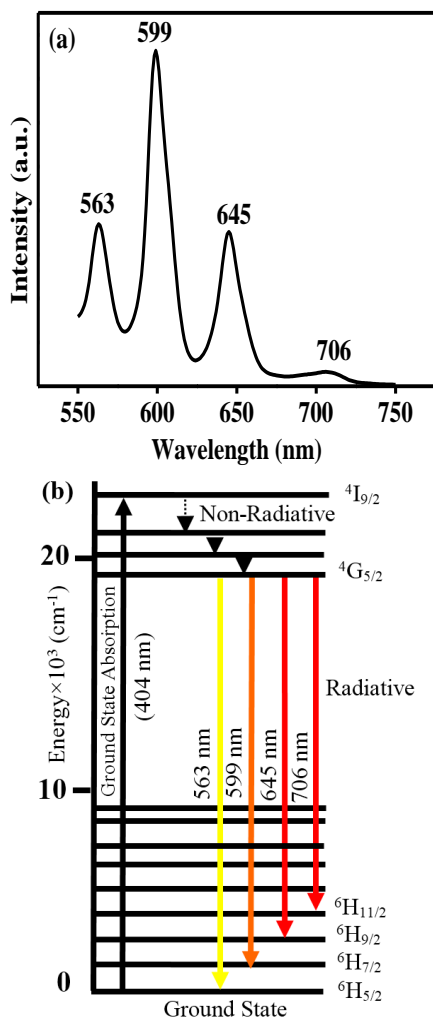


Fig. 5: (a) Luminescence spectra of Sm³⁺ doped MBP ceramic excited at 404 nm (b) Partial energy level diagram Sm³⁺

The emission spectra exhibit four emission bands centered at 563 nm, 599 nm, 645 nm and 706 nm ascribed to ${}^4G_{5/2}-{}^6H_{5/2}$, ${}^6H_{7/2}$, ${}^6H_{9/2}$ and ${}^6H_{11/2}$ transitions, respectively. Strong peaks correspond to reddish-orange emission from ${}^4G_{5/2}$ level to the ${}^6H_{7/2}$ level are observed at 599 nm [21]. The emitting ${}^4G_{5/2}$ level of Sm³⁺ exhibits relatively high quantum efficiency [22]. Among the observed emission transitions of Sm³⁺, transition of ${}^4G_{5/2}-{}^6H_{5/2}$ and ${}^4G_{5/2}-{}^6H_{7/2}$ are purely electric dipole in nature ($\Delta J \leq 6$) and the other two transitions ${}^4G_{5/2}-{}^6H_{9/2}$ and ${}^4G_{5/2}-{}^6H_{11/2}$ contain both electric and magnetic contributions ($\Delta J = 0, \pm 1$) [23]. All transitions of emission spectra of Sm³⁺ can be corresponded to energy level. Fig. 5 (b) describes the energy level of the emission process observed for Sm³⁺ ions doped MBP ceramic.

4 CONCLUSION

For the first time, the influence of Eu³⁺, Dy³⁺ and Sm³⁺ doped MBP ceramic have been prepared and its structural and luminescence properties were studied and reported. Structural analysis indicated that Eu³⁺, Dy³⁺ and Sm³⁺ do not give influence on the structural properties. Meanwhile, luminescence studies show that among the REIs, Eu³⁺ has the

strongest luminescence intensity on MBP ceramic. Present finding suggest that the newly proposed ceramics composition may be beneficial for the laser emission at 593 nm and development optical devices.

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