Photoluminescence Characteristic of Magnesium Boro-Tellurite doped Eu³⁺ Ceramic (Ciri Fotoluminesens bagi Magnesium Boro-Telurit dop Seramik Eu³⁺)

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ABSTRACT

The series samples of $xTeO_2^{-}(70-x)B_2O_3^{-}30MgO$ with $0 \le x \le 30$ mol% have been prepared via the solid-state reaction method. The composition sample of $30TeO_2^{-}40B_2O_3^{-}30MgO$ were chosen as a doped sample in the composition of 100-y($30TeO_2^{-}40B_2O_3^{-}30MgO$)-yEu³⁺ with $0.2 \le y \le 2$ mol% and were heated at $750^{\circ}C$. The XRD results showed that the major phase was $Mg(Te_2O_5)$ while $MgO(B_2O_3)_2$, $MgTe_6O_{13}$, $Mg_2(B_2O_5)$ and MgB_4O_7 was observed as a minor phase. The small phase of EuB_2O_4 and Eu_2Te_4O_{11} were detected by XRD when the composition of $30TeO_2^{-}40B_2O_3^{-}30MgO$ were doped with 1.5% of Eu^{3+} . The EDX analysis of $30TeO_2^{-}40B_2O_3^{-}30MgO$ doped with 1.5% Eu³⁺ sample was confirmed the presence of boron (B), magnesium (Mg), tellurium (Te), oxygen (O) and europium (Eu) elements. From the FESEM images, the surface morphology of doped 1.5% Eu³⁺ samples was agglomerated compared with the undoped sample. The average diameter of the grain size is in the range of 50-100 µm. The emission spectra of the Eu³⁺-doped $30TeO_2^{-}40B_2O_3^{-}30MgO$ ceramic consists of intense and sharp lines ranging from 550-725 nm. The luminescence spectra showed that the emission intensity of $30TeO_2^{-}40B_2O_3^{-}30MgO$ doped with Eu^{3+} was enhanced with the increase of Eu^{3+} ion from 0.2 to 1.5 mol%, which resulted in enhancement of the red emission of the samples. The longest decay time for $30TeO_2^{-}40B_2O_3^{-}30MgO$ doped with 1.5 mol% Eu^{3+} was 0.892 ms.

Keywords: Decay curve; magnesium boro-tellurite; photoluminescence

ABSTRAK

Siri sampel bagi xTeO₂-(70-x)B₂O₃-30MgO dengan $0 \le x \le 30$ mol% telah disediakan melalui kaedah tindak balas keadaan pepejal. Sampel dengan komposisi 30TeO₂-40B₂O₃-30MgO telah dipilih sebagai sampel dop berkomposisi 100-y(30TeO₂-40B₂O₃-30MgO)-yEu³⁺ dengan $0.2 \le y \le 2$ mol% dan telah dipanaskan pada suhu 750°C. Keputusan XRD menunjukkan fasa major adalah Mg(Te₂O₅) manakala MgO(B₂O₃)₂. MgTe₆O₁₃, Mg₂(B₂O₅) and MgB₄O₇ dilihat sebagai fasa minor. Fasa yang kecil bagi Dy(BO₂)₃, Dy₂Te₄O₁₁, EuB₂O₄ and Eu₂Te₄O₁₁ telah dikesan oleh XRD pada komposisi 30TeO₂-40B₂O₃-30MgO dop 1.5% Eu³⁺. Analisis EDX bagi sampel 30TeO₂-40B₂O₃-30MgO dop 1.5% Eu³⁺ menunjukkan unsur boron (B), magnesium (Mg), telurium (Te), oksigen (O) dan europium (Eu). Daripada imej FESEM, morfologi permukaan bagi sampel dop adalah bergumpal berbanding dengan sampel tidak didop. Diameter purata bagi saiz butiran adalah dalam lingkungan 50-100 µm. Spektrum pancaran bagi Eu³⁺-dop 30TeO₂-40B₂O₃-30MgO seramik terdiri garisan yang jelas dan tajam pada julat 550-725 nm. Spektra luminesens menunjukkan keamatan pancaran bagi 30TeO₂-40B₂O₃-30MgO dop 2.5% menunjukkan peningkatan ion Eu³⁺ daripada 0.2 ke 1.5 mol%, menunjukkan peningkatan pancaran merah pada sampel tersebut. Masa pereputan yang paling lama apabila didopkan dengan 1.5 mol% Eu³⁺ pada komposisi 30TeO₂-40B₂O₃-30MgO adalah 0.892 ms.

Kata kunci: Fotoluminesens; lengkung pereputan; magnesium boro-telurit

INTRODUCTION

The high optical quality rare earth (RE) ions doped ceramics have been investigated as attractive lighting sources. Ceramics are the best host materials to incorporate high concentrations of dopant ions such as rare earth and transition metal ions besides having thermal and mechanical properties. These ceramic can be fabricated at lower cost and speedy processes in a large variety of sizes and shapes (Lupei et al. 2005; Mohr et al. 2008). Borate has been studied extensively due to the physical properties like low melting point, high thermal stability and good solubility (Elfayoumi et al. 2010). An interesting behavior of the tellurite based is good mechanical strength, chemical durability, no hygroscopic properties and low process temperature (Babu et al. 2007). Among the host materials, boro-tellurite represents favorable compromise of low phonon energy and a relatively high thermal stability, high chemical durability and ease of fabrication (Joshi et al. 2008; Yanmin et al. 2007). Rare-earth elements which act as dopant yield interesting and useful properties in host crystal. Rare-earth-doped materials also have potential applications for phosphors, display monitor, x-ray imaging and scintillators (Blasse & Grabmaier 1994). Moreover, the

luminescence properties of the ceramic could be improved by doping with rare earth (RE) ions as an activator. Eu³⁺doped are commonly used as red emitting materials for field emission technology and LEDs, which exhibit higher luminescence efficiency compared with other luminous materials (Oikawa & Fujihara 2005). In the present work, magnesium boro-tellurite doped Eu³⁺ ceramic with various Eu³⁺ concentration were synthesized by the solid state reaction method. The effect of Eu³⁺ dopants on the structural and luminescence characteristic are discussed.

EXPERIMENTAL DETAILS

All the powder samples were synthesized by the solid state reaction method. The starting materials such as of boric acid, H₂BO₂ (99.99%), tellurium oxide, TeO₂ (99.99%), magnesium oxide, MgO (99.99%) and europium oxide, $Eu_{2}O_{2}$ (99.99%) were employed as the raw materials. The samples were synthesized according to the compositions of xTeO₂-(70-x)B₂O₃-30MgO with 0 $\leq x \leq$ 30 in appropriate amounts (mol%). The percentage of Eu₂O₃ from 0.2 to 2 mol% was then added into the mixtures. The powders were thoroughly mixed in agate mortar. The mixtures were pressed into pellets using hydraulic press with 10 ton/ cm² pressure. After pelletized; the samples were heated at 750°C for 6 h. The dried pellet was grounded into fine powder. The powders were prepared for the experimental measurement. The structure of the prepared powders was examined by Siemen Diffraction D5000 diffractometer with CuK_a radiation ($\lambda = 1.54$ Å) and 2q scan range of 10 to 80°. The PL and lifetime measurements were performed with a Jasco Fluorescence spectrophotometer FP8500 equipped with a 150-W xenon lamp as an excitation source. The surface morphology was examined by field emission scanning electron microscope (FESEM) model SUPRA 55VP. Elemental analysis was carried out by energy dispersive X-ray (EDX) using X-ray detector attached to the FESEM instrument. All the measurements were performed at room temperature.

RESULTS AND DISCUSSION

The XRD pattern shows the influence of varying composition of the xTeO₂-(70-x)B₂O₂-30MgO with 0 $\leq x \leq$ 30 mol%. It can be observed that all the diffraction peaks in XRD patterns assigned to $Mg(Te_2O_5)$, $MgO(B_2O_3)_2$, $MgTe_6O_{13}$, $Mg_2(B_2O_5)$ and MgB_4O_7 , which were well matches with the JCPDS No. 01-073-3922, 01-076-0666, 00-028-0634, 01-086-0531 and 00-031-0787, respectively. Figure 1 shows the intensity of the peaks increases with increasing xmol% and the phases appear clearly at x = 30 mol%. From the XRD results, the major peaks due to $Mg(Te_2O_5)$ can be observed followed by $MgO(B_2O_3)_2$. $MgTe_6O_{13}$, $Mg_2(B_2O_5)$ and MgB_4O_7 also was observed as a minor peaks. The XRD patterns of 30TeO2-40B2O3-30MgO doped with 1.5% of Eu³⁺ is shown in Figure 2. The pattern shows that a small amount of rare earth ions also can be observed as a minor phase. With the addition of dopant into the sample, the peaks of EuB2O4 and Eu2Te4O11 were included into the XRD pattern. The previous results also showed that rare earth ions phase can be detected (Cheng et al. 2014; Kumar & Buddhuda 2009; Kunimoto et al. 2013).



FIGURE 1. X-ray diffraction pattern of xTeO₂-(70-x)B₂O₃-30MgO with $0 \le x \le 30$ mol% ceramic sample prepared at 750°C



FIGURE 2. X-ray diffraction pattern of 30TeO₂-40B₂O₃-30MgO doped 1.5% of Eu³⁺ ceramic sample prepared at 750°C

EDX analysis was carried out to confirm the presence of rare earth ion in the samples. Figure 3 shows the EDX spectra of 30TeO_2 - $40\text{B}_2\text{O}_3$ -30MgO doped 1.5% of Eu³⁺. The EDX analysis confirmed the presence of boron (B), magnesium (Mg), tellurium (Te) and oxygen (O) and europium (Eu) elements. Figure 4 shows the FESEM images of 30TeO_2 - $40\text{B}_2\text{O}_3$ -30MgO doped 1.5% of Eu³⁺ at 750°C . The doped sample has different morphological structures and grain size compared with the undoped sample. The structure of the doped samples is more agglomerated compared with the undoped sample. The samples have an average grain size of 50-100 µm.

The excitation spectra of $100-y(30\text{TeO}_2-40\text{B}_2\text{O}_3-30\text{MgO})-y\text{Eu}^{3+}$ ceramic with $0.2 \le y \le 2 \mod \%$ at 750°C monitored at 615.68 nm emission are given in Figure 5.

The broad band from 200 to 350 nm is attributable to the charge transfer band (CTB) transition. The CTB plays an important role in its luminescence. The broad absorption band is assigned to the CTB of Eu-O (Sun & Fu 2012), which occurred by electronic transition from the filled 2p orbital of O^{2-} to the partially filled 4f orbital of Eu³⁺. The CTB is related closely to the covalency between O^{2-} and Eu³⁺ and the coordination environment around Eu³⁺ (Tian et al. 2009). It has been reported that CTB in oxides due to Eu³⁺- O^{2-} interaction might arise (Rao et al. 2008). The sharp lines 363.01 nm ($^7F_0-^5D_4$), 382.86 nm ($^7F_0-^5G_3$), 396.61 nm ($^7F_0-^5D_2$), 465.78 nm ($^7F_0-^5D_2$), 474.72 nm ($^7F_0-^5D_2$), 489.07 nm ($^7F_0-^5D_2$), 517.16 nm ($^7F_0-^5D_1$), 527.48 nm ($^7F_0-^5D_1$) and 537.07 nm ($^7F_0-^5D_1$) were observed,



FIGURE 3. EDX spectrum of 30TeO₂-40B₂O₃-30MgO doped 1.5% of Eu³⁺ ceramic sample prepared at 750°C



FIGURE 4. FESEM images of 30TeO_2 - $40\text{B}_2\text{O}_3$ -30MgO(a) x = 30 (b) 1.5% of Eu³⁺ ceramic sample prepared at 750°C (magnification: 10K ×)

respectively. The adsorbed spectra showed that when the wavelength ranged from 350-550 nm, the sharp peaks originated from the transitions with the *f*-configuration from $^{7}F_{0}$ to the excitation states (Visser et al. 1992). No significant shift in peak position was observed for the various Eu³⁺ ion concentrations. The $^{7}F_{0}$ to $^{5}G_{3}$ at 382.86 nm and $^{7}F_{0}$ - $^{5}L_{6}$ transition at 396.61 nm were the two strongest

absorptions. The prominent excitation band at 396.61 nm has been chosen for the measurement of emission spectra of 30TeO_2 - $40\text{B}_2\text{O}_3$ -30MgO doped Eu³⁺ ceramic. However, the intensities of the peaks in the excitation spectra increased in order of 0.2, 0.4, 0.6, 0.8, 1.0, 1.5 and 2 mol%. As the Eu³⁺ ion concentration increases, the CTB of Eu-O also increases and is shifted towards the shorter wavelength (higher energy) region.

The luminescence spectrum of 30TeO₂-40B₂O₃-30MgO doped Eu³⁺ (Eu³⁺ = 0.2, 0.4, 0.6, 0.8, 1.0, 1.5 and 2) mol%) ceramic obtained by excitation of Eu3+ at 396.61 nm are displayed in Figure 6. It can be seen that the emission spectra of the Eu³⁺-doped 30TeO₂-40B₂O₂-30MgO ceramic is composed of intense and sharp lines ranging from 550-725 nm, which are related to transition from the excited ⁵D_o level to ⁷F₁ (J=0-4) levels (Li et al. 2012). The strong emission peaks observed at 593.21, 615.68 and 701.20 nm were assigned to the transitions of ${}^{5}D_{0} {}^{-7}F_{1}$, ${}^{5}D_{0} {}^{-7}F_{2}$, and ${}^{5}D_{0} {}^{-1}F_{2}$ ${}^{7}F_{4}$. Besides, the weak emission was observed at 642.14 and 654.08 nm ascribed to the transition of ${}^{5}D_{0}$ - ${}^{7}F_{3}$. Among these peaks, the red emission peak at 615.68 nm is more dominant than the other peaks. This peak originates from the electric dipole transitions of ${}^{5}D_{a}$, which indicates that Eu³⁺ occupies a non-centro-symmetric site (Meng et al. 2012). The luminescence spectra showed that the emission intensity of 30TeO₂-40B₂O₃-30MgO doped with Eu³⁺ was enhanced with the increase of Eu3+ ion concentration from 0.2 to 1.5 mol%, which resulted in enhancement of the red emission of the samples. When the Eu³⁺ ion concentration continuously increase to 2 mol%, the emission intensity decreases because of the concentration quenching effect. With the increase of Eu³⁺ concentration, the proportion of non-radiative energy transfer between nearby Eu³⁺ ions exceeds the critical value and the luminescence intensity begins to decrease (Cui et al. 2013).

Figure 7 shows the measured fluorescence decay curve of the 30TeO_2 - $40\text{B}_2\text{O}_3$ -30MgO doped Eu³⁺ ceramic for various Eu³⁺ concentrations. With the increase of Eu³⁺



FIGURE 5. Excitation spectra of $100-x(30\text{TeO}_2-40\text{B}_2\text{O}_3-30\text{MgO})-x\text{Eu}^{3+}$ with $0.2 \le x \le 2$ mol% ceramic sample prepared at 750°C



FIGURE 6. Emission spectra of $100-x(30\text{TeO}_2-40\text{B}_2\text{O}_3-30\text{MgO})-x\text{Eu}^{3+}$ with $0.2 \le x \le 2 \text{ mol}\%$ ceramic sample prepared at 750°C



FIGURE 7. Lifetime spectra of 100-*x*(30TeO₂-40B₂O₃-30MgO)-*x*Eu³⁺ with 0.2≤*x*≤2 mol% ceramic sample prepared at 750°C

concentrations from 0.2 to 1.5 mol%, the decay time value of Eu³⁺ ion increased from 0.834 ms to 0.892 ms and decrease to 0.846 ms at 2 mol%. The longest decay time occurred at 1.5 mol% of Eu³⁺. The sample doped with 2 mol% Eu³⁺ had reached a concentration quenching effect and caused shorter lifetime (Fang et al. 2006). The decay curves of 30TeO_2 - $40\text{B}_2\text{O}_3$ -30MgO doped Eu³⁺ ceramic values with the various concentrations of Eu³⁺ ions were listed as shown in Table 1.

CONCLUSION

In summary, the samples of magnesium boro-tellurite and magnesium boro-tellurite doped Eu^{3+} ceramic have been prepared using the solid-state reaction method. From the XRD profiles, the major peaks due to Mg(Te₂O₅) was observed in each profile followed by MgO(B₂O₃)₂, MgTe₆O₁₃, Mg₂(B₂O₅) and MgB₄O₇ observed as weak

TABLE 1. Decay times for $100-x(30\text{TeO}_2-40\text{B}_2\text{O}_3-30\text{MgO})-x\text{Eu}^{3+}$ with $0.2 \le x \le 2$ mol% ceramic sample prepared at 750°C

Concentration of Eu ³⁺ (mol %)	Decay time (ms)	
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0.2	0.834	
0.4	0.853	
0.6	0.858	
0.8	0.860	
1.0	0.866	
1.5	0.892	
2.0	0.846	

peaks. The peaks of EuB_2O_4 and $\text{Eu}_2\text{Te}_4\text{O}_{11}$ were included into the XRD patterns of 30TeO_2 - $40\text{B}_2\text{O}_3$ -30MgO doped 1.5% of Eu^{3+} . The morphology of the ceramic studied using the SEM images shows that the particles are agglomerated and the particles are in micron size. From the luminescence study, the emission intensity of the 615.68 nm increases rapidly with Eu³⁺ concentration up to 1.5 mol%. When the Eu³⁺ concentration is above 1.5 mol%, concentration quenching occurred. The highest value of the decay time was obtained at 1.5 mol% of Eu³⁺. Based on the results of emission spectral, we suggest that these ceramic powders are brightly luminescent and are applicable as novel optical materials.

ACKNOWLEDGEMENTS

The authors would like to thank the Fundamental Research Grant Scheme (FRGS) under research grant Project Number: Q.J130000.2526.03H97 for the financial support. We would also like to thank the Faculty of Science, Universiti Teknologi Malaysia (UTM) and Institute of Ibnu Sina for the facilities provided.

REFERENCES

- Babu, P., Seo, H.J., Jang, K.H., Kumar, K.U. & Jayasankar, C.K. 2007. Optical spectroscopy, 1.5 μm emission, and upconversion properties of Er³⁺-doped metaphosphate laser glasses. *Journal of the Optical Society of America B* 24(9): 2218-2228.
- Blasse, G. & Grabmaier, B.C. 1994. Luminescence Materials. Berlin: Springer-Verlag.
- Cheng, L.Y., Dan, P.G., Fei, W., Ming, Y.Z., Ai, L.Z., Xiao, Y.L., Ying, X.L., Xin, Y.L., Hai, B.B. & Yu, L.P. 2014. On the luminescent properties of Dy³⁺:β-Li₂TiO₃ omment on 'Synthesis and emission analysis of RE³⁺ (Eu³⁺ or Dy³⁺): Li₂TiO₃ ceramics'. *Ceramics International* 40: 11465-11467.
- Cui, R., Deng, C., Gong, X., Li, X. & Zhou, J. 2013. Luminescent performance of rare earths doped CaBi₂Ta₂O₉ phosphor. *Journal of Rare Earths* 31(6): 546-550.
- Elfayoumi, M.A.K., Farouk, M., Brik, M.G. & Elokr, M.M. 2010. Spectroscopic studies of Sm³⁺ and Eu³⁺ co-doped lithium borate glass. *J. Alloys Compd.* 492(1-2): 712-716.
- Fang, T.H., Hsiao, Y.J., Chang, Y.S. & Chang, Y.H. 2006. Photoluminescent characterization of KNbO₃:Eu³⁺. *Materials Chemistry and Physics* 100: 418-422.
- Joshi, P., Shen, S. & Jha, A. 2008. Er³⁺-doped boro-tellurite glass for optical amplification in the 1530-1580 nm. *Journal of Appl. Phys.* 103(8): 083543.
- Kumar, G.B. & Buddhudu, S. 2009. Synthesis and emission analysis of RE³⁺ (Eu³⁺ or Dy³⁺): Li₂TiO₃ ceramics. *Ceramics International* 35: 521-525.
- Kunimoto, T., Honma, T., Ohmi, K., Okubo, S. & Ohta, H. 2013. Detailed impurity phase investigation by X-ray absorption fine structure and electron spin resonance analyses in synthesis of CaMgSi₂O₆: eu phosphor. *Japanese Journal of Applied Physics* 52: 042402.

- Li, S., Xu, D., Shen, H., Zhou, J. & Fan, Y. 2012. Synthesis and Raman properties of magnesium borate micro/nanorods. *Materials Research Bulletin* 47: 3650-3653.
- Lupei, V., Lupei, A. & Ikesue, A. 2005. Transparent Nd and (Nd, Yb)-doped Sc₂O₃ ceramics as potential new laser materials. *Appl. Phys. Lett.* 86: 111-118.
- Meng, F.G., Zhang, X.M., Li, H. & Seo, H.J. 2012. Synthesis and spectral characteristics of La₂MoO₆: Ln³⁺ (Ln=Eu, Sm, Dy, Pr, Tb) polycrystals. J. Rare Earths 30(9): 866-870.
- Mohr, D., Andrea, S.S., Camargo, D., Schneider, J.F., Quieroz, T.B., Eckert, H., Botero, E.R., Garcia, D. & Eiras, J.A. 2008. Solid state NMR as a new approach for the structural characterization of rare earth doped lead lanthanum Zirconate titanate laser ceramics. *Solid State Sci.* 10: 1401-1407.
- Oikawa, M. & Fujihara, S. 2005. Sol-gel preparation and luminescence properties of CeO₂: Ln (Ln = Eu³⁺ and Sm³⁺) thin films. *Journal of European Ceramic Society* 25: 2921-2924.
- Rao, B.V., Rambabu, U. & Buddhudu, S. 2008. Photoluminescence spectral analysis of Eu³⁺: Phosphors. *Physica B* 382: 86-91.
- Sun, Y.H. & Fu, Y.X. 2012. Synthesis and characteristics of nano-size sandwich structure (Y,Gd)BO₃: Eu³⁺ phosphors. *J. Luminescence* 132: 550-557.
- Tian, Y., Qi, X., Wu, X., Hu, R. & Chen, B. 2009. Luminescent properties of Y₂(MoO₄)₃:Eu³⁺ red phosphors with flowerlike shape prepared via co-precipitation method. *J. Phys. Chem. C* 113: 10767-10772.
- Visser, O., Visscher, L., Aerts, P.J.C. & Nieuwpoort, W.C. 1992. Molecular open shell configuration interaction calculations using the Dirac-Coulomb Hamiltonian: The f⁶-manifold of an embedded EuO₆⁹-cluster. J. Chem. Phys. 96(4): 2910.
- Yanmin, Y., Baojiu, C., Cheng, W., Guozhong, R. & Xiaojun, W. 2007. Investigation of modification effect of B₂O₃ component on optical spectroscopy of Er³+ doped tellurite glasses. J. Rare Earths 25(1): 31-35.

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Received: 23 October 2014 Accepted: 5 May 2015