Synthesis and Luminescence Properties of Doped Magnesium Boro-Tellurite Ceramics

Nur Zu Bohari,*, R. Hussin, Zuhairi Ibrahim, Hendrik O. Lintang

*Phosphor Research Group, Department of Physics, Faculty of Science, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor Malaysia
†Ibnu Sina Institute for Fundamental Science Studies, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor Malaysia

*Corresponding author: nzura@gmail.com

Article history
Received: 05 July 2014
Received in revised form: 17 November 2014
Accepted: 1 February 2015

Graphical abstract

Abstract

Glass has been widely utilized in the field of lighting, telecommunication and spectroscopy. Boro-tellurite is one of the suitable glasses used for solid state lighting and laser application. The investigation on the luminescence properties of rare earth doped ceramic is rarely used due to the opacity. In this paper boro-tellurite prepared in ceramic can show the better luminescence with the less advantage. The aim of this paper is to present the effect and advantages in luminescence results of boro-tellurite ceramics doped with the constant amount of rare earth. Doped magnesium boro-tellurite with Eu3+ and Dy3+ ceramic have been prepared using solid state reaction method with the compositions of xTeO2-(70-x)B2O3-30MgO with 10≤x≤40, and have been doped with Eu3+O2 (1mol%) and Dy3+O2 (1mol%). The characterizations of the samples have been investigated by means of X-Ray diffraction, Raman, Infrared and Photoluminescence spectroscopy. From the X-ray diffraction results, two phases are assigned to MgTe2O4 and Mg5B2O7. Raman spectroscopy showed strong bands observed in the vicinity of 140, 175, 220, 266, 332, 403, 436, 646, 694, 723, 757 and 806 cm−1. FTIR spectra showed bands located in the range between 400-800 cm−1 are assigned to the bending mode of Te-O-Te, TeO2 and TeO4. In the range of 800-1400 cm−1, the bands are associated with B-O, B-O-B, BO3 and BO4 bonds. The emission transition D1→F2 corresponded to the red emission (612 nm) was found to be the most intense in all the Eu3+-doped magnesium boro-tellurite ceramics.

Keywords: Magnesium boro-tellurite ceramic, luminescence, doped Eu3+ and Dy3+

Abstrak


Kata kunci: Seramik magnesium boro-tellurite, luminesens, dop Eu3+ dan Dy3+ © 2015 Penerbit UTM Press. All rights reserved.

1.0 INTRODUCTION

Ceramic based on boro-tellurite host matrices doped with rare earth have tremendous applications for lasers, optical amplifier, photo sensitivity, optical storage, and bio-ceramics materials [1-8]. Currently, a great deal of research has been focused on rare earth (RE) doped glasses owing to their extensive applications [9-10]. But, the investigation on the luminescence properties of rare earth doped ceramic is rarely used due to the opacity and hence, limited their applications. Eu3+ ion doped sodium-aluminum-tellurite (Eu3+: NAT) was prepared in opaque ceramics compound [11].
The host material with low phonon energy that can reduce the non-radiative loss, play important role for obtaining highly efficient luminescent properties via multiphonon relaxations and thus achieve strong luminescence [12]. In this study, tellurite oxide based has been utilized due to their desirable physical properties, such as high refractive index, excellent infrared transmittance and high dielectric constant, good chemical durability and low melting temperature. On the other hand, borate has important physical properties such as high transparency, low melting point, high thermal stability, good rare earth ions solubility, resistance to chemicals and can enhance mechanical durability [3]. Addition of alkali oxide (MgO) as network modifier has also been employed since the utilization of modifier doped with boro-tellurite based are rarely reported.

The aim of this work is to prepare doped magnesium boro-tellurite ceramics via solid state reaction route and to study the behavior through X-Ray Diffraction (XRD), Infrared (IR), Raman and Photoluminescence (PL) spectroscopic for both materials. The concentration of Eu$^{3+}$ and Dy$^{3+}$ will remain constant.

### 2.0 EXPERIMENTAL

High purity of H$_2$BO$_3$ (99.99%), TeO$_2$ (99.99%), MgO (99.99%), Eu$_2$O$_3$ (99.99%) and Dy$_2$O$_3$ (99.99%) were used as the raw materials. Two types of sample were prepared for the study; magnesium boro-tellurite ceramic and magnesium boro-tellurite with Eu$^{3+}$ and Dy$^{3+}$ ceramic. The samples with the compositions of xTeO$_2$-(70-x)B$_2$O$_3$-30MgO with 10≤x≤40 mol%, doped with Eu$_2$O$_3$ (1mol%) and Dy$_2$O$_3$ (1mol%) have been prepared using solid state reaction method. Analytical grade reagents of H$_2$BO$_3$, TeO$_2$, MgO, Eu$_2$O$_3$ and Dy$_2$O$_3$ powders in appropriate amounts (mol%) were thoroughly mixed in agate mortar. The mixtures were pressed into pellets using hydraulic press with 10 ton/cm$^2$ of pressure. Pelletized samples were then heat treated at 650 °C for 6 hours. The dried pellet was grounded into fine powder for further characterizations.

Several experiments have been setup to determine the physical nature and characteristics of the prepared samples. The examination of the structure was examined using X-ray diffraction (XRD) using Siemens Diffraction D500 diffractometer with CuKα radiation [13]. Fourier transform infrared spectroscopy (FTIR) was examined using Perkin-Elmer spectrometer (Spectrum 100) [13]. Raman spectroscopy was examined using Bruker model RFS 100/S FT-Raman spectrometer. The emission spectra were obtained using Jasco Fluorescence spectrophotometer, Model FP8000 series, at room temperature.

### 3.0 RESULTS AND DISCUSSION

X-ray diffraction technique was used to identify the crystalline phase of the doped magnesium boro-tellurite with Eu$^{3+}$ and Dy$^{3+}$ ceramics. The XRD patterns, Figure 1, show the influence of varying composition of the xTeO$_2$-(70-x)B$_2$O$_3$-30MgO with 10≤x≤40 mol%. The x-ray diffractionogram showed well-defined peaks which indicate the crystalline and phase formation of the synthesized compounds. There are two main phases; namely MgTeO$_3$ (ICDD: 01-073-3922) and Mg$_2$BO$_3$ (ICDD: 01-073-2107). The intensity increased with B$_2$O$_3$ and decrease with TeO$_2$, ranging from x = 10 to 40. MgTeO$_3$ became a dominant phase in the sample followed by Mg$_2$BO$_3$ phase. The majority phase of MgTeO$_3$ is an evident that the TeO$_2$ contribute to the formation of the phase. The percentage of the crystalline phase can be estimated by comparing the highest peak heights summarized in the Table 1. From the estimation of Table 1, it can be concluded that the MgTeO$_3$ was the dominant phase.

Raman spectrum of xTeO$_2$-(70-x)B$_2$O$_3$-30MgO are presented in Figure 2. Raman spectroscopy show the strong band are observed at 140, 175, 220, 266, 332, 403, 436, 646, 694, 723, 757 and 806 cm$^{-1}$. Raman spectrum show that besides the expected TeO$_4$, Te$_2$O$_4$, TeO$_3$, and BO$_3$ (peak 7 to 12) existent, the vibrations corresponding to the metal ions are also present in ceramics (peak 1 to 6), respectively.

### Table 1 The estimation of percentage of the crystalline phase of xTeO$_2$-(70-x)B$_2$O$_3$-30MgO doped Eu$^{3+}$ and Dy$^{3+}$ ceramic (10≤x≤40 mol%)

<table>
<thead>
<tr>
<th>x</th>
<th>MgTeO$_3$ phase (%)</th>
<th>Mg$_2$BO$_3$ phase (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>58.03</td>
<td>41.97</td>
</tr>
<tr>
<td>20</td>
<td>62.94</td>
<td>37.05</td>
</tr>
<tr>
<td>30</td>
<td>67.94</td>
<td>32.06</td>
</tr>
<tr>
<td>40</td>
<td>76.00</td>
<td>23.99</td>
</tr>
</tbody>
</table>

![Figure 1](image1.png) X-ray diffraction pattern of xTeO$_2$-(70-x)B$_2$O$_3$-30MgO doped Eu$^{3+}$ and Dy$^{3+}$ ceramic (10≤x≤40 mol%)

![Figure 2](image2.png) Raman spectra of xTeO$_2$-(70-x)B$_2$O$_3$-30MgO doped Eu$^{3+}$ and Dy$^{3+}$ ceramic (10≤x≤40 mol%)
The infrared spectrum of \(x\text{TeO}_2-(70-x)\text{B}_2\text{O}_3-30\text{MgO}\) with 10\(\leq x\leq 40\) mol% in the range 1400-4000 cm\(^{-1}\) are presented in the Figure 3. There are four bands in this range when the peaks represent OH- and H-units are at around 3215 cm\(^{-1}\), 2920 cm\(^{-1}\) and 2261 cm\(^{-1}\). The peaks observed between 3375 cm\(^{-1}\) and 4000 cm\(^{-1}\) are the hydroxyl groups due to OH- stretching and the peaks observed between (2800-2900) cm\(^{-1}\) are the hydrogen bond [9]. Based on the Figure 3, the peaks around 1500 cm\(^{-1}\) are due to the B-O stretching of BO\(_3\) units which are observed and the band became smaller (\(x=40\)), indicating a decrease in TeO\(_2\) amounts and increasing B\(_2\)O\(_3\).

![Figure 3 IR spectra of \(x\text{TeO}_2-(70-x)\text{B}_2\text{O}_3-30\text{MgO}\) doped \(\text{Eu}^{3+}\) and \(\text{Dy}^{3+}\) ceramic (10\(\leq x\leq 40\) mol%)](image)

In Figure 4, the IR spectra of \(x\text{TeO}_2-(70-x)\text{B}_2\text{O}_3-30\text{MgO}\) with 10\(\leq x\leq 40\) mol% in the range of (1800-4000) cm\(^{-1}\) is presented. The bands located in the range between (400-800) cm\(^{-1}\) are assigned to the bending mode of Te-O-Te, Te-O\(_2\) and TeO\(_3\). In the range of (800-1400) cm\(^{-1}\), the B-O bond of B-O-B, BO\(_3\) and B\(_2\)O\(_3\) also appeared. The bands located around (1331-1362) cm\(^{-1}\) are assigned to BO\(_3\) units [15, 21] and in the range between (881-1200) cm\(^{-1}\) which is the BO\(_2\) units [10, 14, 16]. The bands positions around 431 cm\(^{-1}\), 564 cm\(^{-1}\), 610-680 cm\(^{-1}\) and 700-780 cm\(^{-1}\) showed the Te-O-Te, TeO\(_2\) and TeO\(_3\) respectively. All of these assignments are in good agreement with the reported literature [10, 17-18]. In Figure 4, the band gradually increased with TeO\(_2\). The intensity of the band in the range of 431-780 cm\(^{-1}\) increased gradually with TeO\(_2\) and the intensity of the band slightly decreased with B\(_2\)O\(_3\) in the range of 881-1362 cm\(^{-1}\).

![Figure 4 IR spectra of \(x\text{TeO}_2-(70-x)\text{B}_2\text{O}_3-30\text{MgO}\) doped \(\text{Eu}^{3+}\) and \(\text{Dy}^{3+}\) ceramic (10\(\leq x\leq 40\) mol%)](image)

The emission spectrum of doped \(x\text{TeO}_2-(70-x)\text{B}_2\text{O}_3-30\text{MgO}\) with 10\(\leq x\leq 40\) mol% is shown in Figure 5. The emission transitions \(\text{D}^{0}\rightarrow\text{F}_6\), \(\text{D}^{0}\rightarrow\text{F}_9\), \(\text{D}^{0}\rightarrow\text{F}_0\), \(\text{D}^{0}\rightarrow\text{F}_2\), \(\text{D}^{0}\rightarrow\text{F}_7\), \(\text{D}^{0}\rightarrow\text{F}_3\), \(\text{D}^{0}\rightarrow\text{F}_4\), \(\text{D}^{0}\rightarrow\text{F}_5\) and \(\text{D}^{0}\rightarrow\text{F}_7\) corresponded to the band position at 484.58, 578.17, 589.89, 612.82, 618.38, 651.23, 683.48, 691.53 and 700.85 nm, respectively. It can be noted that a series of \(\text{Eu}^{3+}\) characteristic emission lines are between 540 nm and 780 nm, which includes the most prominent peak at 612 nm and corresponding to the \(\text{D}^{0}\rightarrow\text{F}_2(J=0, 1, 2, 3, 4)\) transitions [19]. The luminescence spectrum was found to be lowest for the sample \(x=10\) followed by \(x=20, 30\) and 40. The \(\text{D}^{0}\rightarrow\text{F}_2\) transition is more intense than the other transitions as reported in the other literatures [20-22].

The emission peaks of \(\text{Dy}^{3+}\) were observed at 484.58 nm and 578.17 nm (peak 1 and 2) similar with the other reported values [23]. Figure 5 shows the emission peaks of \(\text{Eu}^{3+}\) are more dominant with high intensity compared to the peaks of \(\text{Dy}^{3+}\). The \(\text{Dy}^{3+}\) emission peaks are not present as dominant peak which indicates that \(\text{Dy}^{3+}\) acts as trap centers that cause long afterglow characteristics, rather than the luminescent centers in the host lattice [24].

![Figure 5 Emission spectrum of \(x\text{TeO}_2-(70-x)\text{B}_2\text{O}_3-30\text{MgO}\) doped \(\text{Eu}^{3+}\) and \(\text{Dy}^{3+}\) ceramic (10\(\leq x\leq 40\) mol%)](image)

### 4.0 CONCLUSION

The samples of \(x\text{TeO}_2-(70-x)\text{B}_2\text{O}_3-30\text{MgO}\) with 10\(\leq x\leq 40\) mol% doped with \(\text{EuOx}(1\text{mol%})\) and \(\text{DyOx}(1\text{mol%})\) have been prepared using solid state route. The structural studies of the samples have been investigated using X-ray diffraction (XRD), Infrared and Raman spectroscopy. The XRD profiles show that \(\text{MgTeO}_3\) became a dominant phase in the sample followed by \(\text{Mgb}_2\text{O}_3\) phase. The IR spectrum shows two series of band regions which obtained in 4000-1400cm\(^{-1}\) and the second region of 1400-400cm\(^{-1}\). The ceramics doped with \(\text{Eu}^{3+}\) shows a bright red emission at 612nm which belongs to the electric dipole \(\text{D}^{0}\rightarrow\text{F}_2\) transition of \(\text{Eu}^{3+}\) ions. There are two groups of emission at 484 nm and 578 nm occurring in the emission spectrum of the ceramics, which probably can be applied for white LEDs application.

Acknowledgement

The authors would like to acknowledge the financial supports from the Fundamental Research Grant Scheme (FRGS) under research grant Project Number: R.J130000.7826.4F140 and the authors would like to thanks Faculty of Science, Universiti Teknologi Malaysia for providing the facilities.
References

[23] Lakshminarayana, G. and J. Giu. 2008. Photoluminescence of Pr\(^{3+}\), Sm\(^{3+}\) and Dy\(^{3+}\):SiO\(_2\)-Al\(_2\)O\(_3\)-LiF-Gd\(_2\)O\(_3\) glass Ceramics and Sm\(^{3+}\), Dy\(^{3+}\):GeO\(_2\)-B\(_2\)O\(_3\)-ZnO-LaF\(_3\) Glasses. Physica B. 404: 1169–1180.