PHYSICAL AND SPECTROSCOPIC CHARACTERISATION OF SAMARIIUM DOPED MAGNESIUM TELLURITE GLASS EMBEDDED SILVER NANOPARTICLES

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To my beloved father (Mohammad Yusoff bin Ismail) and mother (Wan Pah binti Wan Mahmud),
to my dearest older sister (Fadilah binti Zaini),
to my valued sibling (Nurul Suhaila, Nurul Aini,
Mohammad Nasaruddin, Nurul Asmira,
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There is nothing in my life that makes me happier and cheerful than your love and care.
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ABSTRACT

Three series of samarium doped magnesium tellurite glasses embedded with silver nanoparticles (Ag NPs) of composition (89-x)TeO$_2$-10MgO-1Sm$_2$O$_3$-xAgCl with 0 ≤ x ≤ 1.0 mol%, (89.6-x)TeO$_2$-10MgO-(x)Sm$_2$O$_3$-0.4AgCl with 0.2 ≤ x ≤ 1.2 mol% and 88.6TeO$_2$-10MgO-(x)Sm$_2$O$_3$-(1.4-x)AgCl with 0.2 ≤ x ≤ 1.0 mol% were prepared using melt quenching technique. It is found that the glass samples are yellowish in colour depending on their composition. The existence of broad hump in X-ray diffraction (XRD) pattern verifies the amorphous nature of glasses and the presence of silver nanoparticles with average diameter of 16.94 nm in the glass matrix is confirmed by transmission electron microscope (TEM) image. The glass density (ρ), molar volume ($V_m$) and ionic packing density ($V_t$) are in the range of (4.91-5.51) g cm$^{-3}$, (27.13-30.46) cm$^3$ mol$^{-1}$ and (0.444-0.498), respectively. The samples exhibit glass stability up to 102°C which indicates the enhancement in ability of glass formation. The fourier transform infrared (FTIR) and Raman spectra reveal modification in network structures which is evident from the shifted vibrational wave-number of TeO$_4$ and TeO$_3$ structural units located around 600 cm$^{-1}$ and 700 cm$^{-1}$, respectively. Two surface plasmon resonance (SPR) peaks are detected at 550 nm for transverse oscillation and 578 nm for longitudinal oscillation from ultraviolet-visible (UV-Vis) absorption spectra. The optical energy band gap and Urbach energy are found in the range of (2.81-3.13) eV and (0.18-0.26) eV, respectively. Refractive index and electronic polarisability have also been calculated and found in the range of (2.35-2.45) and (6.68-7.51) Å$^3$, respectively. The absorption measurement is complemented with determination of bonding characteristic of Sm$^{3+}$ and ligand via calculations of nephelauxetic ratio and Racah parameters. It is found that the addition of Sm$^{3+}$ and Ag$^0$ alters the electron distribution which leads to the increase of the covalent bond between Sm and ligand. The glass samples are excited under 554 nm excitation wavelength and the emission spectra are found to consist of a single emission band corresponding to $^4$G$_{5/2}$→$^4$H$_{11/2}$ transition. The intensity enhancement of such transition rises up to 3 times compare to glass without Ag NPs which is attributed to the local field effect and energy transfer from Ag$^0$ to Sm$^{3+}$. The quality factor, Q is also obtained in the range of 19.20-24.25 which is due to the phonon loss during the non-radiative emission. Meanwhile, decay half-life is determined in the range of (1.4405-1.4459) µs depending on composition. The properties of this glass are very much dependent on the concentration of Sm$^{3+}$ and Ag NPs. This type of glass has a wide potential to be used as red laser medium and in various photonic applications.
ABSTRAK

Tiga siri kaca magnesium tellurite berdopkan samarium oksida yang tertanam zarah nano perak (Ag NPs) dengan komposisi \((89-x)\text{TeO}_2-10\text{MgO}-15\text{Sm}_2\text{O}_3-x\text{AgCl}\) \((0 \leq x \leq 1.0 \text{ mol\%})\), \((89.6-x)\text{TeO}_2-10\text{MgO}-(x)\text{Sm}_2\text{O}_3-0.4\text{AgCl}\) \((0.2 \leq x \leq 1.2 \text{ mol\%})\) dan \(88.6\text{TeO}_2-10\text{MgO}-(x)\text{Sm}_2\text{O}_3-(1.4-x)\text{AgCl}\) \((0.2 \leq x \leq 1.0 \text{ mol\%})\) disediakan melalui teknik pelindapan leburan. Kaca tersebut berwarna kekuningan bergantung kepada komposisinya. Kewujudan puncak yang lebar daripada corak pembelauan sinar-X (XRD) mengesahkan sifat amorfus kaca dan kehadiran zarah nano perak dengan purata diameter 16.94 nm di dalam matrik kaca disahkan melalui mikroskop elektron transmisi (TEM). Ketumpatan kaca \(\rho\), isipadu molar \(V_m\) dan ketumpatan padatan ioni \(V_t\) masing-masing dalam julat \((4.91-5.51) \text{ g cm}^{-3}\), \((27.13-30.46) \text{ cm}^3 \text{ mol}^{-1}\) dan \((0.444-0.498) \text{ Å}^3\). Sampel tersebut mempamerkan kestabilan kaca sehingga 102°C yang menunjukkan peningkatan dalam keupayaan membentuk kaca. Spektrum transformasi fourier infra merah (FTIR) dan Raman menunjukkan pengubahsuaian dalam struktur rangkaian dan dibuktikan melalui anjakan getaran nombor gelombang bagi struktur unit \text{TeO}_4 dan \text{TeO}_3 yang masing-masing terletak di sekitar 600 cm\(^{-1}\) dan 700 cm\(^{-1}\). Dua puncak resonans plasmon permukaan (SPR) dikesan pada 550 nm untuk ayunan melintang dan 578 nm untuk ayunan membujur daripada spektrum penyerapan ultra lembayung-boleh nampak (UV-Vis). Jurang tenaga optik dan tenaga Urbach ditemui mengalami peningkatan 3 kali ganda berbanding dengan kaca tanpa Ag NPs yang disebabkan oleh kesan medan setempat dan pemindahan tenaga dari \text{Ag}\(^0\) ke \text{Sm}\(^{3+}\). Faktor kualiti, \(Q\) juga diperoleh dalam julat 19.20-24.25 yang disebabkan oleh kehilangan fonon semasa berlakunya pancaran tak radiatif. Sementara itu, setengah hayat pereputan juga telah ditentukan dalam julat \((1.4405-1.4459) \mu\text{s}\). Kaca jenis ini mempunyai potensi yang luas untuk digunakan sebagai medium laser merah dan dalam pelbagai aplikasi fotonik.
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<tbody>
<tr>
<td>(\bar{x})</td>
<td>arithmetic mean</td>
</tr>
<tr>
<td>(\rho)</td>
<td>glass density</td>
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<tr>
<td>(V_m)</td>
<td>molar volume</td>
</tr>
<tr>
<td>(V_t)</td>
<td>ionic packing density</td>
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<tr>
<td>(V_i)</td>
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<td>onset crystallization temperature</td>
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<td>(\Delta T)</td>
<td>thermal stability</td>
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<td>(\nu)</td>
<td>vibrational frequency</td>
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<td>(\mu)</td>
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<td>(I)</td>
<td>intensity of transmitted light</td>
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<tr>
<td>(a)</td>
<td>absorption coefficient</td>
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<tr>
<td>(E_{opt})</td>
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<td>(\Delta E)</td>
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<tr>
<td>(h\nu)</td>
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<tr>
<td>(n)</td>
<td>refractive index</td>
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<td>Description</td>
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<tr>
<td>$F$</td>
<td>field strength</td>
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<tr>
<td>$R_m$</td>
<td>molar refraction</td>
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<tr>
<td>$M$</td>
<td>metallization parameter</td>
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<td>$\delta$</td>
<td>bonding parameter</td>
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<tr>
<td>$\bar{\beta}$</td>
<td>average nephelauxetic ratio</td>
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<tr>
<td>$h$</td>
<td>nephelauxetic function</td>
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<tr>
<td>$k_{ion}$</td>
<td>central metal ion</td>
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<tr>
<td>$\tau$</td>
<td>half-life</td>
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<tr>
<td>$Q$</td>
<td>quality factor</td>
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<tr>
<td>ASTM</td>
<td>American Society for Testing and Materials</td>
</tr>
<tr>
<td>TMO</td>
<td>transition metal oxide</td>
</tr>
<tr>
<td>tbp</td>
<td>trigonal bipyramidal</td>
</tr>
<tr>
<td>tp</td>
<td>trigonal pyramidal</td>
</tr>
<tr>
<td>Oeq</td>
<td>equatorial oxygens</td>
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<tr>
<td>Oax</td>
<td>axial oxygens</td>
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<tr>
<td>ZnO</td>
<td>Zinc oxide</td>
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<tr>
<td>MgO</td>
<td>Magnesium oxide</td>
</tr>
<tr>
<td>RE</td>
<td>Rare earth</td>
</tr>
<tr>
<td>BO</td>
<td>Bridging oxygens</td>
</tr>
<tr>
<td>NBO</td>
<td>Non-bridging oxygens</td>
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<td>NPs</td>
<td>Nanoparticles</td>
</tr>
<tr>
<td>SPR</td>
<td>Surface plasmon resonance</td>
</tr>
<tr>
<td>ET</td>
<td>Energy transfer</td>
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<tr>
<td>CCD</td>
<td>charge couple device</td>
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CHAPTER 1

INTRODUCTION

1.0 Introduction

Glass can be defined as an amorphous solid which is stand for absences of long-range order or structureless solid. There is no regularity in the arrangement of its molecular constituent. Morey [1] defines glass as an inorganic substance in which its behaviour is analogous to the liquid state of that substance. According to American Society for Testing and Materials (ASTM), glass is defined as an inorganic product of fusion which has cooled to a rigid condition without crystallizing. Meanwhile, Secrist and Mackenzie [2] define a glass as a non-crystalline solid. The historical of glass definitions obviously refers and reflects to the evolution of glass development regarding to the technological interest and commercially important. Glasses are easily produced from a melt by rapid cooling to a sufficiently low temperature which is well known as melt quenching technique. The fast cooling rate generally in the order of $10^7$ degrees per second may avoid the crystallisation to occur in the glassy phase. Of course, there are many other technique for preparing glass [3]. However, the melt quenching technique has been used in this study since it is the cheapest and the shortest time consuming. Glasses can be fabricated into a variety of shapes and sizes with an appropriate composition [4]. Glass features are essentially depending on its composition [5].
The number of materials to form glasses is rapidly increases [6]. Among the most motivated studies of glassy materials, tellurite based glasses draw much interest because of their unique properties such as high dielectric constant and excellent transmission in the visible as well as IR wavelength regions, good mechanical strength and chemical durability [7-10]. These glasses also possess higher refractive index which is approximately in the range of 2.0 to 2.5 [11-14] and their low melting temperature (about 800°C) contributes to the high possibility of stable glass forming using a conventional melt quenching method [10]. Although, pure tellurium oxide cannot form glass by itself but needs another element known as glass modifier such as alkali metal, alkaline earth metal oxide and transition metal oxide (TMO) to improve the network connectivity then produce a stable tellurite glass [15-16] with increasing non-bridging oxygen [15]. Thus, reduce the rigidity of TeO₂ structure and easily produce disorder structure. TeO₂ glassy and crystalline states are built by co-ordination of Te⁴⁺ ions in TeO₄ groups as trigonal bipyramidal (tbp) form with bridging oxygen [17]. In TeO₄ tbp linkage, two oxygen atoms are located in the axial site, while the other two and the lone electron pair of tellurium are located in the three equatorial sites. Kim [18] acknowledged that the equatorial Te-O bonds are slightly shorter than the axial bonds. Damas et al. [19] reported that the two equatorial oxygens (Oₑq) possessed a distance of 1.9Å from the Te atom, while the two axial oxygens (Oₐx) possesses a distance of 2.1Å from Te atom. Trigonal bipyramids are linked by each other by sharing their vertices which form a continuous three-dimensional structure [20] as shown in Figure 1.1. The basic structure of TeO₂ glass network often changes from TeO₄ to TeO₃⁺₁ and/or TeO₃ in the presence of network modifier. The substitution of network modifier such as MgO and ZnO would produce the stable tellurite glass [21-22]. The addition of such modifiers would modify and increase non-bridging oxygen, consequently open up the glass structure. In this case, the Te-O-Te linkages in TeO₄ will break into TeO₃⁺₁ or TeO₃ structural unit. In addition, it is reported that the alkaline earth metals are good network modifiers for tellurite glass [23-24].
Te-O bonds can also be easily broken and accommodate heavy metal oxides or rare earth (RE) precisely called as dopant. Nelson et al. [25] have proposed two important effects of dopant ions in terms of their local environment. Firstly, each of the dopant ions can occupy an individual site which is determined by the configuration of the structural unit in the melt. Secondly, dopant can modify the spatial geometry of the nearby glass network to outfit their own bonding requirement. Moreover, dopants can also act as network modifiers and thus promote the formation of high number of non-bridging oxygen (NBO) [26]. TeO₂ based glass is good for hosting rare earth ion since they provide low phonon energy (~750 nm), which minimizes non-radiative losses [27-28]. RE doped glass has long held tradition of facilitating lasing character inside the glass matrix. Samarium is one of the important active ion in rare earth family which exhibits strong orange-red luminescence in the visible region and very useful in high density optical storage, under water communication, colour displays and visible solid state lasers. The luminescence properties either down or up conversion phenomena has widely been

Figure 1.1: The TeO₄ tbp structural unit of tellurium oxide. The distances of Te-O bond are also shown [19].
studied in various based glass. These studies show that the emission intensities are strongly dependent of Sm$^{3+}$ concentration and glass composition [29].

It is worth to notice that RE doped glasses may exhibit some unwanted effects such as concentration quenching due to the energy-transfer to neighbouring ions. So in order to enhance the luminescence efficiency and remove this drawback, several methods can be adopted. The embedding of metallic nanoparticles (NPs) inside the glass host thus changing the environment felt by the RE ions is introduced a successful strategy [30-34]. Recently, Sm$^{3+}$ ion is verified as a dopant while Au or Ag NPs are demonstrated as stimulating agents for the enhancements of absorption and emission properties [35]. The metallic NPs assisted strong modifications in the rare earth transition probabilities caused by local field effect and energy transfer are easily detected from emission measurements. The composition, shape and size of NPs play significant roles towards their interaction with external radiation [36].

1.1 Problem Statement

The nano era revolution demands the synthesis of new nanostructured materials, if possible by a simple technique but with remarkable properties and versatile applications [37]. Previous study of nanoglass has been focused on embedding of metallic nanoparticles in glass containing rare earth ions only [36, 38-41]. In order to pursue this area, a well-designed new glass composition should be developed and presented. Rare doped tellurite glass embedded nanoparticles has been reported to improve luminescence intensity due to energy transfer and local field effect [36, 38-41]. The enhancement of luminescence intensity and the avoidance of quenching effect is a challenge effort. Up to date, most of study focused on the embedment of Au NPs in Er$^{3+}$/Yb$^{3+}$ co-doped tellurite glass [42], Er$^{3+}$ doped tellurite glass [43], meanwhile the embedment of Ag NPs on Er$^{3+}$ doped tellurite glass [40], Dy$^{3+}$ doped tellurite glass [41], Sm$^{3+}$:Yb$^{3+}$ co-doped tellurite glass [37]. In sequence,
the embedment of Ag NPs with an optimum concentration into tellurite glass containing single rare earth especially Sm$^{3+}$ is important to be emphasised. Additionally, since there is a lack of report on these glasses, it is of particular important to study these glasses in order to give more information on the influence of Ag NPs and Sm$^{3+}$ ion on the glass. It is therefore, the aim of this work to characterise the glass by means of their physical, thermal, structural, absorption features and the quality of the emission intensity.

1.2 Objectives

In order to solve the problem as stated in Section 1.1, several objectives have been outlined as follows,

1) To prepare glass samples containing Ag NPs and Sm$^{3+}$ ion by melt quenching technique in three glass series of composition,

   a. Series 1: (89-x)TeO$_2$-10MgO-1Sm$_2$O$_3$-xAgCl, where 0≤x≤1.0 in mol%
   b. Series 2: (89.6-x)TeO$_2$-10MgO-xSm$_2$O$_3$-0.4AgCl where 0.2≤x≤1.2 in mol%
   c. Series 3: 88.6TeO$_2$-10MgO-xSm$_2$O$_3$-(1.4-x)AgCl where 0.2≤x≤1.0 in mol%.

2) To determine the influence of substituted Ag NPs and Sm$^{3+}$ ion in the glass on physical and thermal properties by calculating density, molar volume, ionic packing density and thermal parameters, respectively.
3) To investigate the role of Ag NPs and Sm$^{3+}$ ion on structural properties of the glass by measuring the change of band position in Infrared and Raman spectroscopy.

4) To investigate the role of Ag NPs and Sm$^{3+}$ ion on the absorption features of the glass by measuring optical energy band gap, Urbach energy, refractive index, and electronic polarizability up to bonding parameter accomplished from UV-Visible spectroscopy.

5) To explore the effect of Ag NPs and Sm$^{3+}$ ion on luminescence enhancement or quenching effect, spectroscopic quality factor and decay half lifetime of the glass accomplished from Photoluminescence Spectroscopy.

1.3 Scope of Study

This study attempted to identify the characteristic of bulk glass samples in three different compositions prepared by a conventional melt quenching technique. The glass densities are measured by Archimedes method since the glass samples have an irregular shape. The measured densities are very useful to determine the molar volume and ionic packing density. Thermal parameters such as glass transition temperature ($T_g$), onset crystallisation temperature ($T_x$) and melting temperature ($T_m$) are also determined by thermogram curve obtained from Differential Thermal Analyser (DTA). In term of structural modification, the research will focus on the change of band position in Infrared spectra and Raman spectra obtained from IR spectrometer and Raman spectrometer, respectively. In this respect, the discussion will only be focus on the change of wavenumber for TeO$_4$ trigonal bipyramidal, TeO$_{3+1}$ tetrahedral and TeO$_3$ trigonal pyramidal. Meanwhile, the study on the absorption feature obtained from UV-Vis spectrophotometer will covers optical
energy band gap, Urbach energy, refractive index and electronic polarizability up to calculation of Racah parameters of bonding characteristic only. Then the enhancement factor, quality factor and decay lifetime will be accomplished from Photoluminescence spectrometer.

1.4 Significant of Study

Study of metallic silver nanoparticles substituted at TeO$_2$ host site provides useful information on the advancement of the glass knowledge. By knowing the amplitude of enhancement factor of luminescence characteristic, the effectiveness of Ag NPs will become clearer. This study also will contribute to a better understanding on bonding and structural characteristic in order to get an optimum amount of Ag NPs which could explain the enhancement phenomena in luminescence. Furthermore, the fundamental phenomenon on the optical characteristic is no exception to be discussed in this study. According to this, the relationship between optical characteristic, glass structural modification and luminescence enhancement can be well explained. This research is very important in view that the required level of luminescence intensity of samarium ion for multipurpose of usage and very significant in the development of nanoscience. Moreover, the optimize method for controlling the Ag NPs and Sm$^{3+}$ ions in improving the structural and optical characteristics of magnesium tellurite glasses may constitute a basis for their large scale synthesis useful for sundry of applications.
1.5 Thesis organisation

This thesis is made up by five main chapters namely introduction, literature review, methodology, results and discussions, and conclusion and recommendation. In the Chapter 1 (Introduction), a briefly explanation about tellurite glass, problem statement, objective, scope of study, significant of study and thesis organisation are provided. In Chapter 2 (Literature review), the basic theoretical of physical, thermal, structural, absorption and luminescence related to the previous research works are described. In Chapter 3 (Methodology), the glass preparation, method of measurement for each characterisation and principle work of each instrument as well as the characterisation framework are provided. In Chapter 4 (Results and Discussions), the obtained data are analysed by plotting graphs and presenting in table. The analysed data well discussed by comparing to the previous results in past research works. In Chapter 5 (Conclusion and Recommendation), the finding are concluded and summarised. Some recommendations for future works toward the prepared glass sample are listed.
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