EFFECTS OF MANGANESE OXIDE NANOPARTICLES EMBEDMENT ON OPTIC-MAGNETIC FEATURES OF MAGNESIUM BOROTELLURITE DOPED EUROPIUM GLASS

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....dedicated to my lovely parent:

AZIZ IBRAHIM 💙 CHE NONG SU

for their unconditional love, motivation and support..

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ABSTRACT

This thesis reports the modified optical and magnetic properties of europium doped and manganese oxide nanoparticles (Mn_3O_4NPs) embedded magnesium borotellurite glass. Glass samples with composition of (59-x)TeO_2-30B_2O_3-10MgO-1Eu_2O_3-$x$$Mn_3O_4$ with $0.0 \leq x \leq 2.0$ mol % and (59-y)TeO_2-30B_2O_3-10MgO-$y$$Eu_2O_3-1Mn_3O_4$ with $0.0 \leq y \leq 2.0$ mol % were prepared by melt-quenching technique. The amorphous nature of the glass was determined by X-Ray Diffractometer (XRD) and the presence of Mn_3O_4 NPs was verified by using Transmission Electron Microscope (TEM) and High Resolution Transmission Electron Microscope (HRTEM). The thermal parameters were determined by Differential Thermal Analyzer (DTA) and spectroscopic properties were measured by Raman, Ultraviolet-Visible (UV-Vis) and Photoluminescence (PL) spectrometer. Magnetic properties were determined by Vibrating Sample Magnetometer (VSM) and Electron Spin Resonance (ESR) spectrometer. The XRD patterns confirmed the amorphous nature of all glasses and TEM images manifested the growth of Mn_3O_4 NPs with average diameter 15 nm. HRTEM result revealed that the lattice spacing of Mn_3O_4 NPs was 0.308 nm at (112) plane. The thermal analysis showed that the glass transition temperature, T_g increases with the increase of Mn_3O_4 NPs and it was attributed to the arrangement of Mn_3O_4 NPs in the glass matrix. The glass with 1.0 mol % of Mn_3O_4 NPs and Eu_2O_3 showed the highest thermal stability, 126 ^{o}C and the glass forming tendency, 0.76. The Raman spectra displayed Mn_3O_4 NPs assisted alteration in the Te-O-Te, BO_3, BO_4, TeO_3 trigonal pyramidal and TeO_4 trigonal bipyramidal bonding vibrations. The UV-Vis spectra consist of three bands attributed to absorption from ground state ($^7F_0$) to $^5D_0$, $^5D_1$ and $^5D_2$ excited states. Two surface plasmon resonance (SPR) peaks of Mn_3O_4 NPs were detected at 388 nm and 516 nm. The emission spectra of Eu^{3+} ion under 390 nm excitations revealed four prominent peaks centered at 591 nm, 614 nm, 651 nm and 700 nm assigned to the transitions from $^5D_0 \rightarrow {}^7F_J$ (J=1, 2, 3, 4) states, respectively. Quenching effect in the luminescence intensity due to the incorporation of Mn_3O_4 NPs was ascribed to the energy transfer from the Eu^{3+} ion to Mn_3O_4 NPs. The calculated Judd-Ofelt intensity parameters (Ω_λ λ=2, 4, 6), radiative parameter and stimulated emission cross section of Eu^{3+} ions were found to be strongly influenced by Mn_3O_4 NPs. Prepared glass systems exhibit paramagnetic behavior with glass magnetization and susceptibility at room temperature in the range of (4.95-13.31×10^{-2}) emug^{-1} and (4.12-11.09×10^{-6}) emuOe^{-1}g^{-1} respectively. The ESR spectra of all glass samples exhibit two resonance signals with g values at 1.9 and 4.3 with higher signal observed at 1.9. In addition, correlations between the size of Mn_3O_4 NPs with saturation magnetization (M_s) and coercivity (H_c) were established. In conclusion, incorporation of Mn_3O_4 NPs in the glass system has improved the optical and magnetic properties of the glass.

ABSTRAK

Tesis ini melaporkan sifat optik dan magnet terubah suai yang berdopkan europium dan zarah nano mangan oksida (Mn_3O_4 NPs) berbenam kaca magnesium borotellurite. Sampel kaca dengan komposisi $(59\text{-}x)TeO_2\text{-}30B_2O_3\text{-}10MgO\text{-}1Eu_2O_3\text{-}xMn_3O_4$ dengan $0.0 \leq x \leq 2.0$ mol % dan $(59\text{-}y)TeO_2\text{-}30B_2O_3\text{-}10MgO\text{-}yEu_2O_3\text{-}1Mn_3O_4$ dengan $0.0 \leq y \leq 2.0$ mol % disediakan menggunakan teknik pelindapan leburan. Sifat amorfus kaca ditentukan oleh diffraktometer Sinar-X (XRD) dan kehadiran Mn_3O_4 NPs disahkan dengan menggunakan mikroskop elektron penghantaran (TEM) dan mikroskop elektron penghantaran beresolusi tinggi (HRTEM). Parameter terma ditentukan dengan penganalisa terma pembeza (DTA) dan sifat spektroskopi diukur dengan spektrometer Raman, penyerapan ultra lembayung boleh nampak (UV-Vis) dan fotoluminesens (PL). Sifat magnet ditentukan menggunakan magnetometer getaran sampel (VSM) dan spektrometer resonans putaran elektron (ESR). Corak XRD mengesahkan sifat amorfus bagi semua kaca dan imej TEM menunjukkan kewujudan Mn_3O_4 NPs dengan diameter purata 15 nm. Keputusan HRTEM mendedahkan jarak kekisi bagi Mn_3O_4 NPs ialah 0.308 nm pada satah (112). Analisis terma menunjukkan bahawa suhu peralihan kaca, T_g meningkat dengan pertambahan Mn_3O_4 NPs yang disebabkan oleh susunan Mn_3O_4 NPs dalam matriks kaca. Kaca dengan 1.0 mol % Mn_3O_4 NPs dan Eu_2O_3 menunjukkan kestabilan terma tertinggi, 126 ^{o}C dan kecenderungan pembentukan kaca tertinggi, 0.76. Spektrum Raman menunjukkan Mn_3O_4 NPs mempengaruhi perubahan dalam getaran ikatan Te-O-Te, BO_3, BO_4, piramid trigonal TeO_3 dan bipyramidal trigonal TeO_4. Spektrum UV-Vis terdiri daripada tiga jalur yang berpadanan dengan penyerapan dari keadaan dasar ($^7F_0$) kepada keadaan teruja $^5D_0$, $^5D_1$ dan $^5D_2$. Dua puncak resonans plasmon permukaan (SPR) bagi Mn_3O_4 NPs dicerap pada 388 nm dan 516 nm. Spektrum pancaran ion Eu^{3+} apabila diuja pada 390 nm memaparkan empat puncak yang berpusat pada 591 nm, 614 nm, 651 nm dan 700 nm masing-masing merujuk kepada peralihan $^5D_0 \rightarrow {}^7F_J$ (J = 1, 2, 3, 4). Kesan penurunan keamatan luminesens yang disebabkan oleh kehadiran Mn_3O_4 NPs adalah disebabkan berlakunya pemindahan tenaga daripada Eu^{3+} ion kepada Mn_3O_4 NPs. Pengiraan parameter keamatan Judd-Ofelt (Ω_λ = 2, 4, 6), parameter sinaran dan keratan rentas pancaran terangsang ion Eu^{3+} sangat dipengaruhi oleh Mn_3O_4 NPs. Semua kaca yang disediakan bersifat paramagnet dengan kemagnetan kaca dan kerentanan pada suhu bilik masing-masing dalam julat ($4.95\text{-}13.31\times10^{-2}$) emug^{-1} dan ($4.12\text{-}11.09\times10^{-6}$) emuOe^{-1}g^{-1}. Spektrum ESR menunjukkan semua kaca mempamerkan dua isyarat resonans dengan nilai g pada 1.9 dan 4.3 dengan isyarat resonans lebih tinggi pada 1.9. Sebagai tambahan, korelasi antara saiz Mn_3O_4 NPs dengan pemagnetan tepu (M_s) dan coerciviti (H_c) telah ditentukan. Kesimpulannya, kemasukan Mn_3O_4 NPs dalam sistem kaca telah menambahbaikkan sifat optik dan magnet kaca.

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LIST OF SYMBOLS

2θ	-	Angle of diffraction
ΔE	-	Urbach energy
ΔH_{pp}	-	Peak-to-peak line width
ΔS	-	Thermal stability
B	-	Magnetic field
d	-	Crystal lattice planar spacing
E	-	Energy
$\bar{E}$	-	Electric field
E_{opt}	-	Optical band gap
g	-	Gyromagnetic
H_c	-	Coercivity
H_r	-	Resonance magnetic field
hv	-	Photon energy
J	-	Angular momentum
M	-	Magnetization
M_s	-	Remanence magnetization
M_r	-	Saturation magnetization
n	-	Refractive index
O	-	Orbital
S	-	Spin
α	-	Absorption coefficient
μ_B	-	Bohr magneton
v	-	Wavenumber
χ	-	Susceptibility
T_m	-	Melting temperature

T_c	-	Crystallization temperature
T_g	-	Transition temperature

LIST OF ABBREVATIONS

BO	-	Bridging oxygens
DTA	-	Differential thermal analysis
ESR	-	Electron spin resonance
ET	-	Energy transfer
GSA	-	Ground state absorption
HRTEM	-	High resolution transmission electron microscope
JCPDS	-	Joint Committee on Powder Diffraction Standard
J-O	-	Judd Ofelt
NBO	-	Non-bridging oxygen
NPs	-	Nanoparticles
NR	-	Nonradiative
PL	-	Photoluminescence
QEs	-	Quantum efficiency
R	-	Radiative
RE	-	Rare earth
SAED	-	Selected area electron diffraction
SPR	-	Surface plasmon resonance
tbp	-	Trigonal bipyramidal
TEM	-	Transmission electron microscope
tp	-	Trigonal pyramidal
UV-Vis	-	Ultra violet visible
VSM	-	Vibrating sample magnetometer
XRD	-	X-ray diffraction

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Glasses are unique materials that have been used for thousands of years. Glass is defined as material that is produced through melting process and then being cooled to be a solid without going through a crystallization process [1]. Glass has been extensively investigated due to its high temperature resistance, high dielectric constant and good mechanical strength [2]. Furthermore, glass is not only known because of their excellent thermal and mechanical properties but they are potentially to become a good medium for luminescence due to the enhancement of the absorption efficiency of rare earth ions [3]. This excellent property has motivate researcher to further the study in optimizing luminescent and become more suitable material in the development of laser and solid state device.

Over the past few decades, tellurite glasses have gained so much interest over conventional silicate due to their high thermal expansion coefficients, excellent transmission in the visible as well as IR wavelength regions and low melting temperature [4]. These interesting properties making it feasible to be prepared at low temperature. Khafagy *et al.* [5] reported that the structure of tellurite glasses have two basic structural units, i.e as TeO_3 and TeO_4 units. The TeO_3 units dominated in the glass structural network but as the TeO_2 content increase, TeO_3 units transform into TeO_{3+1} then to TeO_4 units [6]. An intensive study on TeO_2 containing glasses has been conducted because of their properties such as exhibit high refractive indices, good chemical durability, better corrosion resistance and good mechanical strength [7].

Recently, tellurite glasses doped with boron oxide have received great scientific interest because these oxides significantly are able to change the properties of tellurite glasses [8][9]. Additionally, borate is one of the most attracting materials where their structural properties have been studied extensively [10]. Conversely, borate based glasses are prospective due to their flexible random network structure consisting of tetrahedral BO_4 and trigonal boron BO_3 units [11]. Besides, due to the excellent rare earth solubility, good infrared transmission and high thermal stability, borate glasses are attractive for the development of new optical devices [12]. However, the strong hygroscopic nature of borate glasses limits their applications [13]. This drawback can be surmounted by stabilizing the borate network with TeO_2 incorporation, which may offer improved chemical durability via the structural modifications of the tetrahedral boron networks [14].

Previous study by Wang *et al.* [15] claimed that TeO_2 is a conditional glass former which explain the incapability of that compound to form glass on its own. As a result, the introduction of borate into tellurite glass network simultaneously enhances the ability of glass formation. The combination of TeO_2 and B_2O_3 is an intrinsically interesting subject of study due to the stability of borotellurite (BT) compound [16]. Further, BT glass needs another element known as glass modifier such as alkaline earth metal oxide and transition metal oxide to improve the network connectivity then produce a stable BT glass [17] with increasing non-bridging oxygen (NBO). The addition of such modifiers would modify and increase the NBO, consequently open up the glass structure [18]. The substitution of network modifier such as MgO would produce stable BT glass [19].

To this day, rare earth ions (REIs) doped glass material becomes an interesting topic in luminescence material. The synthesis and characterizations of REIs doped binary and ternary glasses are intensively performed due to their advantages in developing efficient photonic devices [20]. Dehelean *et al*. [21] acknowledged that REIs doped glasses exhibit high brightness and improved efficiency thus are very prospective for broad array of technological applications. Trivalent Eu^{3+} ion is a well-known activator with simple electronic transitions. The Eu^{3+} ions possess prominent laser emissions in the orange or red region [22] and narrow band emission [23] with longer lifetime. Thus, BT glass has emerged as a favorable host for accommodating large amount of REIs. Maheshvaran *et al.* [3] reported that Eu^{3+} doped BT glass has potential for red-emitting glass due to excellent luminescent properties and can be used as optical materials. Hence, Eu^{3+} doped glass has drawn much interest in technological applications especially for optoelectronic materials [24].

Despite many studies, the Judd-Ofelt (J-O) theory has not been applied uniformly to characterize the spectroscopic properties of Eu^{3+} ion doped glasses. Bo and Teruto [25] used $^5D_0 \rightarrow ^7F_2$, $^7F_4$ and $^7F_6$ emission transitions of the Eu^{3+} ions to obtain the J-O parameters. Van Deun *et al.* [26] studied the absorption spectra of Eu^{3+} ion involving $^7F_0 \rightarrow ^5D_2$,$^5D_4$ and $^5L_6$ transitions, where the calculated J-O parameters of Eu^{3+} ions exhibits good agreement with the measured oscillator strengths. However, the study of J-O for glass containing magnetic NPs accompanied with REIs has not much been reported or been discussed in literature. In the present study the method of Bo and Teruto [25] to calculate the J-O parameters of Eu^{3+} ions doped inside BT glasses containing Mn_3O_4 NPs will be applied.

Currently, the development of multifunctional metallic NPs is in full swing [27] due to the feasibility of sundry applications. The research on the modifications in the structural, magnetic and optical properties of REIs doped glasses by embedding various metallic NPs is however still in progress. In this view, several attempts have been made to improve the optical properties of REIs doped glasses by incorporating various metallic NPs (magnetic and nonmagnetic). Lately, various magnetic NPs embedded glass systems are prepared such as Ni NPs incorporated samarium doped zinc phosphate glass [28] and Fe_3O_4 NPs in erbium doped zinc phosphate glass [29]. The impact of Ni^{2+} and Fe^{2+} magnetic NPs on the physical, structural and magneto-optic properties of REIs doped binary glasses have accrescent interest. Literatures hinted that these types of glasses with tailored properties are greatly potentials for the advancement of magneto-optic devices including isolators, switches and sensors [30].

Synthesis and characterization of magnetic (Fe, Co, Ni and Mn) NPs have ever-growing interest. Amongst all, Mn ions have been frequently used to improve the structural, electrical and magnetic properties of vitreous systems [31]. Manganese ions exist in different valence states in glassy matrices [32]. For example, Mn^{3+} ions in borate glasses exist with octahedral coordination whereas in silicate and germanate glasses they exist as Mn^{2+} ions with both octahedral and tetrahedral coordination [33]. Moreover, these well-known paramagnetic ions (Mn^{2+} and Mn^{3+}) are identified as strong luminescence activators [34]. The incorporation of Mn_3O_4 in glass has paramount importance due to their excellent physical and structural properties [31]. These transition metal ions contribute multi-valence states in the glass network and remarkably influence the properties. The appearance of super-paramagnetic behaviour, softness and large surface area of manganese nanoparticles make them highly potential magnetic materials [35] like manganese zinc ferrites useful for high density magnetic storage devices [36]. High saturation magnetization and magnetocrystalline anisotropy of Mn_3O_4 NPs are useful for creating excellent traps for excited electrons in the glass host. Such electron trapping are advantageous to surmount data corruption in magnetic data storage [37].

Despite much research the impact of Mn_3O_4 NPs on the structural properties of Eu^{3+} doped BT glass system is not yet explored. The incorporation of controlled concentrations of magnetic NPs in BT glass provides an opportunity to develop new stable magnetic glasses useful for nonlinear optical sensor and electronics devices. Additionally, literature shows that not many efforts are dedicated towards the incorporation of Mn_3O_4 NPs in BT glass system for determining their role in improving the structural and optical properties. This motivated to investigate the REIs doped glasses containing Mn_3O_4 NPs. Therefore, a new series of Mn_3O_4 NPs embedded and Eu^{3+} ions doped BT glass systems are prepared and evaluate the Mn_3O_4 NPs concentration dependent on thermal, structural and optical properties. Synthesized glasses are characterized using X-ray Diffraction (XRD), High Resolution Transmission Electron Microscopy (HRTEM), Differential Thermal

Analysis (DTA), Raman Spectroscopy, UV-Visible Spectroscopy and Photoluminescence (PL) Spectroscopy measurements. Meanwhile, Vibrating Sample Magnetometer (VSM) and Electron Spin Resonance (ESR) will be used to study the magnetic moment of the local magnetic properties due to the nature of spin-spin interaction.

1.2 Problem Statement

Plasmonic nanoglass is a new research paradigm with numerous application possibilities. Metallic NPs (such as gold, silver, copper, etc.) embedded REIs doped glass became attractive during past two decades. The inclusion of gold (Au) and silver (Ag) NPs in glass containing REIs [27][38] are exploited to enhance the quantum efficiency to achieve high performance lasing glass system. Yusoff and Sahar [39] have proposed that the enhancement of photoluminescence intensity is deduced by energy transfer from NPs to REIs and large local field in the vicinity of the REIs. Although significant effort continues in the development of the metallic NPs regrettably not many studies are dedicated towards the dispersing magnetic NPs such as manganese, nickel, ferrite and cobalt into rare earth doped glass. To overcome this limitation, the investigation of RE-doped glasses incorporated with magnetic NPs elements are suggested and become interest for magnetic studies.

Research of NPs effect on spectroscopic properties in RE doped oxides glasses have been widely studied [40][41]. It is known that, NPs have been able to enhance quantum efficiency which consequently leads to improve the optical characteristics of oxide glasses [38]. However, there are limited reports found about the influence of Mn_3O_4 NPs in BT glass doped with optimum concentration of europium. Yet, their careful synthesis, detailed characterisation and systematic Judd Ofelt analysis are not reported extensively. Therefore, this research is also devoted to discover laser efficiency of Eu^{3+} ions doped BT glasses with NPs embedment via Judd Ofelt calculation.

In addition to that, the growth and nucleation of magnetic NPs favor the alteration of the local structure of the glass system. Carefully controlled size of Mn_3O_4 NPs through appropriate heat treatment is one of the promising methods to modify and improve the magnetic properties of synthesized glass. The incorporation of Mn_3O_4 NPs in the BT glass with tunable size and their effects on magnetic properties are not extensively studied. However it is a challenging task due to easy crystallization of discovered glass host [42]. In spite of that, this has motivated the researcher to investigate the RE doped glasses containing Mn_3O_4 NPs elements. The role of Mn_3O_4 NPs in the europium doped magnesium BT glass in optical and magnetic properties is far from being understood and requires further attention. There are only some reports on the influence of Eu^{3+} ions doped magnesium BT glass towards optical properties [43]. Therefore, the effects of Mn_3O_4 NPs concentration changes on the thermal, structural and optical properties will be evaluated. Then, the magnetic properties are accomplished from the magnetic moment of the local magnetic properties due to the nature of spin-spin interaction.

1.3 Objectives of Study

The objectives of this study are as follows:

i. To optimize the concentration of Mn_3O_4 NPs embedded into europium doped magnesium BT glass via melt-quenching method.

ii. To determine the influence of Mn_3O_4 NPs concentration on the thermal, structural, optical and magnetic properties of Eu^{3+} doped BT glass.

iii. To complement the experimental spectroscopic data using JO theoretical calculation of intensity parameter.

iv. To control the size of Mn_3O_4 NPs by varying heat treatment durations and investigate its effects on spectral and magnetic features modifications in these glass system.

1.4 Scope of Study

In this study, 3 series of glass of different composition were prepared by melt quenching technique:

a. Series I : (59-*x*)TeO_2-30B_2O_3-10MgO-1Eu_2O_3-*x*Mn_3O_4 where ($0.0 \leq x \leq 2.0$ in mol %)
b. Series II : (59-*y*)TeO_2-30B_2O_3-10MgO-*y*Eu_2O_3-1Mn_3O_4 where ($0.0 \leq y \leq 2.0$ in mol %)
c. Series III : 58TeO_2-30B_2O_3-10MgO-1Eu_2O_3-1Mn_3O_4 glasses at different heat treatment durations

These glasses are chosen due to the optimal performance of TeO_2-B_2O_3-MgO-Eu_2O_3 glass system [44]. As increasing the concentration of TeO_2, BT glass will be more transparent. Nevertheless, the BT glass phase will become opaque if the concentration of B_2O_3 is richer than TeO_2. Burger *et al.* [45] suggested that the optimum concentration of TeO_2 is in the range of 3.9 to 73.6 mol % able to form glass in BT system. Meanwhile, Yardımcı *et al.* [46] determined that the glass forming range for concentration of B_2O_3 in B_2O_3-TeO_2 is system about 5 to 30 mol % and as the concentration increase, the crystallization starts to occur The addition of MgO up to 15 mol % in glass system will increase the structural compactness of glass network [18]. The incorporation of MgO as network modifiers in BT glass cause the formation of more non bridging oxygen (NBO) and 1.0 mol % of Eu^{3+} as a dopant is the optimized concentration and have potential for solid state applications [47].

However, the role played by Mn_3O_4 NPs as magnetic NPs in the structural features of the magnesium BT glass and the interaction of this element in the glass network is still a subject under study. Therefore, in current study the special attention is given to the inclusion of Mn_3O_4 NPs in glass matrix to modify the thermal, structural, optical and magnetic properties of glass. The phase of the glass will be determined by X-ray Diffraction (XRD) and the existence and size of Mn_3O_4 NPs in glass matrix investigated using High Resolution Transmission Electron Microscopy (HRTEM). Then, controlling the size of Mn_3O_4 NPs through heat treatment process with different heat treatment durations above glass transition temperature, T_g which is determined from Differential Thermal Analysis (DTA). In terms of structural and optical properties influence by Mn_3O_4 NPs will be determined by Raman spectroscopy, UV-Visible spectroscopy and Photoluminescence (PL) spectroscopy. Additionally, the magnetic properties will be accomplished from Vibrating Sample Magnetometer (VSM) and Electron Spin Resonance (ESR).

1.5 Significance of Study

Study of BT glass host embedded with Mn_3O_4 NPs provides useful information on the advancement of the glass knowledge. The rapid quench process is used to achieve well transparent glasses which are physically and chemically stable and Eu^{3+} doped BT glass will improve the luminescence properties. Furthermore, embedding Mn_3O_4 NPs in glass network as an alternative for understand the magnetic properties in order to determine the optimum concentration of Mn_3O_4 NPs. This study is great importance to understand and explain the magnetic behaviour of Mn_3O_4 NPs in glass. This may help in the discovery of a new magneto-device material that may contribute towards the development of NPs embedded RE doped photonics glass.

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