SPECTROSCOPIC STUDIES OF ERBIUM DOPED ZINC TELLURITE GLASS EMBEDDED WITH GOLD NANOPARTICLES

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To

My beloved family….

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ABSTRACT

Series of glasses based on (70-x)TeO_2 – 30ZnO – 0.5Er_2O_3 – xAu, where $0.0 \leq x \leq 0.5$ mol % were prepared using melt-quenching technique. The nature of the glass was confirmed using X-ray diffraction and the size of Au NPs (GNPs) was estimated by using transmission electron microscope image. It was found that the glass was amorphous in nature with an average diameter size of GNPs of about 2.6 ± 1.6 nm. The thermal stability of the glass was determined by means of differential thermal analysis (DTA). From the DTA curve, the glass transition temperature (T_g), crystallization temperature (T_c) and melting temperature (T_m) was identified and thermal stability was calculated. The structural characteristic was investigated using Fourier transform infra red spectroscopy in the range of 400 cm^{-1} to 3500 cm^{-1}. The spectra of the glass shows two absorption peaks around 646 cm^{-1} and 748 cm^{-1} corresponding to the TeO_4 and TeO_3 structural units, respectively. The absorption properties of these samples were obtained by using UV-Visible spectrometer which showed six absorption peaks. The values of optical band gap (E_{opt}) and Urbach energy (E_u) were calculated from the absorption peak and were found to be in the range of 2.57 - 2.64 eV and increased as the concentration of GNPs was increased, while (E_u) was found in the range 0.39 - 0.41 eV. The emission characteristic of this glass was characterized using photoluminescence spectroscopy. It was observed that there were two distinctive emissions centered at 650 nm and 845 nm which are assigned to $^4F_{9/2}$ - $^4I_{15/2}$ and $^4I_{13/2}$ - $^4I_{15/2}$ transition, respectively under 488 nm excitation wavelength. It was observed that sample of 0.3 mol % GNPs exhibits the highest enhancement due to energy transfer from GNPs to Er^{3+} ion.

ABSTRAK

Beberapa siri kaca berdasarkan (70-x)TeO_2 – 30ZnO – 0.5Er_2O_3 – xAu, dengan $0.0 \leq x \leq 0.5$ mol % telah berjaya disediakan dengan menggunakan teknik pelindapan leburan. Sifat kaca telah disahkan dengan menggunakan analisis pembelauan sinar-X dan saiz zarah emas, Au dianggarkan menggunakan imej mikroskop imbasan elektron. Hasil menunjukkan bahawa kaca adalah bersifat amorfos dengan purata diameter saiz zarah emas adalah 2.6 ± 1.6 nm. Kestabilan terma kaca telah ditentukan dengan menggunakan analisis pembezaan terma (DTA). Melalui analisis lengkuk pembezaan terma ini parameter seperti suhu transisi kaca (T_g), suhu penghabluran kaca (T_c), suhu lebur (T_m) telah dikenalpasti dan kestabilan terma juga telah dihitung. Ciri struktur kaca pula dikaji menggunakan spektroskopi infra merah tansformasi Fourier dalam julat 400 cm^{-1} hingga 3500 cm^{-1}. Spektrum kaca ini menunjukkan dua puncak sekitar 646 cm^{-1} dan 748 cm^{-1} yang masing-masing mewakili unit struktur TeO_4 dan TeO_3. Sifat penyerapan kaca pula diperoleh dengan menggunakan spekroskopi UV-Vis yang memberikan enam puncak serapan. Nilai bagi jurang tenaga optik (E_{opt}) dan tenaga Urbach (E_u) telah dihitung daripada puncak serapan dan didapati berada dalam julat 2.57 - 2.64 eV dan meningkat dengan pertambahan kepekatan zarah nano emas manakala nilai E_u berada dalam julat 0.39 - 0.41 eV. Ciri pancaran kaca ini pula dianalisis menggunakan spektroskopi fotoluminesen. Terdapat dua puncak pancaran yang ketara masing-masing pada 645 nm dan 845 nm, yang merujuk kepada transisi $^4F_{9/2}$ - $^4I_{15/2}$ dan $^4I_{13/2}$ - $^4I_{15/2}$, di bawah pengujaan panjang gelombang 488 nm. Sampel yang mengandungi zarah nano emas sebanyak 0.3 mol % mempunyai keamatan pancaran tertinggi disebabkan perpindahan tenaga dari GNPs ke ion Er^{3+}.

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LIST OF SYMBOLS

T_c	Crystallization Temperature
T_g	Transformation Temperature
n	Refractive index
d	Atomic distance
λ	Wavelength
θ	Angle
ω	The angular frequency
α	The absorption coefficient
E_{opt}	Optical band gap energy
E_u	Urbach energy
$\hbar$	Plank constant
ΔE	Width of band tail

LIST OF ABREVIATIONS

GNPs	Gold nanoparticles
XRD	X-ray diffraction
FT-IR	Fourier transformed infrared
TEM	Transmission electron microscopy
UV	Ultra violet
Vis	Visible
ASTM	American Society for Testing Material
PL	Photoluminescence
NIR	Near infra red
MIR	Middle Infrared
RE	Rare-earth
Tp	Trigonal pyramid
Tbp	Trigonal bypyramid
Er_2O_3	Erbium oxide
ZnO	Zinc oxide
NR	Non radiatively
CET	Cooperative energy transfer
ET	Energy transfer
LSPR	Localized surface plasmon resonance
ESA	Energy state absorption

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CHAPTER 1

INTRODUCTION

1.1 Introduction

Glasses are one of the oldest as well as one of the newest materials in the world that find a variety of used in everyday life. Glass is an amorphous material that can be formed by some techniques such as sol gel processing of solution, vapor deposition, melt quenching or by neutron irradiation of crystalline material (Doremus and Narottam, 1986) but by all these techniques, cooling from the liquid states is the most important and most widely used (Uhlmann and Kreidel,1983). Glass material is not new. It has been used since 4000 years ago in Egypt. It is different from crystalline material because it does not possess long range order and has no periodic arrangement. The interesting fact about glass is it acquires many unique properties such transparency, clear and not easily corroded.

Tellurite glasses are finding widespread applications in the field of photonics like chalcogenide glasses due to some characteristics features such as low phonon energy, high refractive index and excellent infrared transmission (Zakery, *et al*., 2007). It has been reported that, these glasses are good candidates for hosting rare-earth (RE) ions because of their low-phonon energy environment, good optical properties and chemical durability (Sun, 1998) (Erariah and Bull, 2010). The erbium-doped tellurite glass also have shown optical and chemical properties suitable for photonic applications such as optical limiter, laser light modulator and are thermally stable for fiber drawing.

Recently, metallic nanostructures is a subject of considerable interest because they are endowed with unique optical properties and functionalities contrast to their bulk counterparts as reported by Som et al. (2010). In addition, tellurite glass embedded with metallic nanoparticles (NPs) recently has been the subject of intensive investigations because of their ability to enhance the luminescence of tellurite glass. Previous studies have been shown that glasses doped with RE ions and metallic NPs have the ability to enhance the luminescence and improved nonlinear optical properties of tellurite glass They are becoming promising for practical applications in photonics as optical amplifier, optical recording, laser active media and infrared-to-visible converters (Carmo *et al.*, 2009). Nanoparticles (NPs) may originate changes of the material's luminescence characteristics as well as enhancement of the nonlinear optical properties (Kassab *et al*., 2008).

For enhanced efficiency and improved up-conversion, absorption cross-section has to be increased. Most concepts for this enhancement rely on energy transfer (ET) from a species with a large absorption cross-section to RE ion. Use of two or more rare-earth ions together and energy transfer between them (Kumar, 2007) or use of the metallic NPs with RE ions has been found a successful way to enhance luminescence of the glass (Kassab, 2011) (Piasecki *et,al*., 2010). In order to get enhancement on optical characteristics in these nano-composite glasses, the concentration of RE ions should be low enough to avoid the quenching effect. Therefore, glasses containing metallic NP doped with low concentration of RE ions are particularly of interest to us.

In spite of few spectroscopic studies, the role of NPs and enhancement of optical properties of tellurite glass is far from being understood. The spectroscopic characterizations of this tellurite nanocomposite are essential for the optimization and applications that needs careful sample preparation, fabrication and spectroscopic investigations. In this study, tellurite glass has been used as a host while erbium oxide as a dopant and will be embedded with gold nanoparticles (GNPs) in order to investigate the effects of concentration of metallic nanoparticles by means of spectroscopic characteristics. The relation between the concentration and spectroscopic characteristic used to determine the optimum composition of GNPs to prepare a high effiency of tellurrite glass as a host especially in laser system and photonic field.

1.2 Problem Statements

Rare-earth doped tellurite glasses embedded with metallic nanoparticles has been receiving special interest due to their ability to enhance the performance of tellurite glass for their applications. Even though there are numbers of research on tellurite glass has been done, yet the characteristics of Er^{3+} ions doped glass embedded with gold nanoparticles (GNPs) has not been fully investigated. In addition, in spite of few experiments on tellurite doped GNPs , the clear explanation about the role played by GNPs are still lacking. Few studies have been done in this system but are limited to certain properties. Therefore, in the present study we will investigate the role played by GNPs on optical properties by spectroscopic techniques which are UV-Vis, Photoluminescence and FTIR spectrometer.

1.3 Research Objectives

The objectives of this work are:

i) To prepare a series of glass samples based on by melt quenching technique.
ii) To determine the existence of NPs.
iii) To determine the thermal parameters.
iv) To characterize the vibrational spectroscopy of the glass
v) To characterize the optical properties of the glass.
vi) To characterize the emission behavior of the glass.

1.4 Scope of Study

In order to achieve the objectives, this research has been carried out within the stated scope as follows:

i) The preparations of (70-x)Te_2O - 30ZnO – 0.5Er_2O_3 – xAu glass where x = (0.1, 0.2, 0.3, 0.4, 0.5) mol% by melts quenching technique. The composition of glass is chosen due to the high stability and highest glass forming ability as investigated Sahar et.al., 2013.
ii) The determination of NPs using Transmission Electron Microscopy (TEM).
iii) The determination of thermal parameters using Diffrential Thernal Analysis (DTA).

iv) The characterization of optical properties using UV-Vis Spectroscopy.

v) The characterization of vibrational spectrum using Fourier Transform Infra Red (FTIR) Spectroscopy.

vi) The characterization of emission behavior using Photoluminescence (PL) Spectroscopy.

1.5 Significance of study

This study is fundamentally important to explain the role played by gold nanoparticels inside tellurite glass by analyzing the absorption, emission, and FTIR spectra of the glass. Hence, from this systematic experimental of fabrication and spectroscopic studies of this sample it would give better suggestions about how to increase the efficiency of tellurite glass for their applications.

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