Journal of Molecular Structure 1117 (2016) 64–68

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: http://www.elsevier.com/locate/molstruc

Ligand field and Judd-Ofelt intensity parameters of samarium doped tellurite glass

Y.A. Tanko, S.K. Ghoshal, M.R. Sahar*

Advanced Optical Materials Research Group, Department of Physics, Faculty of Science, Universiti Teknologi Malaysia, 81310 Skudai, Johor, Malaysia

ARTICLE INFO

Article history:
Received 14 November 2015
Received in revised form
14 February 2016
Accepted 25 March 2016
Available online 28 March 2016

Keywords:
Tellurite glass
Melt quenching technique
UV–Vis optical absorption
Ligand field parameters
Judd-Ofelt intensity parameters

ABSTRACT

We report the samarium ions (Sm^{3+}) contents dependent ligand field and Judd-Ofelt (JO) intensity parameters (Ω_2, Ω_4, Ω_6) of zinc tellurite glass. The amorphous nature of the melt-quench synthesized glasses is confirmed using XRD. The lower energy region of the absorption spectra is used to calculate JO intensity parameters and the UV edge is exploited to determine the Nephelauxetic ratio, bonding, and Racah parameters. The Nephelauxetic ratio and Racah parameter is reduced and the bonding parameter is enhanced with the increase of Sm^{3+} concentration. The enhancement in covalency is found to increase the non-bridging oxygen and crystal field strength by delocalizing more d-shell electrons. Furthermore, Nephelauxetic function revealed an increase due to the reduction of localized d-electrons that is aroused from the overlap of d-orbital and ligand orbital. The JO intensity parameters displayed the $\Omega_4>\Omega_6>\Omega_2$ trend. Increase in Ω_2 and decrease in Ω_2 and Ω_2 with the increase of Sm^{3+} concentration indicated an increase in the Sm–O covalency and coordination in the asymmetry of the prepared glasses. The large vale of spectroscopic quality factor (greater than unity) makes the proposed glass system prospective for various optical devices fabrication.

1. Introduction

Over the years, various rare earth ions (REIs) doped inorganic glasses revealed tremendous promise for developing solid state lasers, waveguide lasers, optical amplifiers and fluorescent display [1–3] as well as other visible and infrared optical devices. Significant information such as radiative lifetime, stimulated emission cross-section, spectroscopic quality factor, and transition energy of these REIs doped glasses provided better understanding to enhancing or developing new optical devices [4,5]. The spectroscopic characteristics of REIs in these glasses depend on the nature and composition of the host material. Among oxide glasses, tellurite glass is more advantageous over borate, silicate and phosphate glasses for applications in optical devices because of their low phonon energy which reduce the non-radiative probability of the rare earth ions, low melting temperature, better thermal and chemical stability, large refractive index, good chemical and thermal stability etc. [6–8].

Routinely, Judd-Ofelt (JO) [9,10] theory is used to determine the transition intensity of the REIs. Three sensitive intensity parameters (Ω_t with t = 2, 4, 6) of the REI is utilized to characterize their environment (in terms of covalency and symmetry) and the strength of the transition. These JO intensity parameters include branching ratios, emission cross section and radiative lifetime. These values are further exploited to optimise the best configuration of the ion–host to enhance the materials for optical applications. Moreover, the rigidity, long range effect and degree of covalency between the rare earth ion and ligands anions are described by the intensity parameter [11,12]. These intensity parameters provide greater knowledge about the bonding nature of the glass and the Nephelauxetic effect of a given system [11]. The Ω_2 parameter is enhanced by covalent bonding, which leads to a reduction in the asymmetry of REI ligand field with an increase in the Nephelauxetic effect [11,13]. Conversely, Ω_4 and Ω_6 specifies the rigidity of the glass structure which is related to the local basicity and degree of distortion in the REIs [11,13,14]. In addition, the crystal field strength (Dq) and the inter-electron interaction (Racah) parameters (B and C) are used in defining the degree of covalency or iconicity of the ligand bonding [15]. Despite much experimental studies, the relationship between the ligand field and JO parameters in Sm^{3+} ions doped tellurite glasses is not established yet.

* Corresponding author.
E-mail address: mrahim057@gmail.com (M.R. Sahar).

http://dx.doi.org/10.1016/j.molstruc.2016.03.083
0022-2860/

We evaluate the ligand field and JO parameters of Sm^{3+} ions doped zinc tellurite glass by analysing the UV–Vis absorption spectra. Sm^{3+} ions concentration dependent refractive index, crystal field strength, Racah parameters and Nephelauxetic ratios are determined. The achieved improved ligand field interaction of the glass may be useful for the development of optical storage devices and solid state lasers.

2. Experimental procedure

Following the conventional melt-quenching method a series of tellurite glasses are prepared. The achieved glass composition is $(80-x)TeO_2-20ZnO-xSm_2O_3$, where $x = 0.6$, 0.9, 1.2 and 1.5 mol% as summarized in Table 1 with codes. Analytical grade anhydrous powders of TeO_2, ZnO, and Sm_2O_3 (Sigma Aldrich of 99.9% purity) are used as starting glass constituents. They are thoroughly mixed before placing being completely melted inside an electric furnace at 950 °C for 15 min. Upon achieving the desired viscosity, the melt is then poured into a stainless steel mould and annealed inside a furnace at 300 °C for 3 h to reduce the mechanical stress that may cause embrittlement. The samples are then cooled down to room temperature, cut, grinded, and polished for optical measurement.

A Bruker D8 Advance XRD diffractometer with Cu–Kα radiations (λ = 1.54 Å) operated at 40 kV and 100 Ma is used to confirm the amorphous state of the prepared glasses. Data are collected at a scanning angle 2θ in the range of 10 to 80° at a rate of 0.05°/sec. Glass density is measured by Archimedes method using toluene as immersion liquid. The ultraviolet–visible and near infra-red (UV–Vis–NIR) absorption spectra in the wavelength range of 400–2000 nm are recorded using Shimadzu UV-3101PC scanning spectrophotometer (Kyoto, Japan). The room temperature emission spectra are measured via a Perkin Elmer LS-55 luminescence spectrometer, where a pulsed xenon lamp is acted as an excitation source.

3. Result and discussion

3.1. X-ray diffraction

The X-ray diffraction patterns of the prepared glasses are shown in Fig. 1. The complete absence of any sharp peak indicates their true amorphous nature.

3.2. Optical absorption

Fig. 2 shows the optical absorption spectra of Sm^{3+} doped tellurite glass. Fig. 2a and b represents the absorption transitions in the higher and lower energy region, respectively. Higher energy region is comprised of three transition bands such as ν_1, ν_2 and ν_3, which are assigned to the transition of $^6H_{5/2} \rightarrow {}^4F_{3/2}$, $^4I_{13/2}$ and $^4K_{11/2}$, respectively. These bands are used to determining the Racah parameters. Meanwhile, the hypersensitive transition at lower energy region is used to evaluate the JO parameters.

Table 1
Nominal glass compositions and their codes.

Codes	Composition (mol %)		
	TeO_2	ZnO	Sm_2O_3
TZS1	79.4	20	0.6
TZS2	79.1	20	0.9
TZS3	78.8	20	1.2
TZS4	78.5	20	1.5

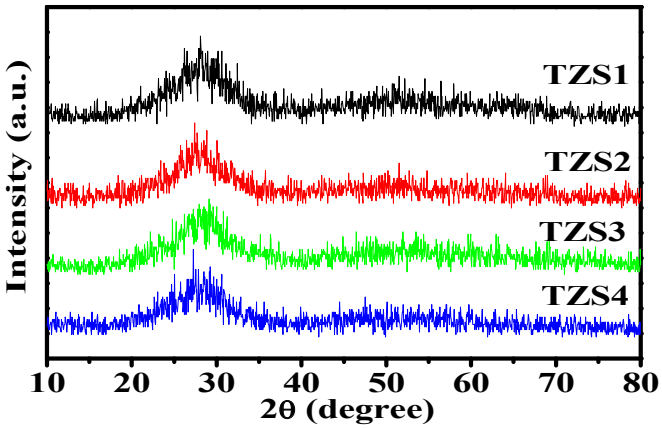

Fig. 1. XRD pattern of the synthesized samples.

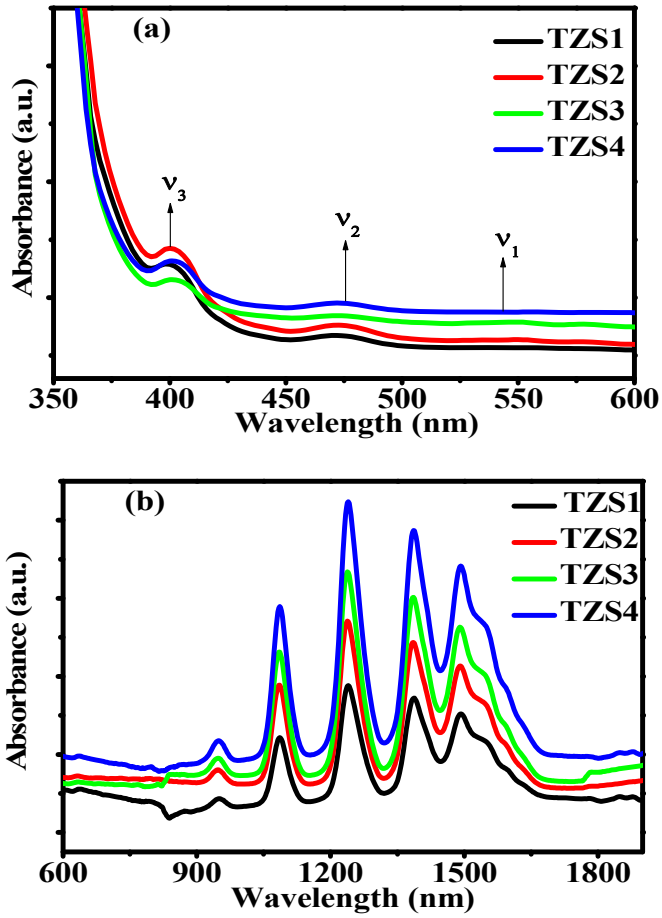

Fig. 2. UV–Vis–NIR absorption spectra of all glass samples in the region of (a) higher energy region and (b) lower energy.

3.3. Degree of covalency

3.3.1. Nephelauxetic ratio and bonding parameter

The Nephelauxetic ratio (β) of the observed transition bands (Fig. 2a) are determined using:

$$\beta = \frac{\nu_T}{\nu_R} \quad (1)$$

where ν_T and ν_R are the wavenumber (cm^{-1}) of a selected transition