

Chapter II

Materials and Methods

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2.1 Introduction

Spectroscopic investigations of rare earth doped glasses provide valuable information that includes energy level structure, radiative properties, stimulated emission cross-sections, etc. These insights play a key role to improve the existing materials or to develop new optical devices like lasers, sensors, hole burning high-density memories, optical fibers and amplifiers [1]. Study of optical properties of the Ln^{3+} ions in glasses is important in estimating the lasing characteristics of any material. So, the optical spectroscopy is an excellent tool to obtain the electronic structure of absorbing/emitting centers (atoms, ions, molecules, defects, etc.) and their environments [2]. It deals with the radiation absorbed, reflected, emitted or scattered by a substance. The optical performance of the glasses is influenced by the glass composition, thermo optical, thermo mechanical, optical quality and chemical durability of the glasses [3]. The optical properties of Ln^{3+} ions in glasses depend on the chemical composition of glass network former and modifier.

This chapter presents a detailed description of the methods used in the preparation of heavy metal borotellurite glasses and instrumental methods employed to study the optical properties. The structural characterization of the prepared samples has been carried out through X-ray diffraction, FTIR and Raman spectra measurements. The amorphous nature of the prepared glasses was confirmed by recording the x-ray diffraction patterns. The FTIR spectra studies were used to identify the various functional groups present in the prepared glasses. Raman spectra were used to study the vibrational energy levels of the prepared material. Optical properties were studied using UV–Vis–NIR absorption, luminescence and decay measurements. The UV–Vis–NIR absorption spectra were used to explore the nature

of the bonding between rare earth ion and its ligand oxygen. In addition, it is used to determine the oscillator strength of the absorption bands. The radiative parameters of the prepared glasses were evaluated from the luminescence spectra to check their suitability in lasers and WLED applications.

2.2 Experimental

2.2.1 Synthesis of glasses

Different techniques have been employed by different groups to prepare the glasses. According to Zarzycki [4], the techniques are (i) melt quenching (ii) thermal evaporation (iii) sputtering (iv) glow- discharge decomposition (v) chemical vapour deposition (vi) gel-dissociation (vii) electrolytic deposition (viii) chemical reaction (ix) reaction amorphization (x) shockwave transformation and (xi) shear amorphisation.

Among these techniques, the melt quenching technique is a promising route for the preparation of high quality optical glasses.

2.2.2 Advantages of melt quenching techniques

Melt quenching technique is one of the most convenient and conventional technique for producing bulk glasses [5]. It has many advantages over the chemical vapour deposition, sol-gel process, etc. Some of the advantages are

- Large flexibility of composition of glasses
- Most convenient and conventional technique for producing bulk glass
- Quenching of melt doesn't require stoichiometry among constituents
- Preparation of glasses with a wide variety of compositions (sometimes ten kinds of constituents at various ratios from a few to more than ten percent is possible).

2.2.3 Melt quenching technique

The glass or amorphous solid is formed by the quenching of molten material. It is obtained by fusion of more than one chemical component in its pure form. When the rate of cooling is sufficiently fast to preclude crystal nucleation and growth, the disordered state of the liquid is frozen and a glass is formed.

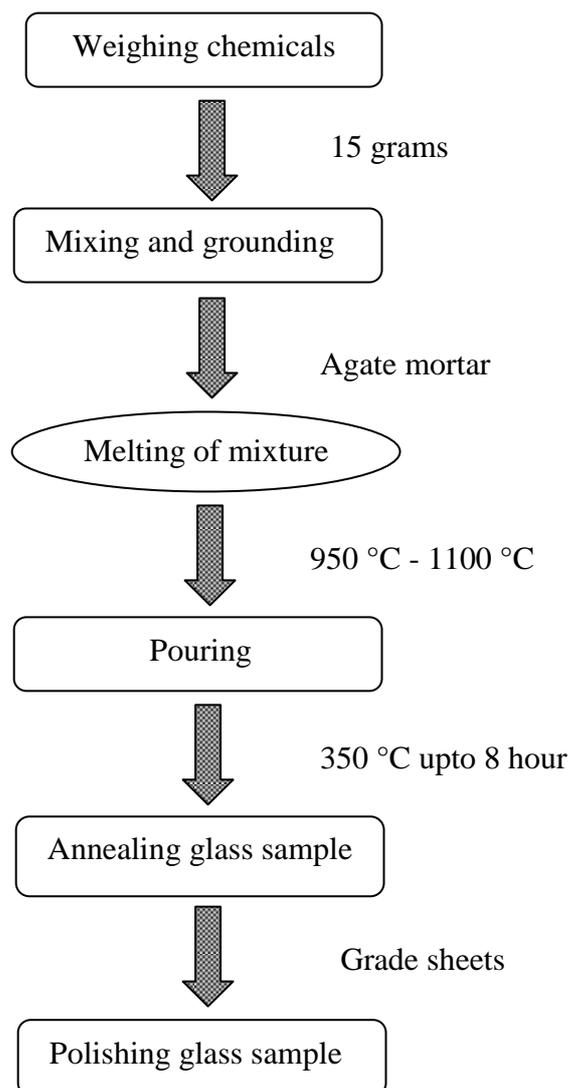


Figure 2.1: Steps involved in the preparation of heavy metal borotellurite glasses by melt quenching technique.

High purity analytical grade (AR) chemicals with 99.99 % were used for the present work. About 15 g batches of chemical compositions were well mixed and thoroughly ground in an agate mortar. The fine homogeneous mixture taken in a

porcelain crucible was kept inside an electric furnace. The time duration of melting and melting temperature depend on the glass composition, which is approximately 1100 °C for 30 min. The melt was stirred frequently at constant intervals in order to improve its homogeneity. The melt was quickly quenched by pouring it into a thick preheated brass mold held at 350 °C. The melt was pressed using another polished brass plate to optimize the thickness of the glass ($\approx 1.5\text{-}2.5$ mm). To remove the internal stress and thermal strain, the glass samples were annealed at 350 °C for 8 hours. Then they were allowed to reach room temperature gradually in its own course of time. The glass samples thus obtained were well polished, before using them for any optical studies.

2.3. Measurement of physical properties

Physical parameters like density, thickness, refractive index, dielectric constant, concentration of RE³⁺ ions, reflection losses, polaron radius and inter-ionic distance of the glasses are important in characterizing the RE doped glasses.

(i) Density

The density (ρ) is defined as the ratio of mass of the material to its volume. It is determined by Archimedes principle at room temperature. When an object is immersed in a fluid, the buoyancy is equal to the weight of fluid displaced by the object. In this measurement, xylene is used as an immersion liquid. A monopan balance is used for weight measurements. The density (in g/cm³) is estimated using the formula,

$$\rho = \frac{W}{W - W_1} \times 0.865 \quad (2.1)$$

where, W = weight of the prepared glass sample in air (g)

W_1 = weight of the glass sample fully immersed in xylene (g)

0.865 = density of xylene at room temperature.

(ii) Refractive index

Refractive index (n_d) of the glasses was measured using an Abbe refractometer at the 589.3 nm (sodium yellow line). Bromonaphthalin ($C_{10}H_7Br$) was used as a contact liquid between sample and prism of the refractometer.

The dielectric constant (ϵ) was obtained from the refractive index of the glass using [6] the relation.

$$\epsilon = n_d^2 \quad (2.2)$$

The reflection loss from the glass surface was calculated from the refractive index using the Fresnel's formula [7] as given below

$$R = \left[\frac{(n_d - 1)}{(n_d + 1)} \right]^2 \times 100 \quad (2.3)$$

The molar refractivity R_M for each glass was calculated using the formula [8] given below,

$$R_M = \left[\frac{(n_d^2 - 1)}{(n_d^2 + 2)} \right] \frac{M}{\rho} \quad (2.4)$$

where, M is the average molecular weight and ρ is the density of the sample in $gm\ cm^{-3}$. The electric polarizability was estimated using the relation [9].

$$\alpha_e = \frac{3(n_d^2 - 1)}{4\pi N(n_d^2 - 2)} \quad (2.5)$$

where, N is the number of rare earth ions per unit volume and n_d is the refractive index.

(iii) Concentration

The concentration of rare earth ions (C) in the prepared glasses (mol/L) were calculated from the expression

$$C = \frac{y}{MW} \frac{d}{x} \times 1000 \quad (2.6)$$

where, y = mass of the Ln ion (gm)

x = total mass of the chemical composition (gm)

d = density of the glass sample (g/cm³)

MW= molecular weight of the Ln ion (g/mol)

The concentration in mol/L can be converted into ions/cm³ by multiplying it with a factor NA/1000, where NA is the Avogadro number.

The polaron radius and inter-ionic separation were evaluated below equation [10]

$$r_p = \frac{1}{2} \left(\frac{\pi}{6N} \right)^{1/3} \quad (2.7)$$

$$\text{and } r_i = \left(\frac{1}{N} \right)^{1/3} \quad (2.8)$$

The field strength were calculated using the following relation

$$F = Z/r_i^2 \quad (2.9)$$

where, Z is the oxidation number of the RE ion, r_i is the interionic distance of the prepared glass samples.

2.4 Material Characterization

2.4.1 X- ray diffraction measurements

The XRD spectra of the prepared samples were recorded using PANalytical XPERT- PRO X-Ray diffractometer using CuK α (30 mA, 40 kV) radiation source with $\lambda=1.540 \text{ \AA}$.

2.4.2 Fourier Transform Infrared spectra (FTIR)

The vibrational features of the molecular unit of the prepared glass can be identified by the Fourier transform infrared spectra. The FTIR spectra of the samples were recorded in the range 4000–400 cm⁻¹ using Perkin-Elmer BX-II spectrometer with a spectral resolution of 4 cm⁻¹ employing the KBr pellet technique.

2.4.3 Raman spectra

Imaging Spectrograph STR 500 SEKI Laser Raman Spectrometer with a resolution of 1/0.6 cm⁻¹/pixel (SEK, Japan) was employed in the measurement of

Raman spectra. These measurements were carried out using Argon laser with $\lambda = 514$ nm.

2.4.4 UV–Vis –NIR Absorption spectra

The UV–Vis absorption spectra were obtained using Perkin-Elmer Lambda 35 in the wavelength range 200–1100 nm at a resolution of 1.0 nm. A deuterium lamp is used in the ultraviolet region and halogen lamp is used in the visible region. The NIR absorption measurements were made using Jasco V–670 spectrophotometer in the wavelength range 1100–1800 nm at a resolution of 1.0 nm.

2.4.5 Luminescence Spectra

The photoluminescence measurements were made using Perkin-Elmer LS55 spectrometer in the wavelength range 200–900 nm with a resolution of 1.0 nm. Luminescence spectra were recorded using pulsed 150 W Xenon lamp source. The slit width of the monochromators may be varied to give better resolutions between 2.5 nm to 15 nm for the excitation monochromator and between 2.5 nm to 20 nm for the emission monochromator in the order of 0.1 nm. For each data collection cycle, spectral data were obtained through a red sensitive photomultiplier. The data signals obtained undergo integration, conversion, averaging and digital filtering before the computer receives the data.

2.4.6 Photoluminescence lifetime

The decay measurements were carried out through a digital storage oscilloscope (Tektronix TDS 1001B) coupled with personal computer. These measurements were carried out using a 75-W xenon pulsed lamp source at 50 ms time per flash and sample window of spectrofluorimeter.

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