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Structural and optical properties of Ho_2TeO_6 micro-crystals embedded in tellurite matrix

C. Joshi, Y. Dwivedi, S.B. Rai *

Laser & Spectroscopy Laboratory, Department of Physics, Banaras Hindu University, Varanasi 221005, India

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Abstract

In the present work, Ho^{3+} doped tellurite glasses and glass ceramics have been explored. Micro-sized Ho_2TeO_6 crystals have been successfully prepared in TeO_2 matrix using two step heat treatment method. Structural, thermal and optical properties have been investigated using different characterization techniques. Variations in above mentioned properties were observed to improve when these crystals grew in TeO_2 matrix. We have reported several anti-Stokes and Stokes emissions extended from UV to NIR region on excitation with 532 and 976 nm laser radiations. The unique structure of Ho_2TeO_6 crystal was expected to play a crucial role in enhancement of the optical properties of glass ceramics.

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Keywords: D. Glass ceramic; Tellurite glass; Anti-Stoke's emission; FTIR analysis; Upconversion

1. Introduction

Rare earth (RE) ion activated materials remain a hot topic of investigation as these materials have been extensively used in various applications viz. high performance magnet, luminescent devises, laser materials, telecommunications, biomedical and many others [1–4]. Peculiar electronic, optical and chemical properties of RE ions are seen from their 4f electrons in different environments. One of the most discussed properties of RE ions is the upconversion process. Because of the long lived radiative levels, upconversion emissions are frequently realized and utilized to simulate different colors. The optical properties of the RE ions are function of the chemical composition and local environment around the ions. Recently, glasses dispersed with nano-crystals gained the special attention because of their prospective use as a promising host for RE ions [5–9]. These glass ceramics are two phase systems consisting of a base glass within which crystals are grown by controlled nucleation of the crystal phase and subsequent crystallization in a precursor glass by thermal process. These lattices are advantageous as they have higher mechanical and chemical stability and have low phonon frequencies.

Among rare earth ions, Ho^{3+} ion has been extensively investigated owing to the observation of laser action in infrared and visible regions [10,11]. It is one of the important active ions applied to upconversion luminescence because of its favorable energy level structure. It has a high lying green emitting level ($^5F_4$, $^5S_2$) and metastable levels ($^5I_7$ and $^5I_6$) from where efficient infrared excited state absorption (ESA) processes take place. Also, many non-radiative energy transfer processes such as cross-relaxation and upconversion can help in building upconverted population.

Tellurite glasses [12,13] are of technical interest because of their low melting temperatures, lower phonon vibrations (600–800 cm^{-1}) and non-hygroscopic properties. Besides these characteristics, tellurite glasses have many other superiorities over other glassy systems such as their high refractive index [14], anomalous partial dispersion in the visible region, high third-order non-linear susceptibility [15,16], good host for RE ions [17] and optical amplifying properties [18] as well as good transmittance in the near infrared region (NIR) [19]. In many cases, these properties are combined with good chemical and crystallization properties

* Corresponding author. Tel.: +91 542 230 7308; fax: +91 542 236 9889.
E-mail address: sbrai49@yahoo.co.in (S.B. Rai).

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[20] to make it as one of the suitable hosts for such type of applications.

In the present work, for the glass preparation, we have taken TeO_2 as network former and Li_2CO_3 and ZnF_2 as network modifiers. Introducing zinc fluoride (ZnF_2) to this glass matrix restricts the lattice vibration considerably. It acts as modifier as well. Fluorine ions break the Te–O bonds while Zn^{2+} ions occupy interstitial positions to form Zn–O–Te linkages because of the close ionic radii of Te^{4+} (0.7 Å) and Zn^{2+} (0.74 Å) ions [21]. Also, addition of ZnF_2 into TeO_2 glass matrices results in lowering its viscosity [22].

In this paper, we report a study on the optical, thermal and structural properties of rare earth ion Ho^{3+} doped oxyfluoro tellurite glasses. We have also described the influence of zinc fluoride on the luminescence and upconversion processes in tellurite glasses and glass ceramics.

2. Experimental

Glass samples were prepared using these chemicals as starting materials according to following compositions in mol.%:

$$74\,TeO_2 + 25\,Li_2CO_3 + 1\,Ho_2O_3, \quad \text{referred as Li : TeO}_2\text{, and}$$

$$69\,TeO_2 + 25\,Li_2CO_3 + 5\,ZnF_2 + 1\,Ho_2O_3, \quad \text{referred as Zn : Li : TeO}_2$$

The conventional melt-quench method has been used for the preparation of glass samples. The concentration of Ho^{3+} was kept below to the concentration quenching limit. All powder materials used were of analytical grade. The well mixed starting materials were first melted at 900 °C in a platinum crucible for 30 min in an electric furnace. The molten mixture (free from air bubbles) was quenched by squeezing it into a rectangular steel cast preheated to 200 °C. The glasses were then cooled to room temperature gradually. The given compositions of all samples were optimized according to their maximum luminescent intensities. The as-prepared glass samples were further heated to 390 °C for 2 h to obtain their ceramics.

In order to determine the characteristic glass transition temperature, crystallization temperature, and melting temperature, differential temperature analysis (DTA) of the glass samples was carried out by a Rigaku Thermoplus analyzer (DSC8270). The crystalline structure of the glass ceramic samples was verified by the powder X-ray diffraction (XRD) using CuKα radiation (1.5406 Å) with nickel filter. The crystallite size was calculated using Scherrer relation. The UV–vis–NIR absorption spectra were obtained at room temperature using a Shimadzu UV 1201 spectrophotometer. Perkin Elmer Spectrum RX1 was used to record the FTIR absorption spectra of the samples. The up and down-conversion emission spectra were recorded using 976 nm wavelength from a diode laser and 532 nm wavelength from Nd:YAG laser as excitation sources. An iHR320, Horiba Jobin Yvon, spectrometer was used to detect the fluorescence signal.

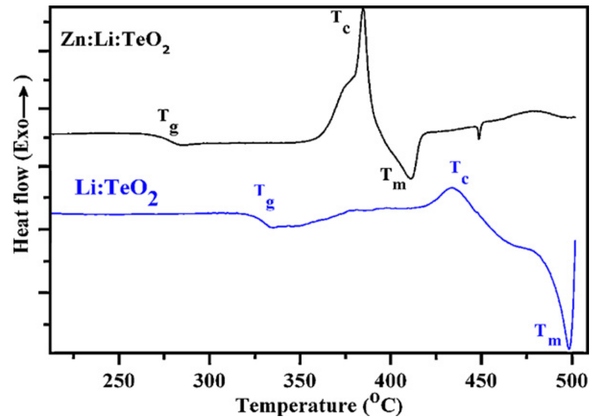

Fig. 1. Differential thermal analysis curves of $Li:TeO_2$ and $Zn:Li:TeO_2$ glass samples.

3. Results and discussion

3.1. Thermal characterization

DTA curves of $Li:TeO_2$ and $Zn:Li:TeO_2$ glasses are shown in Fig. 1. DTA scan of $Li:TeO_2$ exhibits an endothermic hump corresponding to the glass transition temperature (T_g) at 322 °C which is followed by three exothermic peaks corresponding to crystallization temperature (T_c) at 382 °C, 397 °C and 433 °C and another endothermic event corresponding to the melting temperature (T_m) at 499 °C. The two exothermic peaks at 382 °C and 397 °C are due to the co-existence of oxide phases of tellurite glass (γ-TeO_3 and α-TeO_3 polymorphics), while the stable α-TeO_3 phase appears at 433 °C temperature. The lack of sharp endothermic and exothermic peaks in the DTA curves clearly indicates the formation of homogeneous glass. On the contrary of $Li:TeO_2$ glass, the glass transition temperature of $Zn:Li:TeO_2$ glass reduces to 271 °C and a sharp crystallization peak at 385 °C overlying a broad peak centered at 375 °C is observed, which is entirely different compared to $Li:TeO_2$ glass. The endothermic process corresponding to the melting point temperature (T_m) is observed at 412 °C. The change in T_g clearly reflects that how ZnF_2 affects the structure and gets arranged in the glass. A decrease in glass transition temperature implies a decrease in the rigidity of the network.

The glass stability can be determined qualitatively by a difference of T_c and T_g, i.e. ($T_c - T_g$) and its larger value leads to high thermal stability of the glass. Its value is found to be 111 °C in case of $Li:TeO_2$ glass while it is 114 °C in case of $Zn:Li:TeO_2$ glass. Another relevant parameter called Hruby's parameter (H_R) has been calculated using the relation

$$H_R = \frac{T_c - T_g}{T_m - T_c}$$

where the terms have their usual meaning. H_R gives information about the stability of the glass against devitrification and its value is found 1.68 in $Li:TeO_2$ glass while it is 4.22 in $Zn:Li:TeO_2$ glass.