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Er^{3+}-doped zinc tellurite glasses revisited: Concentration dependent chemical durability, thermal stability and spectroscopic properties

M.R. Dousti [a,*], R.J. Amjad [b], M.R. Sahar [c], Z.M. Zabidi [d], A.N. Alias [d], A.S.S. de Camargo [a,*]

[a] Instituto de Física de São Carlos, Universidade de São Paulo, Av. Trabalhador Sãocarlense 400, São Carlos, SP 13566–590, Brazil
[b] Department of Physics, COMSATS Institute of Information Technology, Lahore 54000, Pakistan
[c] Advanced Optical Materials Research Group, Department of Physics, Faculty of Science, Universiti Teknologi Malaysia, Skudai 81310, Malaysia
[d] Applied Science Department, Universiti Teknologi Mara Cawangan Pulau Pinang, 13500 Permatang Pauh, Pulau Pinang, Malaysia

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ABSTRACT

Tellurite glasses are interesting materials with extensive infrared transmission window, relatively low phonon energy, high refractive indexes and the ability to incorporate reasonably high amount of rare earth ion dopants. These characteristics make them popular candidates for infrared and visible emissions. Particularly, Er^{3+}-doped tellurite glass compositions have been actively studied for broadband near infrared applications where the requirement for low dimension needs to be compensated by higher doping ion concentration. In this work, we revisit Er^{3+}-doped zinc tellurite glasses, which are among the most thermally and chemically stable tellurite compositions. The glasses were prepared by the melt-quenching technique and the favorable effects of increasing dopant concentration on chemical durability, water resistivity and thermal stability (up to 140 °C) are discussed. The photophysical properties of the glasses were studied by absorption and luminescence spectroscopic techniques. The Stokes and anti-Stokes emissions of erbium were analyzed and it was verified that the width of the emission band at 1532 nm strongly depends on Er^{3+} concentration varying from 60 to 82 nm for 0.5 and 2.5 mol% of Er_2O_3, respectively. The intensity of green and red upconversion emissions was evaluated and the increased efficiency of red emission with increasing concentration is attributed to energy transfer mechanisms between infrared energy levels.

1. Introduction

In the last decades, the impressive technological advances in telecommunications, lighting and lasing devices have pushed a fast development of new luminescent and optical materials, among which glasses occupy a strategic position [1–5]. Contrary to natural and synthetic crystals, glasses can be tailored and obtained faster, at lower costs, and in a much larger variety of sizes and shapes, for the most diverse applications. Besides that, glasses can usually incorporate higher concentration of active dopant ions such as the trivalent rare earth ions (RE). The tremendous commercial advantages that these characteristics represent, associated with the growing demand for more efficient, fast-responsive and multifunctional materials,have motivated the search for new glass compositions. The most commonly explored oxide compositions are based on silicates [6], phosphates [7] and borates [8]. Although these glasses present, in general, good thermal and mechanical stabilities, their high melting temperatures, hygroscopicity and low RE dispersion hinder desired applications. Furthermore, regular oxide glasses present high phonon energies (~1000 cm^{-1}) which results in larger probability of non-radiative deactivation of RE excited states. As an alternative to overcome that particular disadvantage, fluoride glasses are largely studied, but their mechanical, chemical and thermal stabilities are less to be desired [9]. More recently, special attention has been paid to heavy metal oxide (HMO) glasses such as antimony, bismuth, germanate and tellurite glasses [10]. Particularly, tellurite glasses present promising features such as lower working temperature.

One of the earliest reports on the preparation of tellurite glass was by Brady [11]. He noticed that the tellurium dioxide is a poor glass former, requiring the addition of a modifier to trigger the formation of a glass from TeO_2 powder. A typical concentration of 10 mol% of any modifier is required to form tellurite glasses. Two crystalline phases exist in pure TeO_2; paratellurite (α-form) [12] and tellurite (β-form) [13]. In both forms, four coordinated tellurium ions and four bridging oxygens constitute a completely interconnected network. Incorporation of modifier and intermediate groups breaks the Te–O–Te network and forms the TeO_{3+1} and TeO_3 groups. In general, three major different tellurite groups can exist in the glassy form, known as $Q^4{}_4$, $Q^3{}_4$ and $Q^2{}_3$ which

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* Corresponding authors.
E-mail addresses: mrdousti@ifsc.usp.br (M.R. Dousti), andreasc@ifsc.usp.br (A.S.S. de Camargo).

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consist of 4, 3 and 2 bridging oxygens, respectively and 0, 1 and 1 non-bridging oxygens. The very good RE solubility, low phonon energies, and high refractive indexes (1.8–2.5) make these glasses promising materials as substitutes for oxide glasses in technological applications, especially in the infrared. The third-order nonlinear susceptibility ($\chi^{(3)}$) of tellurite glass has been measured by Kim et al. as 14.0×10^{-13} esu, which is much higher than those of silicate glasses (0.28×10^{-13} esu) [14], and a non-linear refractive index, $n_2 = 10.48$ for $90TeO_2$–$10La_2O_3$ decreases to 6.84 for $80TeO_2$–$20La_2O_3$ glass sample [14]. For $(100 - x)Te_2O$–xLi_2O glasses, the $\chi^{(3)}$ of 24×10^{-13} and 38×10^{-13} esu were measured for $x = 20$ and 25 mol%, respectively [15]. The structure of zinc tellurite glasses was investigated by Sidek et al. [16], Hoppe et al. [17] and Sahar et al. [18–20]. They showed that the introduction of ZnO to the TeO_2 network shifts the Raman band at 626 cm^{-1} to 669 cm^{-1} for pure TeO_2 and $15ZnO$–$85TeO_2$ glasses, respectively. The addition of zinc oxide to TeO_2 matrix increases the density, refractive index and Urbach energy, while polarizability, molar volume and optical band gap are gradually decreased. Hoppe et al. [17] showed that introduction of ZnO in TeO_2 glass system decreases the total Te–O coordination number while TeO_4 trigonal bipyramid (tbp) groups transform to TeO_3 units. The bond distances for two existing species of Te–O band were measured to be 1.9 Å and 2.1 Å. The coordination number changes as follows: addition of second oxide to corner-connected TeO_4 in TeO_2 network breaks the Te–O–Te bridging and converts two TeO_4 units to TeO_3 units with one non-bridging oxygen for each.

Zinc-tellurite glasses are among those with highest thermal stability (T_x–$T_g > 100$ °C [20]) but they can be melted below 1000 °C. They show high thermal expansion coefficients (150–$200 \times 10^{-6} \cdot {}^{o}C^{-1}$) and low deformation temperature, around 250–350 °C [21]. Chemical durability of tellurite glasses were studied by Stanworth [22]. Tellurite glass shows large durability against water, alkaline and acid environments. A weight loss of the order of 5×10^{-7} and 20×10^{-7} $g \cdot cm^{-2} \cdot day^{-1}$ was measured for $18PbO$–$82TeO_2$ and $22PbO$–$78TeO_2$ glasses, respectively. The durability of lead-tellurite glass in water is reduced by introduction of modifiers such as lithium oxide and sodium oxide, while this effect is more rigorous by adding the boron oxide in tellurite glass. Tellurite glasses containing BaO, Li_2O, Na_2O and As_2O_5 showed heavy attacks and reduction of water durability. Moreover, it has been shown that the chemical durability and water resistance of zinc tellurite glasses increase with increasing rare earth in doped samples [23], and decreases by introduction of silver NPs [24].

Tellurite glasses doped with erbium ions are studied wide and large [25–30]. The yellowish color of the undoped zinc-tellurite glass changes to orange color by addition of erbium ions [31], although green color is also reported for the undoped zinc tellurite glass sample [32]. Er^{3+} ions show green and red luminescence under various excitation wavelengths (e.g. ~376, 480, 800, 980 and 1532 nm). The anti-Stokes upconversion emissions (excitation at 980 and 1532 nm) and the Stokes near-infrared emissions (excitation at 980 nm and emission at around 1532 nm) attracted large attention due to their applications in lasers, sensors, upconverting devices and amplifiers. Moreover, the enhancement of upconversion luminescence of Er^{3+}-doped zinc tellurite glasses embedding metallic nanoparticles has been recently observed [25,31,33–35]. The NIR broadband emission of the Er^{3+}-doped tellurite glasses is a promising feature of these glass compositions. The FWHM of this band in tellurite glasses is larger (60–80 nm [36–38]) than those reported for soda lime silicate (~19 nm [39]) and aluminum silicate (59.3 nm [40]) glasses.

The aim of this work is to revisit the important properties of the erbium doped zinc tellurite glasses prepared by a simple melt-quenching method. The studied composition was $(80 - x)TeO_2$–$20ZnO$–xEr_2O_3 (where $x = 0$, 0.5, 0.7, 1.0, 1.3, 1.5, 1.7, 2.0 and 2.5 mol%). Investigations on chemical durability towards exposure to water and a more aggressive, acidic environment are presented. In addition, thermal stability and optical properties, including Stokes and anti-Stokes emissions and excited state lifetimes, are presented as a function of Er^{3+} ion molar concentration.

Table 1
Labels and corresponding glass compositions (mol%), theoretical and experimental densities ($g.cm^{-3}$), ionic densities ($ion.cm^{-3}$) and characteristic temperatures (°C) [20].

Label	TeO_2	ZnO	Er_2O_3	ρ_{exp}	ρ_{th}	N_{Er} ($\times 10^{21}$)	T_g	T_x	ΔT
ZTEr0.0	80.0	20	0.0	5.10[16]	5.66	0.00	325	439	114
ZTEr0.5	79.5	20	0.5	5.12	5.67	0.59	321	420	99
ZTEr1.0	79.0	20	1.0	5.27	5.69	1.14	322	442	120
ZTEr1.5	78.5	20	1.5	5.30	5.70	1.70	–	–	–
ZTEr2.0	78.0	20	2.0	5.35	5.71	2.25	323	460	137
ZTEr2.5	77.5	20	2.5	5.37	5.73	2.80	335	475	140

2. Experimental

The Er^{3+}-doped glass samples with composition $(80 - x)TeO_2$–$20ZnO$–xEr_2O_3 (where $x = 0$, 0.5, 0.7, 1.0, 1.3, 1.5, 1.7, 2.0 and 2.5 mol%) were prepared by the conventional melt-quenching technique. The homogeneously mixed powders were melted at 850 °C for 1 h and subsequently poured and annealed on preheated stainless steels molds at 300 °C, for 3 h. The samples were left inside the furnace to cool down to the ambient temperature. Then, the glasses were cut and optically polished for optical measurements. Very fine powders of samples were also prepared for structural and thermal analysis, as well as for photophysical measurements. The glass compositions and corresponding labels are listed in Table 1, in addition to some of the physical properties.

The calorimetric and thermal properties of glasses were measured using a differential thermal analyzer (DTA, Model: Pyris Diamond TG-DTA, Japan) by heating with a rate 10 °C/min. The samples were heated from room temperature to 650 °C under N_2 atmosphere with 200 mL/min rate of flow. The fine powders of glasses were mixed with KBr to measure the Fourier Transform Infrared (FTIR) spectra of the samples using a Perkin Elmer spectrometer model Spectrum One. The density values of the glasses were determined by Archimedes' principle taking into account the weight of the samples in air and in water as the immersion liquids.

The UV–VIS–NIR absorption spectra were measured in a Perkin-Elmer spectrophotometer model Lambda 1050. The excitation and emission spectra, as well as the lifetime decay curves were measured in a Horiba Fluorolog fluorimeter, which is equipped with CW and pulsed Xe lamps as excitation sources. The signals were collected by a photodiode detector model PPD-850 in the visible, and by a Hamamatsu photomultiplier in the infrared. The spectra were corrected by the lamp profile and detectors response. The upconversion spectra were measured with excitation by a 976 nm laser with tunable power, DMC model Lasertool. The excited state lifetime values of Er^{3+} ions were

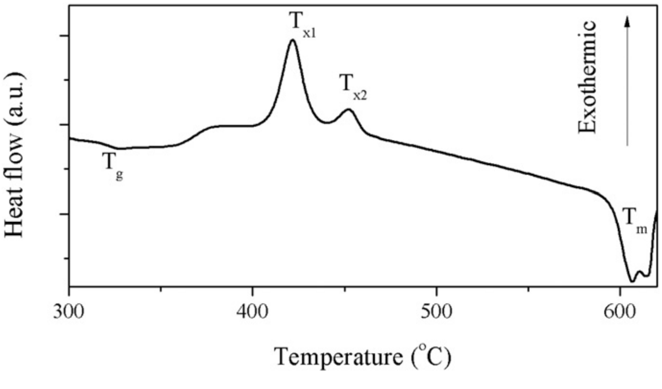

Fig. 1. Representative differential thermal analysis of the ZTEr1.0 glass sample.