Chalcogenide Letters Vol. 12, No. 12, December 2015, p. 653 - 663

RAMAN SPECTROSCOPY AND RAMAN GAIN COEFFICIENT OF TELLURONIOBIUM- ZINC-LEAD OXYGLASSES DOPED WITH RARE EARTH

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The host glasses with composition $75TeO_2$-$10Nb_2O_5$-10ZnO-5PbO doped with different concentration of xEr_2O_3 have been prepared. The structure of the glasses through Raman spectroscopy from 200 to 1300 nm was investigated. The Raman gain coefficients of these glasses evaluated from spontaneous Raman scattering experimental result by using 532 nm Laser type Diode-pumped, solid state (DPSS). The present glasses have broader bandwidths of gain amplification from 225 to 1125 cm^{-1}. The amplification band width of present glasses is 4.9 times largest than the silica glasses. This indicates that this glass can be use as a potential for fiber Raman amplifier.

(Received September 29, 2015; Accepted December 4, 2015)

Keywords: Oxide glasses; Raman spectroscopy; Rare earth

1. Introduction

Tellurite glasses used in technological applications such as solid state batteries, fuel cells, gas sensors, infrared filters, optical fibers, modulators and host materials for laser applications [1-3]. Recently in high-speed optical communications, investigation new materials can be increased information flow (short and long distance networks) for an access to new spectral bandwidth are of interest.TeO_2- based glasses are a good candidates for these applications; it has broad transmission range from 0.3 to 5 µm and hence they have highest Raman cross section as compared to other glasses system [4].Moreover it has Raman gain equal 58 times that of fused silica, which the Raman gain responses evaluate by measuring the Raman spontaneous response [5- 7]. The stimulated Raman scattering is one of the most extensively studied nonlinear optical phenomena applicable to optoelectronic devices such as fiber Raman amplifiers, fiber Raman lasers, microsphere Raman lasers [8], silicon Raman laser [9] and so on. Raman gain media are more advantageous than Rare-earth ions-doped media, since the Raman gain can be obtained at any wavelength depending on the available pump wavelength. In other words, a pump spectrum determines a gain spectrum. Such freedom of the Raman gain spectrum enables advanced devices such as multi-wavelength pumping broadband fiber Raman amplifiers [10] and cascaded Raman lasers [11]. We note that herein the vibration mode of glasses depended on composition and excitation wavelength. Many author [12–22] estimated that the addition of oxides such as P_2O_5, WO_3, Nb_2O_5, BaO, SrO and MoO_3 to tellurite glasses leads to expand broad band and high the Raman gain coefficient. In this paper we studied the Raman characteristics of TeO_2/Nb_2O_5/ZnO/PbO/Er_2O_5glasses that reveal the highest Raman gain coefficient and broader bandwidth Raman gain amplification compared with other glasses system such as tellurite, silicate, phosphate and borosilicate.

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2.Experimental

By using the conventional quench-melting method the Er^{3+} ions doped glass systems with a composition of $75TeO_2$-$10Nb_2O_5$-5PbO-10ZnO-xEr_2O_3 (where x = 0.00, 2500, 3750, 5000, 6250, 7500and 8750 ppm) were prepared. The glasses were put in a platinum crucible and melting at 920 °C for 45 min; the crucible was constantly stirred in order to obtain a homogeneous melt. Then the melt was poured onto graphite mould and the quenched samples were annealed at 320 °C for 2 h and then cooled inside the furnace down to room temperature.

The vertical (VV) polarized spontaneous Raman spectra of the prepared glass were acquired using a Thermo Scientific DXR Raman Microscope spectroscopy setup with 532 nm excitation [(532 nm Laser type Diode-pumped, solid state (DPSS)] and acquisition time was set to 30 seconds. The incoming signal vertically surface of the bulk sample, and V-polarized Raman scattered signal was collected in the backscattering geometry with a 100x microscope objective.

3. Result and discussion

The prepared glasses excited by using DPSS at wave number (ν_l=1.880×10^4 in cm^{-1}) with a power of ≈ 0.1mW. Herein fig. 1a, b and fig. 2a-h shows the reduced Raman spectroscopy and deconvolution of normalized Raman spectra of prepared glasses respectively. Although the Raman intensity are related to the polarizability of the network modifying ions, the larger polarizable ions contribute more to intensify the high intensity of peak, hence the intensity of Raman spectra increased with increasing of doping Er^{3+} ion from 2500 to 8750 ppm. We note that the TeO_2 network consists of several asymmetric structural units like that TeO_4 trigonal bipyramids (tbp), TeO_{3+1} polyhedra and TeO_3 trigonal pyramids (tp). Moreover the TeO_4 group has two axial and two equatorial oxygen atoms, besides the transformation of TeO_4tbp convert toTeO_{3+1} and TeO_3tp units is strongly affected by doping with Er^{3+} ions [1, 23]. Also introduction of a network modifier to TeO_2 based glasses leads to changes the Te coordination polyhedron from TeO_4 to TeO_3 through breaking Te-O-Te bonds, along with the formation of non bridging oxygen (NBO) atoms. The Raman bands deconvoluted into six symmetrical Gaussian peaks and the peak position of present glasses were summarized in Table 1. The structure of these glasses investigated as; the band labeled (A) around at 368- 394 cm^{-1}in sample 2 to 7 can be contributed to the axial bending vibration mode (O_{ax}- Te-O_{ax}) at corner sharing sites, otherwise it is not appeared in sample 1 may be hidden by the strong Raman response of TeO_2 matrix or of very low intensity. The band as labeled (B) around 440- 497 cm^{-1} can be attributed to symmetrical or bending vibrations of Te-O-Te linkages at corner sharing sites[28–31].A band labeled (C) around 526-566 cm^{-1} can be attributed to anti symmetrical stretching of the continuous network composed ofTeO_4tbps[28–31]. A band labeled (D) around 649- 667 cm^{-1} can be attributed to anti symmetrical stretching of the continuous network composed ofTeO_4 tbps [28–31]. A band labeled (E)around 755- 807 cm^{-1}can be attributed stretching vibrations of Te-O− and Te=O bonds containing nonbridging oxygen in TeO_3tps andTeO_{3+1}polyhedraor Te_2O_7bridged tetrahedra (Te-O-Te antisymmetric stretch) [28–33]. A band labeled (F) around 834- 925 cm^{-1} can be attributed to stretching of Nb and its neighboring NBO in NbO_6 octahedra [28].When the concentration of Nb_2O_5 content is lower leads to most of Te^{4+} ions exist as [TeO_4] tbps and form Te–O chains in the glasses matrix, but a few of [TeO_3] bps exist in the glass network. The Nb^{5+} ions exist as [NbO_6] octahedra to link the chains which the apical-sharing [TeO_4] tbps are more stable than the edge-sharing ones. Moreover may be Nb^{5+} ions in tellurite glasses exist partially in both NbO_6 octahedra (i.e. connect to non-bridging oxygen, NBO), and NbO_4 tetrahedra (means that chain to bridging oxygen, BO).Where NbO_4 tetrahedra take part in as network formers, forming three dimensional structure units contributing to restore bridging bonds and will increase the number of TeO_4 (tbp) groups just diminishing the TeO_3 (tp) groups.

Table 1: Glasses composition in mol% and peak position in cm^{-1} of prepared glasses.

Sample code	**Glasses composition**	**Peak position in cm^{-1}**					
		A	**B**	**C**	**D**	**E**	**F**
Sample1	$75TeO_2$- $10Nb_2O_5$- 5PbO- 10ZnO	not appeared	440	not appeared	649	755	869
Sample2	$75TeO_2$- $10Nb_2O_5$- 5PbO- 10ZnO- 2500ppm Er_2O_3	368	442	526	679	766	834
Sample3	$75TeO_2$- $10Nb_2O_5$- 5PbO- 10ZnO- 3750ppm Er_2O_3	386	493	565	666	803	917
Sample4	$75TeO_2$- $10Nb_2O_5$- 5PbO- 10ZnO- 5000ppm Er_2O_3	390	495	566	663	803	919
Sample5	$75TeO_2$- $10Nb_2O_5$- 5PbO- 10ZnO- 6250ppm Er_2O_3	394	497	566	664	804	921
Sample6	$75TeO_2$- $10Nb_2O_5$- 5PbO- 10ZnO- 7500ppm Er_2O_3	390	496	566	667	807	925
Sample7	$75TeO_2$- $10Nb_2O_5$- 5PbO- 10ZnO- 8750ppm Er_2O_3	393	497	566	665	807	925

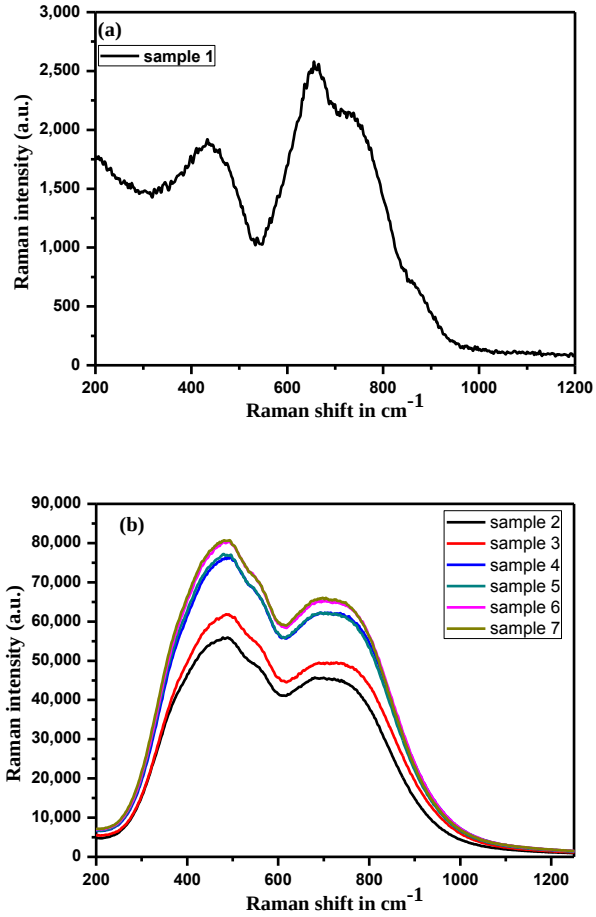

Fig. 1: Raman spectra for studied glasses ***(a)****: sample 1(75TeO_2- 10Nb_2O_5- 5PbO- 10ZnO),* ***(b)*** *sample 2 (75TeO_2- 10Nb_2O_5- 5PbO- 10ZnO - 2500ppm Er_2O_3), sample 3 (75TeO_2- 10Nb_2O_5- 5PbO- 10ZnO -3750ppm Er_2O_3), sample 4 (75TeO_2- 10Nb_2O_5- 5PbO- 10ZnO- 5000ppm Er_2O_3), sample 5 (75TeO_2- 10Nb_2O_5- 5PbO- 10ZnO- 6250ppm Er_2O_3), sample 6 (75TeO_2- 10Nb_2O_5- 5PbO- 10ZnO-7500ppm Er_2O_3), sample 7(75TeO_2- 10Nb_2O_5- 5PbO- 10ZnO- 8750ppm Er_2O_3).*

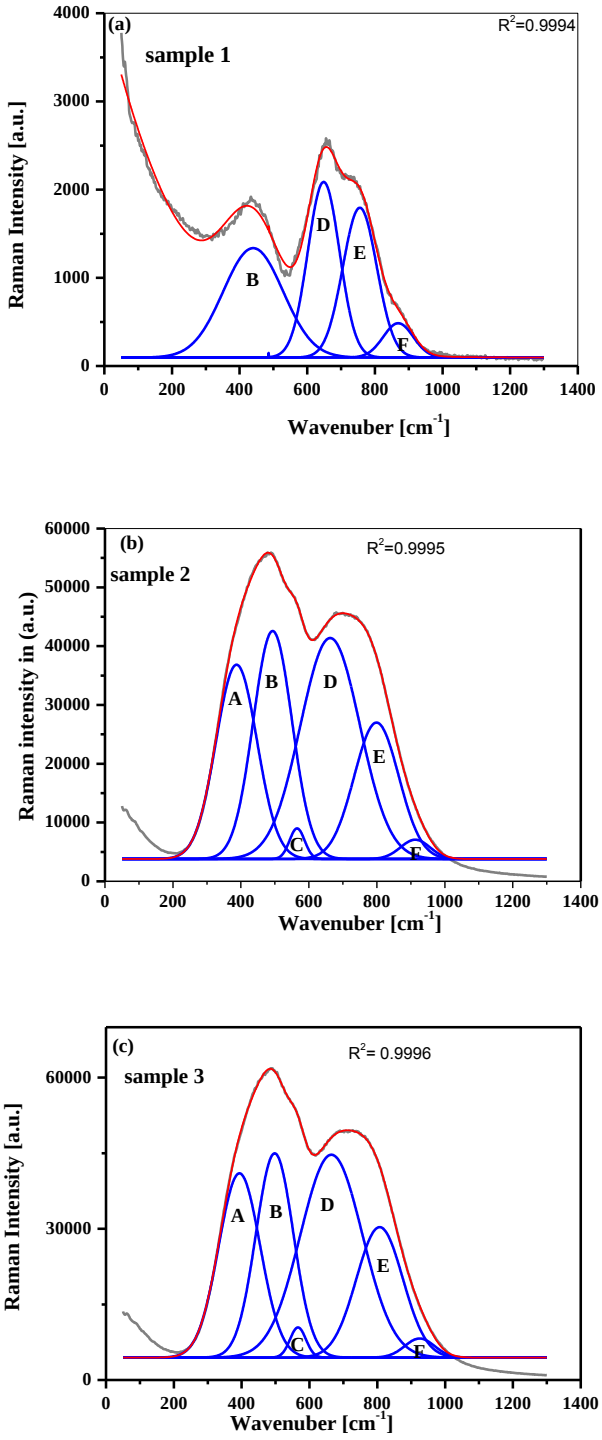

Fig. 2a, b, c: Deconvolution of Raman spectra of prepared glasses (sample 1, sample 2, and sample 3)

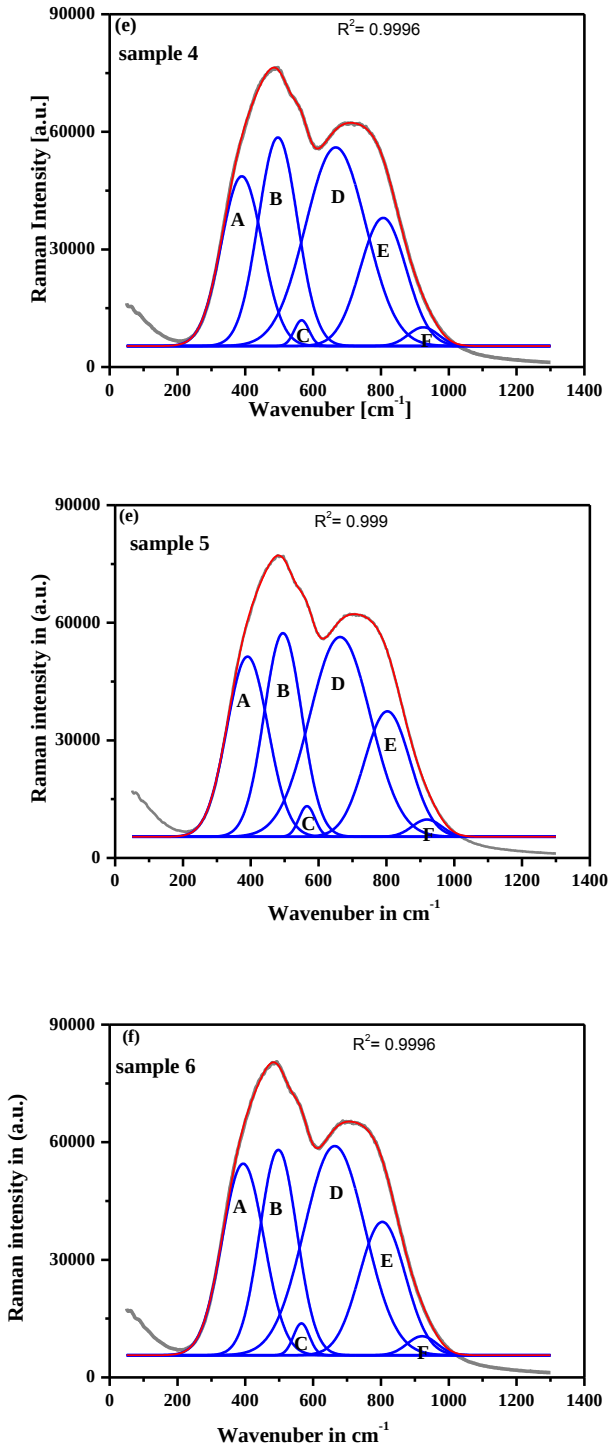

Fig. 2d, e, f: Deconvolution of Raman spectra of prepared glasses (sample 4, sample 5, and sample 6)

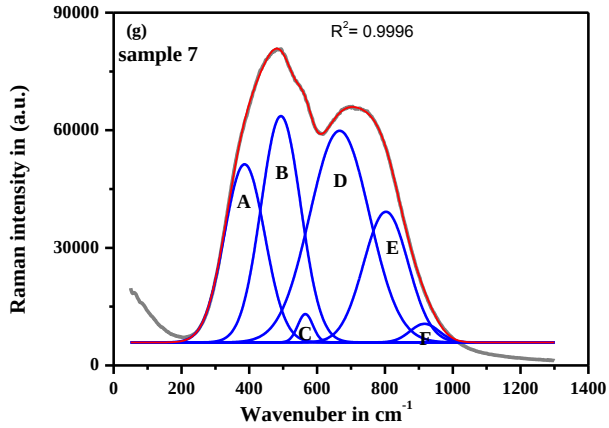

Fig. 2g: Deconvolution of Raman spectra of sample 7.

While the Nb^{5+} ions in form of NbO_6 octahedra occupy interstitial positions as net work modifiers. Addition of ZnO content from 0 to 15 wt% in a TeO_2-Nb_2O_5 base glass has two effects on the network structures; (1) it modified few Nb^{5+} ions from network modifiers to network formers and increases BO ions, (2) It changes the Te^{4+} bond from TeO_4 tbp to TeO_3 tp and increases NBO ions. Komatsu and co-workers [34] estimated the bands around 440 and 665 cm^{-1}, these correspond to Te-O-Te chains and TeO_4 units in the TeO_2-Na_2O-ZnO-PbO glasses, respectively. Also they reported that when addition of PbO lead to increased the intensity of the band at 765 cm-1 corresponding to $[TeO_3]/[TeO_{3+1}]$ units and PbO at 3 mol%, the lead enters the tellurite network as $[PbO_6]$ octahedra. By similarity from the Raman spectra we can calculate the ratio of transform ($TeO_4 \rightarrow TeO_3$ and TeO_{3+1}) in the matrix of studied glasses. The ratio of the value intensity of band (e) to band labeled (d) denotes that fraction ratio TeO_3 and TeO_{3+1} /TeO_4 results were shown in Table (2). From this data the ratio values are in the range from 0.86 to 0.66, this means that the glass without Er_2O_3 modifier has highest NBO compared with other glasses doped with rare earth also a result obtain that the TeO_4 units are transformed little by little to TeO_{3+1} and TeO_3 when increasing Er^{3+} ion concentration (see Table 2 column 2). The presence of Er^{3+} in these glasses leads to the peak position shift to higher values of wavenumber.

Table 2: Ratio between TeO_{3+1}, TeO_3 to TeO_4, Raman gain coefficients, g, and full weight half maximum (FWHM) of prepared glasses

Sample code	Ratio of stretching vibrations of Te-O− and Te=O bonds containing NBO oxygen in TeO_3 tps and TeO_{3+1} polyhedra / BO in TeO_4	Raman gain ($\times 10^{-10}$ m.W^{-1})	FWHM (cm^{-1})
Sample 1	0.86	0.17	252
Sample 2	0.66	3.72	500
Sample 3	0.68	4.2	501
Sample 4	0.68	5.14	496
Sample 5	0.66	5.24	497
Sample 6	0.68	5.43	496
Sample 7	0.66	5.50	500

The reduced spectra in which thermal population and absolute frequency dependence is corrected were obtained using equation:

$$R(w) = \frac{w}{[N(w,T)+1](w_0-w)^4} \cdot I(w) \qquad (1)$$

Where I(w) is the reduced intensity, w is the Raman shift (cm^{-1}), w_0 is the frequency of the excitation radiation, N(w,T) is the Bose-Enisten factor,

$$N(w,T) = \frac{1}{\exp\left(\frac{hw}{2\pi K_B T}\right)-1} \qquad (2)$$

Where h is Planck's constant K_B is the Boltzman constant, and T is the measurement temperature (300 K).

The Raman gain spectra can be calculated from spontaneous Raman scattering spectra, the ratio of the number of Stokes photons scattered spontaneously into a solid angle $d\Omega$ is given by;

$$\frac{d\sigma}{d\Omega} = \left[\frac{w_s^3 w_p}{(4\pi\epsilon_0 C^2)^2}\right] \cdot \langle |\alpha_R|^2 \rangle \qquad (3)$$

Where α_R= Raman polarizability, ε_0= permittivity of free space (8.8542×10^{-12} F/m), w_s= Stokes frequency, w_p= pump frequency, C is the speed of light.

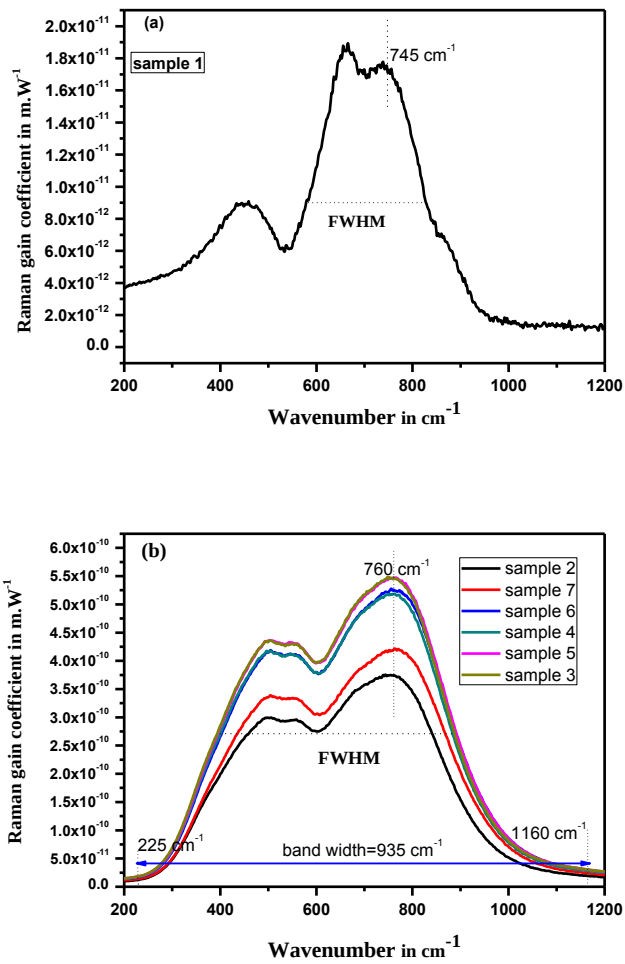

*Fig. 3: Raman gain and FWHM for studied glasses **(a)**: sample 1(75TeO$_2$- 10Nb$_2$O$_5$- 5PbO- 10ZnO), **(b)** sample 2 (75TeO$_2$- 10Nb$_2$O$_5$- 5PbO- 10ZnO - 2500ppm Er$_2$O$_3$), sample 3 (75TeO$_2$- 10Nb$_2$O$_5$- 5PbO- 10ZnO -3750ppm Er$_2$O$_3$), sample 4 (75TeO$_2$- 10Nb$_2$O$_5$- 5PbO- 10ZnO- 5000ppm Er$_2$O$_3$), sample 5 (75TeO$_2$- 10Nb$_2$O$_5$- 5PbO- 10ZnO- 6250ppm Er$_2$O$_3$), sample 6 (75TeO$_2$- 10Nb$_2$O$_5$- 5PbO- 10ZnO-7500ppm Er$_2$O$_3$), sample 7 (75TeO$_2$- 10Nb$_2$O$_5$- 5PbO- 10ZnO- 8750ppm Er$_2$O$_3$).*

The Raman gain coefficient, g, is related to the spontaneous Raman scattering cross section as [25].

$$g(\nu) = \frac{\sigma(\nu).(\frac{1}{(\nu_l-\nu)})^3}{C^2.h.n^2(\nu_l-\nu)} \qquad (4)$$

Where, σ, is the spontaneous Raman cross section. The reported value of the Raman gain coefficient of silica, g_{SiO2}=1.86×10^{-13} m·W^{-1} at the Stokes shift of 440 cm^{-1}for the 532 nm excitation [26] was used as the reference. Figure 3a and b, show the Raman gain spectra of prepared glasses. The Raman gain coefficient value at 760 cm^{-1}of prepared glasses increase from 0.17 to 5.5×10^{-10} m· W^{-1} with increasing Er$_2$O$_3$ concentration from 0.0 to 8750ppm. The FWHM value of Raman gain increase from 252 to 500 cm^{-1} with increasing Er$_2$O$_3$ concentration from 0.0 to 8750ppm (see Table 2). From literature reported in Ref. [28- 33] Raman gain value of the glass85%TeO$_2$ – 15%WO$_3$ and 85%TeO$_2$ – 10%Nb$_2$O$_5$ – 5% MgO were 38 and 26× 10^{-13} m/W respectively. Raman gain coefficient of TeO$_2$-ZnO–Na$_2$O, TeO$_2$–Na$_2$O–ZnO–PbO, TeO$_2$–WO$_3$–

Nb_2O_5 and TeO_2–WO_3–Bi_2O_3 glasses were found to be 20–30 times that of fused-silica. The broader bandwidth were reported in the tellurite glass containing 15 mol. % MoO_3 exhibits the bandwidth 1.7 times larger than the silica glass and the Raman gain coefficient is as high as 38 times that of the silica glass. The tellurite glass containing 15 mol % MoO_3 and 15 mol % P_2O_5 shows the bandwidth 1.9 times larger than the silica glass and high Raman gain coefficient which is as high as 37 times that of the silica glass. In the present work the prepared glasses has highest value of Raman gain coefficient compared with other glasses were reported in the literature [28-33]. Moreover these glasses have bandwidth as high as 4.9 times larger than the silica glass. Hence this indicates that this glass can be used in gain media such as broadband Raman amplifier. The formation $TeO_3$and TeO_{3+1} units at 760 cm^{-1}, Nb^{5+}, $Pb^{2+}$and Er^{3+} may be are character more polarizability ion in this glasses matrix than compare with other glasses leads to higher Raman gain.

4. Conclusion

High polarizability oxide PbO and Er^{3+} ion added to host glass matrix with composition TeO_2- Nb_2O_5- PbO- ZnO leads to getting high Raman spectra intensity, Raman gain coefficient and extend the bandwidth amplification. Characteristic units for TeO_4, TeO_{3+1} and TeO_3phases were detected in the structure of the investigated glasses. The fraction ratio between TeO_3 and TeO_{3+1} phase to TeO_4 decreases from 0.86 to 0.66 with doping Er^{3+} ion.75TeO_2- 10Nb_2O_5- 5PbO-10ZnO- 8750ppm Er_2O_3 has the highest value of Raman gain coefficient equal 5.5×10^{-10} $m\cdot W^{-1}$ and bandwidth as high as 4.9 times larger than the silica glass.

Acknowledgements

This work was financially supported by the Department of Physics, Faculty of Science, Al- AzharUniv., Cairo Branch, Egypt.

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