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INFRARED AND RAMAN SPECTROSCOPIC INVESTIGATIONS of xSrO-(40-x) As_2O_3 –$60TeO_2$ GLASS SYSTEM

S. Rajesh[1] , P. Satyagopal Rao[2], Suresh.Sripada[3]

[1,2,3] *JNTUH CEJ Kondagattu-505501, Jagtial, T.S, (INDIA)*

ABSTRACT

xSrO-(40-x) As_2O_3 *–60*TeO_2 *glass system with 0<x<35 mol% was prepared and investigated by FT-IR and Raman Spectroscopies in order to determine its structure and the changes induced by the increasing of SrO content. The results offered by FT-IR and Raman spectroscopies suggest a structure formed by* AsO_3, TeO_4 *tbp, and* TeO_3 *tp units.*

Key Words: As_2O_3***.***Teo_2 ***Glass Matrix, FT-IR, Raman***

I INTRODUCTION

Tellurite glasses have been studied from several different points of view because of their peculiar properties such as chemical durability,highrefractive index, high dielectric constant, good thermal stability and strength, corrosion resistance and low melting temperature [1-3]. The high non-linear refractive index of TeO_2 containing glasses is attributed to the non-bonding lone electron pair $5s^2$ of tellurium.These properties of TeO_2 are considered to have important commercial applications in infrared filters, optical amplifiers, memories and laser hosts.Tellurium glass has the lowest maximum phonon energy among common oxide glasses due to the heavier mass of tellurium atom [4, 5]. It has been reported that the pure TeO_2 can't be vitrified except in the presence of trace impurities or under very peculiar conditions [6, 7]. However combined with metal oxide modifiers the system yields glasses possessing interesting characteristics such as infrared transmission (0.4 to 6 μm) and large linear & non-linear refractive indices [8]. Because of their technological potentials, several studies such a IR, Raman, NMR and XRD have been devoted to the relation between optical properties and the structure of these systems [9-11]. It generally accepted that tellurium is a conditional glass former and the addition of As_2O_3 augments the glass formation ability and the optical transparency in the blue region. As_2O_3 glasses have high transmission potential in the far infrared region due to which they were recognized as low loss materials for long distance optical transmissionwhen compared with the conventional glasses like B_2O_3, SiO_2 and GeO_2[12].As_2O_3 glasses have exceptionally high Raman scattering coefficients and found to be suitable for active fiber Raman amplification. Arsenic telluride glasses have different practical applications such as switching and memory devices. The electro negativity of TeO_2 is in the range of other good glass formers cat ions such as P, As, Ge…etc[13]. The incorporation of As_2O_3 in to the TeO_2 glass matrix expected to affect the far infrared transmission of TeO_2 glasses to a less extent since the frequencies of some of the fundamental modes of vibrations of As_2O_3 structural groups lie in the region of vibration of TeO_2 structural groups[14].Few studiesavailable on structural investigations and dielectric spectroscopic properties of TeO_2-As_2O_3glasses [15-17]with rear earth oxide and some heavy metal oxides to reveal the structural characteristics of As_2O_3, TeO2 glasses. The purpose of presentstudy to investigate by means of FT-IR and Raman spectroscopies to reveal the structural characteristics of SrO-As_2O_3-TeO_2 glasses and the modifications that appears in this structure with the addition of SrO content.

II MATERIALS AND METHODS

2.1 Glass Preparation

In the present study xSrO+(40-x)As_2O_3+60TeO_2(where x=10-35 mol%) glasses were prepared by melt quenching method. Appropriate amounts of reagent grade SrO (SD-Fine), As_2O_3 (SD-Fine) and TeO_2 (Sigma-Aldrich) chemicals were thoroughly mixed in an agate mortar and were melted in a porcelain crucible in the temperature range 800 to 850^{0}C in a electrical muffle furnace for half an hour until a bubble free transparent liquid formed. The resultant melt was then poured on to the steel mould and pressed with another steel plate to obtain a thin glass of pellet shape.

2.2 Glass Characterization

The amorphous state of the glass was checked out by X-Ray diffraction spectra. The XRD patterns obtained are characteristic to vitreous solid in the given compositional range and are given in the Figure.1.However as seen from Figure.1. IR spectra were the most advantageous tools and have been extensively employed over the years to investigate the structure of glasses; we have used it to determine structure of Tellurite glasses of various amounts of As_2O_3 and TeO_2. The FT-IR spectra of the obtained glass samples was recorded at room temperatureusing KBr beam splitter technique in the spectral range from 600 cm^{-1} to 4000 cm^{-1} on Brukerspectrometermodel (TENSOR27).The Raman spectra were considered as a source of information about structural properties of the glasses and their composition dependences. First the study was performed for the xSrO+(40-x)As_2O_3+60TeO_2system in interval between x= 10 to 35 mol% in the wavenumber range from 50 cm^{-1} to 4000cm^{-1} with BRUKER RFS Raman spectrometer. The excitation source of Raman measurements was an Nd:YAG laser operating at 1064nm.

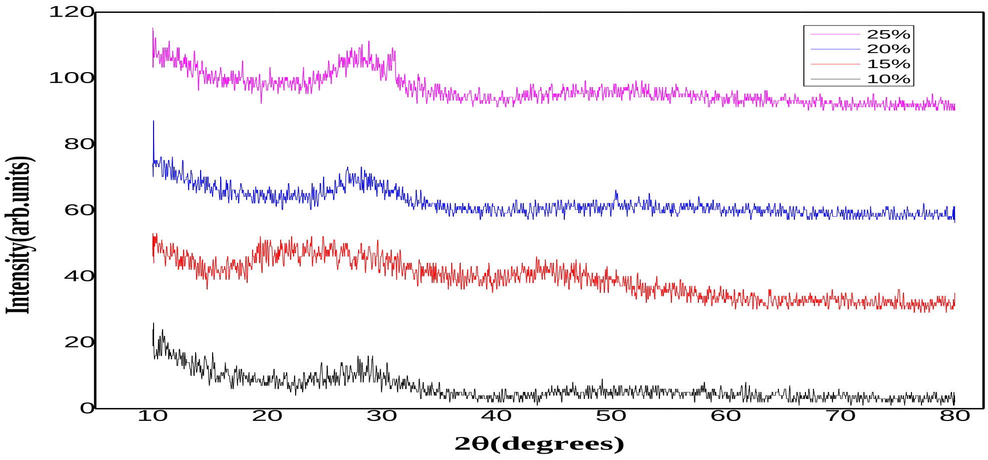

Figure.1. XRD pattern of xSrO+ (40-x) As_2O_3+60TeO_2 glass system.

III RESULTS AND DISCUSSION

3.1 FT-IR Spectral Studies

x SrO+(40-*x*) As_2O_3+60 TeO_2 glass system(10<*x*<35 mol%) was investigated in the range of 600 cm^{-1} to 4000 cm^{-1} by FT-IR spectroscopy. The FT-IR absorption spectra are presented in Figure (2) and the structural assignments are presented in Table (1).There are five regions of absorption bands 630-644 cm^{-1}, 770-710 cm^{-1}, 890-864 cm^{-1} and 1101-1086 cm^{-1}, 1440-1438 cm^{-1} are noticed in the present glass system. The spectra exhibited different absorption bands due to various structural units of TeO_2 and As_2O_3.It is very familiar that IR spectra of crystalline TeO_2 is expected to exhibit two absorption bands at 772 $cm^{-1}(\nu_1)$ and at 650 $cm^{-1}(\nu_2)$ due to ν_s-TeO_{2eq} and ν_s-TeO_{2ax} vibrations with $C_{2\upsilon}$ symmetry respectively[18]. In the present glass system the bandsobserved at 630-644 cm^{-1} is attributed to TeO_4 tbp and a similar band was observed at 663 cm^{-1} resulting from vibration of Te-O_{ax} bond and is attributed to TeO_4 tbp[21]. The third region of present glass system around 770-710cm^{-1} is due to symmetric vibrations of Te-O_{eq} bond and is attributed to TeO_3 tp structural units and the intensity of this band increases with the increasing of SrO content and is shifted to lower wavelength side.The increasing intensity of this band suggests an increasing of TeO_4 tbp structural units. It was observed that IR band at 893cm^{-1} in [TeO_2-Nb_2O_5-ZnO]is attributed toTeO_3 trigonal pyramids with NBO[22]. The same absorption band in present glass system noticed in the region 864-890 cm^{-1} when SrO is increased from 10 mol% to 35 mol% respectively.It well known that IR spectrum of crystalline As_2O_3 is expected four prominent bands ν_1 (1050 cm^{-1}), ν_2 (625 cm^{-1}), ν_3 (812 cm^{-1}), ν_4 (495 cm^{-1}) due to vibrations of As_2O_3 structural units [19]. In the present glass system the band at 632 cm^{-1} is attributed to the symmetric bending vibrations of AsO_3 structural groups[14].It is noticed that the increasing of SrO results the decreasing of intensity of this band.The band observed in the region 890-864 cm^{-1} is attributed to doubly degenerate stretching vibrations of AsO_3 units. This band is shifted to lower wavelength side as SrO concentration increases and its intensity is increasing. This behavior suggests the increasing of As_2O_3 units and also of TeO_3 tp units with NBO[27]. The band at 1101-1086 cm^{-1} is attributed to totally symmetric stretching vibrations of AsO_3 structural units[20].The presence of AsO_3, TeO_4 tbp and TeO_3 tp units in the structure of the present glass matrix is confirmed by the bands exhibited by these structural units.For pure SrO powder peaks were observed at 1699 cm^{-1}, 1458 cm^{-1}, 1026 cm^{-1}, 855 cm^{-1} with broad bands from 585 $cm^{-1}$to 600 cm^{-1} and 409 cm^{-1} to 450 cm^{-1} [23]. In the present glass system the bands at 1440 and 1654 cm^{-1} are confirms the existence of SrO in the glass matrix.

Figure 2.IR spectra of xSrO+(40-x)As_2O_3+60TeO_2 glass system with 10<x<35 mol%

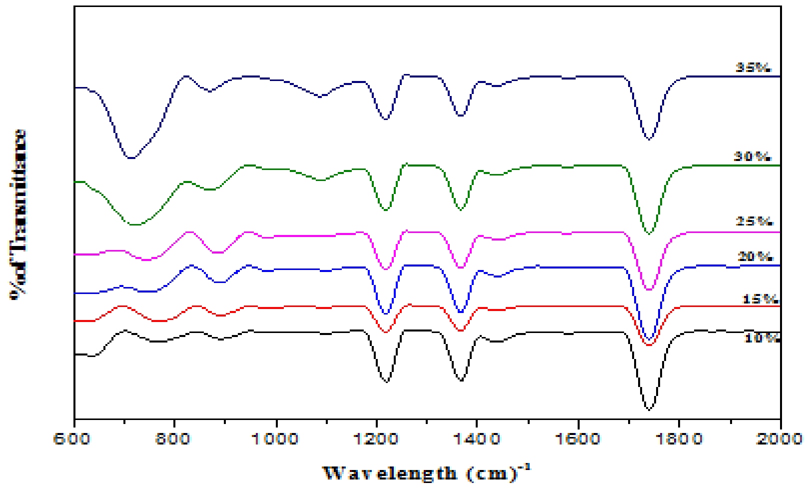

Table 1. Assignment of IR and Raman bands of the glass system xSrO+(40-x)As_2O_3+60TeO_2

Wavelength cm^{-1}		Assignment	
FT-IR	Raman	FT-IR	Raman
	452		Symmetric bending vibrations of Te-O-Te vertex linkages between different TeO_4(tbp), TeO_{3+1} polyhedra
644	645	Totally symmetric bending vibrations of AsO_3 unts, Stretching vibrational mode of TeO_4 tbp with bridging g oxygen.	Stretching vibrations of TeO_4 tbp units
747	758	Stretching vibrational mode of TeO_4 tbp with 4 bridging oxygen.	Stretching mode of TeO_3(tp) with NBO's, vibrations of the continuous TeO_4(tbp) network, As-O-As stretching vibrations
864		Doubly degenerate stretching vibrations of AsO_3 units, stretching vibrational mode of TeO_3 tp with NBO	As-O-As stretching vibrations
1101		Totally symmetric stretching vibrations of AsO_3 units	

3.2 Raman Spectral Studies

xSrO+(40-x)As_2O_3+60TeO_2 glass system with 10<x<35 mol% was investigated by Raman spectra. The Raman spectra of present glass system shown in the Figure (3) and the structural arrangements are mentioned in Table (1). There are three major bands regions are observed in the present glass system: Band 1:452-461 cm^{-1}, Band 2: 658-689 cm^{-1}, Band 3: 737-771 cm^{-1}. The peak about 452 cm^{-1} resulting from the symmetric stretching and bending vibrations of Te-O-Te linkages.These are formed by sharing vertices of TeO_4 tbp's, TeO_{3+1} polyhydra and TeO_3 tp's. The existence of this peak indicates a continuous network consisting of TeO_n(n=4,3+1, 3) polyhedra[24]. The intensity of the band from 452 cm^{-1} is increasing due to fact that the addition of SrO is favoring the formation Te-O-Te vertex linkages between different TeO_4 tbp. The peak about 658 cm^{-1} was assigned to anti-symmetric vibrations of Te_{4}-$_{eq}O_{ax}$-Te_4, Te_{3+1}-O---Te_{3+1}, Te_3-O---Te_{3+1}, Te_{4}-$_{eq}$O---Te_{3+1}, Te_{4}-$_{ax}$O-Te_{3+1}, and Te_{4}-$_{ax}$O-Te_3 linkages with different bond lengths.The variation in the Raman intensity due to a difference in polarizability between the long and short Te-O bonds [25]. The peak at 658 cm^{-1} shows a decrease of fraction of Tellurium forming TeO_4 tbp's and TeO_{3+1} polyhedra. This suggest that a part of TeO_4 tbp's and TeO_{3+1} polyhedra change in to TeO_3 tp's. The Raman peak around 770 cm^{-1} is due to stretching mode of TeO_3 tp's with NBOs and the vibrations of the continuous TeO_4 tbp's network over which As-O-As stretching vibrations can be superposed [26]. The appearance of this shoulder confirms the presence of As-O-As bonds even at high content of SrO concentration.

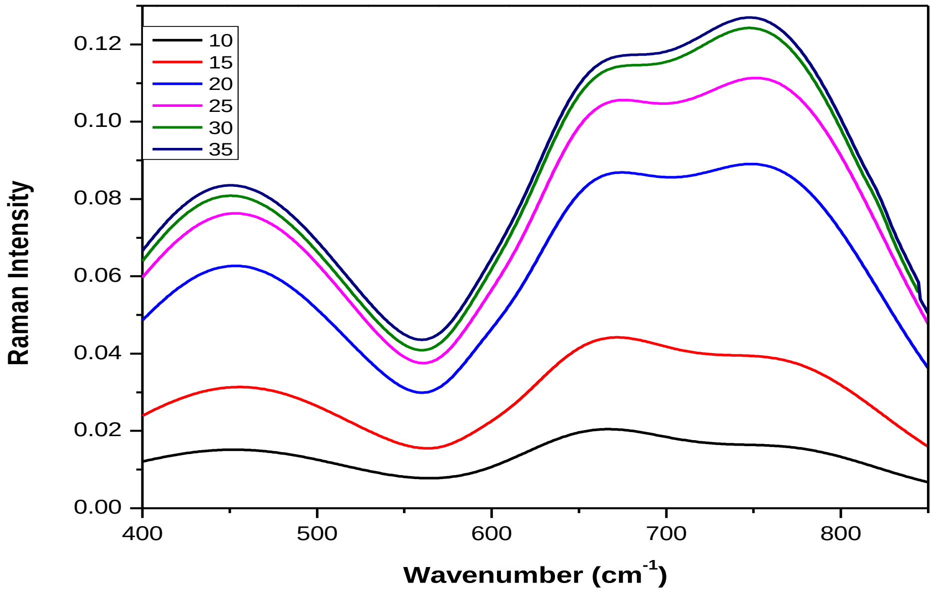

Figure 3. Raman spectra of *x*SrO+(40-*x*)As_2O_3+60TeO_2 glass system

IV CONCLUSIONS

We have presented the IR and Raman studies on SrO-As_2O_3-TeO_2 glass system. The spectra obtained suggest a glassy structure of this system. The infrared spectra of these glasses suggest that the structure of this system is modifying with the addition and increasing of SrO content. The spectrum of the glass matrix suggests a structure formed from AsO_3, TeO_4 tbp, TeO_3 tp units. Then addition of modifier results in the decreasing of intensities of the bands present in the spectrum of the glass matrix. This suggests the presence of the SrO leading to the disordering of the structure. The bands characteristic to AsO_3, TeO_4 tbp, TeO_3 tp units became more intense. This behavior suggests that the SrO units became distinctive units in a structure formed from AsO_3, TeO_4 tbp, TeO_3 tp units.The Raman results show the progressive transformation of the TeO_4 units to TeO_3 units via TeO_{3+1} unit with increasing SrO content where the presence of As-O-As bonds cannot be excluded. The addition of SrO is leading to a disordering of the structure proposed by the spectrum of the glass matrix. With the increasing of SrO content the intensity of these bands is increasing showing that the SrO content favored the formation of TeO_4 tbp, TeO_3 tp units. The Raman results confirm the infrared results of this complex glass system.

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