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FT-IR and Raman spectroscopic studies of ZnF_2–ZnO–As_2O_3–TeO_2 glasses

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Abstract

The effect of fluorine substitution on the spectral properties of the $x$$ZnF_2$–(20-$x$)ZnO–40$As_2O_3$–40$TeO_2$ (x = 0, 4, 8, 12, 16 and 20 mol%) glass system was investigated by FTIR and Raman spectroscopies. The results demonstrate that TeO_4 and TeO_3 were among the primary structural units in the investigated glasses in addition to As_2O_3 pyramids and ZnO_4 structural units. The addition of fluorine results in the reduction of Te—O—Te linkage due to a gradual transformation of trigonal bipyramidal TeO_4 through TeO_{3+1} to trigonal pyramidal TeO_3, which decreases the connectivity of the tellurite glass former network. The theoretical optical basicity of the studied glasses decreases with increasing ZnF_2 content.

Keywords: Glasses; EDAX; FTIR; Raman

1. Introduction

Tellurium oxide-based glasses have been the subject of current research due to their interesting electrical, optical and magnetic properties [1,2]. In addition to having a unique structure [3,4], telluride glasses also have good mechanical strength and chemical durability [5–8], a low melting temperature [9], large linear and non-linear refractive indices [10,11] and good optical transmission at infrared [12,13] and visible wavelengths [14–17]. These properties make tellurite glasses good candidates for the development of optical devices [18]. Furthermore, tellurium oxide-based glasses exhibit higher dielectric constants and electrical conductivity [19,20].

The basic structural unit of tellurium oxide in binary tellurite glass is the trigonal bipyramid (tbp) with a lone pair of electrons, and it forms a Te–O–Te bond during glass formation. The physical and structural properties of binary tellurite glasses such as V_2O_5–TeO_2, TeO_2–Nb_2O_5 and TeO_2–B_2O_3 have been investigated with ESR spectra [21], X-ray absorption spectroscopy [22] and extended X-ray absorption fine structure [23] studies. The change in the coordination of Te from the TeO_4 triogonal bipyramid to the TeO_3 trigonal pyramid (tp) group through the formation of an intermediate polyhedron TeO_{3+1} and then to the TeO_3 units [24] has

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been studied in TeO_2 glasses with increasing content of network modifiers such as alkali and alkaline oxides. Rajendran et al. [4,25] methods the structural and elastic properties of vanadate bismuth tellurite and TeO_2–BaF_2 glasses employing ultrasonic studies.

Tellurium oxide under normal conditions does not have the ability to form a glass without a modifier such as alkali, alkaline earth oxide and/or other types of glass formers [7,26,27]. The addition of arsenic oxide (As_2O_3) to tellurium oxide glasses improves the glass forming ability and the optical transparency in the blue region. As_2O_3, a strong glass network former, was being used as a fining agent to remove air bubbles in glasses. Few studies on As_2O_3 glasses mixed with alkali halides, rare earth oxides and some heavy metal oxides were reported [28–30] as having a narrow glass-forming region. In zinc arsenate glasses, the presence of ZnO improves the mechanical properties as well as the chemical and thermal resistivities and reduces the sublimation characteristics of arsenate [31,32]. Recently, Bala Murali Krishna et al. [33–35] studied the optical, structural and dielectric spectroscopic properties of ZnO–As_2O_3-based glasses doped with chromium and molybdenum ions. In the present study, a strong glass network former, As_2O_3, has been chosen for incorporation into the TeO_2 glass system. In general, As_2O_3-mixed glasses possess exceptionally high Raman scattering coefficients and are suitable for active fibre Raman amplification [36]. Furthermore, the addition of As_2O_3 into the TeO_2 glass system is expected to affect the far-infrared transmission to a lesser extent than other compounds because the fundamental modes of vibration of the As_2O_3 structural groups lie in the region of vibration of the TeO_2 structural groups [36].

Binary zinc tellurite glasses have been extensively studied [37–41]. Zinc atoms are suggested to play an important role in forming a glass network and the fraction of ZnO in binary zinc tellurite glasses can strengthen the whole network structure due to its bridging oxygen ion. Several studies of infrared and optical absorption were published for zinc tellurite glasses [42–45]. It has been reported that absorption properties in TeO_2–ZnO glasses exhibited a strong dependence on the ZnO content. A ZnO–TeO_2 glass was used as the basis for a multi-component optical system. The addition of modifiers such as ZnF_2 to the ZnO–TeO_2 glass matrix or the substitution of fluorine ions for oxide ions is expected to increase the glass forming range and glass stability, lower the viscosity and improve the transparency substantially in addition to making the glass more moisture resistant [46,47].

Several studies on the introduction of fluorine ions into oxide ions were reported for zinc tellurite glasses [48,49]. Because a fluorine ion has nearly the same radius as an oxygen ion, the probability of substitution of the oxygen ions with fluorine ions is high, but the fluorine ions could also occupy interstitial positions. Additionally, fluorine has a higher electronegativity than oxygen, and because two fluoride ions would take the place of one oxide ion, which would cause the breakdown of the glass network structure, the glass transition and deformation temperatures would be expected to decrease with the substitution of fluoride ions in place of oxide ions.

To the best of our knowledge, fluorine substituted zinc arsenic tellurite glasses have not previously been reported. We recently reported [50] the physical and optical properties of zinc arsenic tellurite glasses based on the ZnF_2–ZnO–As_2O_3–TeO_2 composition. Apart from these reported properties, there is a lack of data in the literature on the structural characteristics of these glasses. Therefore, the objective of this research is to characterize the ZnF_2–ZnO–As_2O_3–TeO_2 glass system using FTIR and Raman spectroscopies.

2. Experimental study

In the present study, zinc tellurite glasses of the system $x$$ZnF_2$–(20-$x$)ZnO–40$As_2O_3$–40$TeO_2$ (x = 0, 4, 8, 12, 16 and 20 mol%) were prepared by a melt quench technique. High purity (99.99%) zinc fluoride (ZnF_2), zinc oxide (ZnO), tellurium oxide (TeO_2) (all Sigma Aldrich) and arsenic oxide (As_2O_3) (May and Baker) were used as the starting materials. The detailed experimental procedure for the preparation of the glass samples was described in our previous paper [50]. The energy dispersive spectroscopy (EDS) measurements were conducted using a Thermo instruments model FEI XL30 ESEM attached to a scanning electron microscope (SEM). The structure of the glass samples was studied using FTIR and Raman spectroscopies. The FTIR absorption spectra were recorded with a Bruker Optics spectrometer (Tensor 27, Germany) using the KBr Pellete technique. Room temperature Micro Raman spectra were recorded using a Renishaw (UK) spectrometer with a 50 mW internal Argon laser source at an excitation wavelength of 514 nm. The spectral resolution was 1 cm^{-1}.

3. Results

3.1. EDS

Energy dispersive X-ray analysis (EDS) is commonly used to determine the chemical composition of