

Structural and magnetic investigations of $\text{Fe}_2\text{O}_3\text{--TeO}_2$ glasses

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Abstract

A series of tellurite glasses containing Fe_2O_3 with the nominal composition $x(\text{Fe}_2\text{O}_3)\text{--}(1-x)(\text{TeO}_2)$, where $x = 0.05, 0.10, 0.15,$ and 0.20 , have been synthesized and investigated using X-ray photoelectron spectroscopy (XPS) and magnetization techniques. The Te 3d core level spectra for all glass samples show symmetrical peaks at essentially the same binding energies as measured for TeO_2 indicating that the chemical environment of the Te atoms in these glasses does not vary significantly with the addition of Fe_2O_3 . Furthermore, the full-width at half-maximum (FWHM) of each peak does not vary with increasing Fe_2O_3 content which suggests that the Te ions exist in a single configuration, namely TeO_4 trigonal bipyramid (tbp). The O 1s spectra are narrow and symmetric for all compositions such that oxygen atoms in the Te–O–Te, Fe–O–Fe and Te–O–Fe configurations must have similar binding energies. The analysis of the Fe 3p spectra indicates the presence of Fe^{3+} ions only, which is consistent with the valence state of the Fe ions determined from magnetic susceptibility measurements.

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1. Introduction

Tellurium oxide (TeO_2) based glasses are important in the fields of glass science and technology due to their electrical and optical properties. TeO_2 is of particular importance as this conditional glass network former has a low melting point when combined with an alkali metal oxide or a transition metal (TM) oxide [1,2]. The formation of these glasses may also be accompanied by a change in the local TeO_2 structure. For example, the addition of alkali metal ions in tellurite glasses can result in the transformation of some TeO_4 trigonal bipyramid (tbp) structural units into TeO_3 trigonal pyramid (tp) with non-bridging oxygen [3]. Similar transformations of the TeO_4 structural unit into the TeO_3 tp structure were found with increasing V_2O_5

content in $\text{V}_2\text{O}_5\text{--TeO}_2$ glasses and with increasing WO_3 content in $\text{WO}_3\text{--TeO}_2$ glasses [4,5]. However, our recent studies on CuO- and MoO_3 -tellurite glasses [6,7] detected no TeO_3 structural units in the XPS spectra, although the existence of both TeO_4 and TeO_3 structural units were found in the ternary $\text{Fe}_2\text{O}_3\text{--Na}_2\text{O--TeO}_2$ glass system [8]. Thus studies of the tellurite glass structure and its corresponding effect on the electronic properties continue to be investigated by a multitude of techniques.

Several spectroscopic techniques have been used to investigate the structure of tellurite glasses, including IR [9], Raman [10], NMR [11], X-ray absorption [12] and neutron diffraction [13]. Similarly, X-ray photoelectron spectroscopy (XPS) is a powerful technique for studying the local glass structure as a function of the TM oxide concentration as well as distinguishing between bridging oxygen (BO) and non-bridging oxygen (NBO) [14]. In the present study the effect of Fe_2O_3 on the local glass structure in the tellurite glass system is investigated by XPS, and is

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part of our continuing studies of the glass structure in transition metal-doped tellurite glasses [6–8]. Besides checking on the whether any TeO_4 units transform into TeO_3 units at high Fe_2O_3 content, the oxidation state of the Fe ions can be deduced from the XPS spectra. Temperature-dependent magnetic susceptibility measurements in combination with inductively coupled plasma spectroscopy (ICP) provide an independent measure of the Fe valence state in these glasses as well as characterize the nature of the magnetic interactions between the Fe ions.

2. Experimental details

2.1. Sample preparation

All glasses were prepared by melting dry mixtures of reagent grade Fe_2O_3 and TeO_2 in alumina crucibles to form nominal $x(\text{Fe}_2\text{O}_3)-(1-x)(\text{TeO}_2)$ compositions with $x = 0.05, 0.10, 0.15,$ and 0.20 . Since oxidation and reduction reactions in a glass melt are known to depend on the size of the melt, on the sample geometry, on whether the melt is static or stirred, on thermal history, and on quenching rate, all glass samples were prepared under similar conditions to minimize these factors. Approximately 30 g of chemicals were thoroughly mixed in an alumina crucible to obtain a homogenized mixture for each Fe_2O_3 concentration. The crucible containing the nominal mixture was then transferred to an electrically heated melting furnace maintained at 900–1000 °C. The melt was left for about an hour under atmospheric conditions in the furnace during which the melt was occasionally stirred with an alumina rod. The homogenized melt was then cast onto a stainless steel plate mold to form glass rods of approximately 5-mm diameter and 2 cm in length for XPS measurements. After casting, the specimens were annealed at 200 °C for ten hours and stored in a vacuum desiccator to minimize any further oxidation of the glass samples. The actual compositions of the glasses were determined by inductively coupled plasma spectroscopy (ICP) and are presented in Table 1. Although the inclusion of alumina from the crucibles used in the melting of the glass mixtures can be a possible source of impurities, no signals for aluminum were detected in either the XPS or ICP measurements on these glasses. X-ray diffraction performed on the samples confirmed the amorphous nature of these glasses.

Table 1
Nominal and actual composition (molar fraction) of various tellurite glasses containing Fe_2O_3

Nominal		Actual (from ICP)	
Fe_2O_3	TeO_2	Fe_2O_3	TeO_2
0.05	0.95	0.046	0.954
0.10	0.90	0.089	0.911
0.15	0.85	0.135	0.865
0.20	0.80	0.153	0.847

The relative uncertainty in the ICP results is $\pm 5\%$.

2.2. XPS measurements

Core level photoelectron spectra were collected on a VG scientific ESCALAB MKII spectrometer equipped with a dual aluminum–magnesium anode X-ray gun and a 150-mm concentric hemispherical analyzer using Al $K\alpha$ ($h\nu = 1486.6$ eV) radiation from an anode operated at 130 W. Photoelectron spectra of Te 3d, Fe 2p, Fe 3p, and O 1s core levels were recorded using a computer-controlled data acquisition system with the electron analyzer set at a pass-energy of 20 eV for the high resolution scans. For self-consistency, the C 1s transition at 284.6 eV was used as a reference for all charge shift corrections. This peak arises from hydrocarbon contamination and its binding energy is generally accepted as remaining constant, irrespective of the chemical state of the sample. For XPS measurements, a glass rod from each composition was cleaved in the preparation chamber at a base pressure of 2×10^{-9} mbar before being transferred to the analysis chamber where the pressure was maintained at $\sim 2 \times 10^{-10}$ mbar. A non-linear, least-squares algorithm was employed to determine the best fit to each of the O 1s, Fe 3p, and Te 3d spin-orbit doublet spectra with two Gaussian–Lorentzian curves in order to represent bridging and non-bridging oxygen, the two possible Fe oxidation states (Fe^{3+} and Fe^{2+}), and the two possible Te tbp and tp structural units, respectively. The fractions of non-bridging oxygen, Fe^{3+} , and tbp units were determined from the respective area ratios obtained from these fits. Based on the reproducibility of similar quantitative spectral decompositions of spectra taken from other surfaces on the same glass samples, uncertainties of $\pm 5\%$ for NBO content and $\pm 10\%$ for both Fe^{3+} and TeO_4 units were estimated for these area ratios. A period of approximately 2 h was required to collect the data set for each sample.

2.3. Magnetic measurements

The temperature-dependent DC magnetic susceptibility was measured using a SQUID magnetometer (Quantum Design model MPMS-5S) in a magnetic field of 5000 Oe over a temperature range 5–300 K at temperature intervals of 2.5 K. The susceptibility of the sample holder was negligible for all samples, and the overall accuracy of the magnetic measurements is estimated to be approximately 3% due to the uncertainty of the magnetometer calibration.

3. Results

3.1. Te 3d spectra

Fig. 1 displays the Te 3d spin-orbit core level spectra for all glass samples investigated. It is clear from the figure that the peak intensity decreases with increasing Fe_2O_3 content, while the peak positions remain essentially the same for all glass compositions. The binding energies (BE) of the $\text{Te}3d_{5/2}$ are measured to be 576.2 ± 0.1 eV with a

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