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Atomic environment changes induced by rare earths addition to heavy metal glasses

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The study aims to evidence the local order changes in Bi_2O_3-GeO_2 heavy metal glasses by addition of gadolinium oxide. The elemental analysis carried out by X-ray photoemission spectroscopy shows that in the first surface layers the oxygen and germanium contents are higher than the calculated values for bulk samples, while the content of gadolinium and bismuth atoms is lower than the expected values for bulk samples. Non-equivalent sites of bismuth atoms are evidenced in the glasses with low Gd_2O_3 content ($x \leq 3$ mol %). The gadolinium addition to Bi_2O_3-GeO_2 glass matrix determines the diminishing of bridging oxygens number and implicitly a depolymerisation of the glass structure. On the other hand, the decrease of full-width at half-maximum of O 1s photoelectron peaks denotes the diminishing of the structural disorder in samples. According to the values of O 1s photoelectrons binding energy, the investigated samples are a mixture of ionic and covalent oxide compounds.

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*Keywords:*Heavy metal glass, Rare-earth, Bi_2O_3-GeO_2 glass, Gd_2O_3

1. Introduction

Heavy metal glasses [1] attracted large interest due to their properties such as high density, high refractive index, excellent IR transmission and high polarisability [1-3]. Germanate glasses containing oxides of heavy metals are promising candidates for new materials for non-linear optical and magneto-optical devices [4]. Glasses based on the heavy metal oxide have the capacity to accept rare earth ions in a relatively high amount [5]. Rare-earth doped oxide glasses are excellent materials for optoelectronics [6-8].

Bismuth-germanate glasses are highly susceptible to structural modifications in the near-surface layer [9]. X-ray induced photoelectron spectroscopy (XPS) provides information on the first 20-50 Å of the sample surface and allows investigations of very near-surface layers from which the photoelectron peaks occur. Bismuth-germanate glasses have been investigated to a less extend [10-15].

The formation of magnetic clusters in Bi_2O_3-PbO glass with Gd_2O_3 has been studied in our previous paper [16].

The purpose of this work is to study by X-ray photoemission spectroscopy the local order changes in Bi_2O_3-GeO_2 heavy metal glasses with gadolinium oxide content.

2. Experimental

High content Bi_2O_3 glasses belonging to $xGd_2O_3 \cdot (100-x)[87.5Bi_2O_3 \cdot 12.5GeO_2]$ system, with $1 \leq x \leq 10$ mol %, have been obtained by rapid cooling of the melts.

The samples were prepared from Gd_2O_3, GeO_2 and Bi_2O_3 of p.a. purity. The reagent mixtures were melted in sintercorundum crucibles at 1250°C and quenched at room temperature. The structure of the as prepared samples was investigated by X ray diffraction with a Shimatzu XRD-6000 diffractometer using CuK_α radiation. XPS measurements were performed using a PHI 5600ci Multi Technique system with monochromatised Al K_α radiation from a 250 W X-ray source ($h\nu$ = 1486.6 eV). During the measurements the pressure in the analysis chamber was in the 10^{-9} Torr range. Low energy electron beam was used to achieve charge neutrality at the sample surface. High resolution core level scans were acquired for the C 1s, Bi 4f, Ge 3d, Gd 4d and O1s photoelectron peaks. The absolute binding energies of the photoelectron spectra were determined by referencing to the C 1s transition at 284.6 eV that result most probably during the measurements as adsorbed species. The position and full width at half maximum of photoelectron peaks were estimated using spectra simulation based on summation of lorentzian and gaussian functions.

3. Results and discussion

The X-ray diffraction patterns of as prepared samples are structureless and confirm their vitreous state.

Electron Spectroscopy for Chemical Analysis (ESCA) was used to establish the elemental composition of samples from XPS survey spectra (Fig. 1).

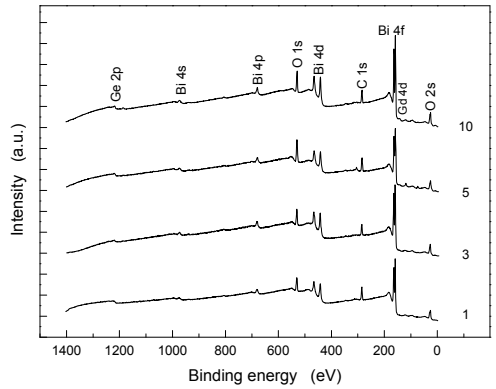

Fig. 1 XPS suvey spectra.

ESCA analysis involves only the top layers of the sample, making it an extremely surface sensitive technique. The elemental composition for the investigated samples is given in Table 1. In all samples the oxygen content in the first surface layers is higher than the calculated content for bulk samples. The same result is observed for germanium atoms.

In the XPS studies of oxide glasses, the binding energy of O 1s electrons in oxygens bonded to different cations seems to be the most informative measurement with respect to the structure of the glass [17]. This binding energy is a measure of the extent to which electrons are localized on the oxygen or in the internuclear region and hence of the constraints on the network, as reflected by the physical properties. The O 1s core level spectra of the investigated $xGd_2O_3 \cdot (100\text{-}x)[87.5Bi_2O_3 \cdot 12.5GeO_2]$ system are presented in Fig. 2.

Table 1.

x (mol%)	Composition (at %)							
	O 1s		Ge 3d		Gd 4d		Bi 4f	
	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.
1	59.47	64.09	2.67	4.58	0.43	0.06	37.43	31.27
3	59.48	63.38	2.62	5.13	1.29	0.75	36.61	30.74
5	59.49	63.49	2.56	4.67	2.15	1.47	35.80	30.36
10	59.52	63.07	2.41	4.97	4.29	2.49	33.78	29.47

The asymmetric peaks are occurring from bridging oxygens (BO) at higher binding energy and nonbridging oxygens (NBO) at lower binding energy. The electron binding energies are reduced by increase in electron density at the oxygen atoms and this is reflected in the photoelectron spectrum, giving rise to non-bridging oxygen peak.

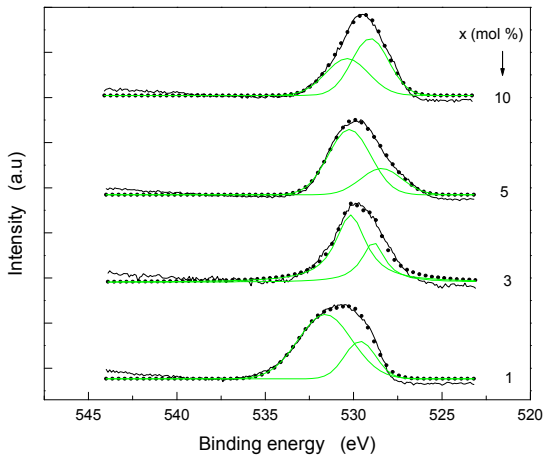

Fig.2. Experimental (solid line) and simulated (short dots) O 1s core level photoelectron.

The fraction of BO relative to the total number of oxygens (N_{BO}/N_O) was estimated from the areas corresponding to O 1s photoelectron peaks in the simulated spectra. As can be seen from Table 2, the ratio N_{BO}/N_O is diminished by gadolinium addition from 75 to 28 % as Gd_2O_3 content increases from 1 to 10 mol.

Table 2.

x (mol %)	FWHM (eV)	N_{BO}/N_O (%)
1	4.3	75
3	3.2	69
5	3.5	32
10	3.2	28

It was established [18] that O 1s binding energy of different oxides varies in the range from 528.0 to 533.5-eV and these values correspond to different degree of ionicity in the bonds of oxygen atoms with the cation atoms. The glasses we investigate could be considered a mixture of ionic and covalent oxide compounds, according to the binding energies of O 1s photoelectrons.

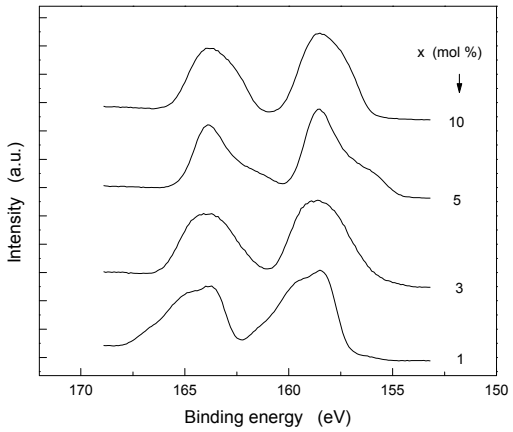

Fig. 3. Bi 4f core level photoelectron spectra.

The Bi 4f high resolution spectra (Fig. 3) present a spin orbit splitting very close to 5.3 eV. The positions of the photoelectron peaks are shifted to some higher energies relative to pure Bi 4 $f_{7/2}$ (157 eV) and Bi 4 $f_{5/2}$ (162.31 eV). The binding energies (BE) are close to the values reported for other bismuth oxide compounds [19-21]. A slight binding energy shift of Bi 4f photoelectron peaks to lower BE values is noticed with increase of Gd_2O_3 content, denoting that the polarisation of Bi depends on gadolinium concentration and results in an decrease of covalence degree of Bi-O bond allowing the depolymerisation of (BiO_5, BiO_6)*n* chains [22]. At the same time, one remarks non-equivalent sites of bismuth atoms in the glasses with low Gd_2O_3 content.

4. Conclusions

Heavy metal oxide glasses in $xGd_2O_3 \cdot (100-x)[87.5Bi_2O_3 \cdot 12.5GeO_2]$ system were obtained by quick melt undercooling. In all samples the oxygen content in the first surface layers is higher than the calculated content for bulk samples. On the surface layers, also the germanium content is higher, while the content of gadolinium and bismuth atoms is lower than the expected values for bulk samples. Non-equivalent sites of bismuth atoms are evidenced in the glasses with low Gd2O3 content ($x \leq 3$ mol %).

The gadolinium addition to Bi_2O_3-GeO_2 glass matrix determines the diminishing of bridging oxygens number and implicitly a depolymerisation of the glass structure. According to the values of O1s binding energy, the investigated samples are a mixture of ionic and covalent oxide compounds.

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