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X-ray photoelectron spectroscopic studies of lead-bismuthate glasses with rare earths

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Lead-bismuthate glasses with cerium and erbium ions have been prepared and investigated by X-ray photoelectron spectroscopy (XPS). The Pb 4f, Bi 4f, O 1s, Er 4p, Ce 3d and Ce 4d binding energies have been measured in order to clarify the electronic structure of oxide glasses. The asymmetric Pb 4f and Bi 4f peaks for all studied glasses indicate the presence of PbO_n and BiO_n units. The O 1s spectrum was deconvoluted into two peaks and the variation of the ratio of the peak areas is discussed.

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1. Introduction

Heavy metal oxide glasses are very attractive hosts for rare earth ions due their possible technological applications in optoelectronics and telecommunications. From various spectroscopic methods such as infrared, Raman spectroscopy [1-5] it has been established that the basic structure of these lead-bismuthate glasses is build up by BiO_3, BiO_6 and PbO_3, PbO_4 units. Lead and bismuth oxides under normal condition could not form glass individually without a modifier like a rare earth oxide or a glass former oxide.

X-ray photoelectron spectroscopy (XPS) of glasses and other insulators can provide physicochemical information concerning both surface and bulk properties that is obtainable by no other means [6].

In this paper we report the investigation of the local atomic structure of two lead-bismuthate glasses with different Er_2O_3 and CeO_2 content.

2. Experimental

Glasses of the $[3Bi_2O_3 \cdot PbO]$ composition doped with different quantities of rare-earth oxides were prepared by mixing Bi_2O_3, PbO and Er_2O_3 and/or CeO_2 of reagent grade purity. The mentioned oxides were mixed in suitable proportions to obtain the desired compositions. The mixtures were milled in an agate ball mill for 30 minutes and then were melted at 1200ºC for 15 minutes. The glass samples were obtained by pouring the melts on a stainless steel block.

XPS spectra of the glasses were recorded on a PHI 5600ci Multi Technique spectrometer with monochromatised Al K_α radiation from a 250 W X-ray source ($h\upsilon$ = 1486.6 eV). During the measurements the pressure in the analysis chamber was in the 10^{-9} Torr range. 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 the half maximum of the photoelectron peaks were estimated using spectra simulation based on Gaussian function.

3. Results

X-ray photoelectron survey scans, in the binding energy region 0-1400 eV, were recorded for each glass sample and a typical wide-scan X-ray photoelectron spectrum for $xEr_2O_3(1-x)[3Bi_2O_3 \cdot PbO]$ glass sample is shown in Fig. 1. The main photoelectron peaks are identified on the spectra. The high resolution Pb 4f and Bi 4f spectra are shown in Figs. 2 and 3. Upon careful inspection of the Pb 4f and Bi 4f spectra an asymmetry is observable. The position of the photoelectron peaks are presented in Table 1.

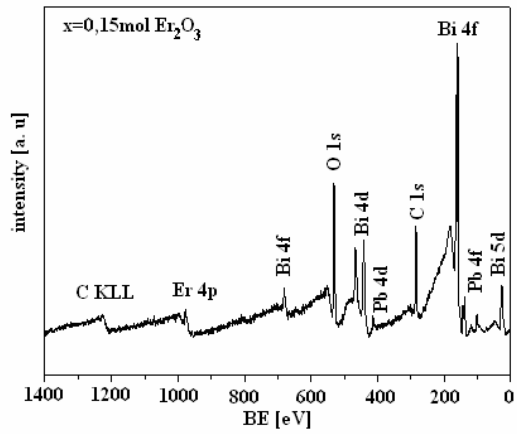

Fig. 1. X-ray photoelectron survey scan for $xEr_2O_3(1-x)[3Bi_2O_3 \cdot PbO]$ glass sample.

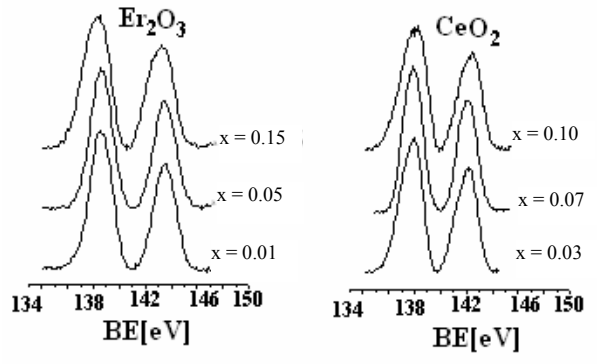

Fig. 2. High resolution Pb 4f spectra .

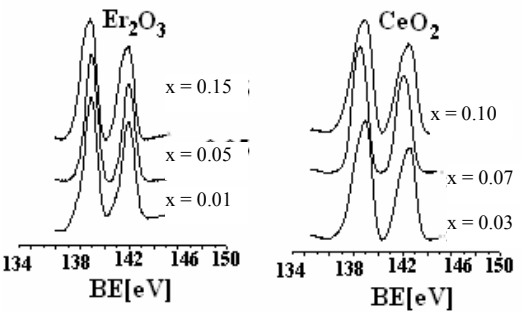

Fig. 3. High resolution Bi 4f spectra.

Table 1. Core level electron binding energies (BE), full-width at half-maximum (FWHM) and spin orbit splitting for Pb 4f and Bi 4f photoelectrons in xRE(1-x)[3Bi_2O_3·PbO] glasses.

x [mol]	BE [eV]		FWHM [eV]		Spin orbit splitting [eV]
	Pb 4 $f_{7/2}$	Pb 4 $f_{5/2}$	Pb 4 $f_{7/2}$	Pb 4 $f_{5/2}$	
$xEr_2O_3(1-x)[3Bi_2O_3·PbO]$					
0.01	137.96 138.75	143.16 144.05	1.79 1.49	1.40 1.23	5.18 5.30
0.05	137.95 138.74	143.15 143.74	1.61 1.53	1.44 1.62	5.02 5.00
0.15	137.87 138.94	142.34 143.56	1.78 1.08	1.19 1.40	4.47 4.62
$xCeO_2(1-x)[3Bi_2O_3·PbO]$					
0.03	137.83 138.86	142.32 143.57	1.80 1.15	1.28 1.35	4.49 4.71
0.07	137.98 138.94	142.44 143.45	1.37 1.18	0.96 1.48	4.46 4.51
0.10	137.98 139.15	142.66 143.95	1.98 1.23	1.29 1.37	4.68 4.80
	Bi 4 $f_{7/2}$	Bi 4 $f_{5/2}$	Bi 4 $f_{7/2}$	Bi 4 $f_{5/2}$	
$xEr_2O_3(1-x)[3Bi_2O_3·PbO]$					
0.01	157.97 159.34	162.95 164.58	1.98 1.48	1.20 1.60	4.98 5.24
0.05	157.62 159.31	162.92 164.61	1.32 1.60	0.62 1.65	5.30 5.30
0.15	158.55 159.61	163.78 164.93	1.88 1.02	1.62 1.13	5.23 5.32
$xCeO_2(1-x)[3Bi_2O_3·PbO]$					
0.03	158.66 159.77	163.81 165.06	1.97 1.13	1.55 1.24	5.15 5.29
0.07	158.59 159.50	163.55 164.55	1.55 1.01	1.23 1.26	4.96 5.05
0.10	158.57 159.78	163.94 165.18	2.13 1.21	1.75 1.22	5.37 5.40

Table 2. Information obtained from the O 1s photoelectron spectra by fitting with two Gaussian peaks assigned to bridging oxygen (BO) and nonbridging (NBO) oxygen and the BO/O_T ratio.

x [mol]	BE [eV]		FWHM [eV]		BO/O_t [%]
	BO	NBO	BO	NBO	
$xEr_2O_3(1-x)[3Bi_2O_3{\cdot}PbO]$					
0.01	531.09	530.24	2.17	1.98	61.62
0.05	530.96	530.37	2.35	2.10	68.88
0.15	530.83	529.86	2.68	2.28	72.84
$xCeO_2(1-x)[3Bi_2O_3{\cdot}PbO]$					
0.03	530.60	529.46	2.37	2.83	77.63
0.07	530.90	530.00	2.39	1.87	70.79
0.10	530.97	529.62	2.39	2.65	68.69

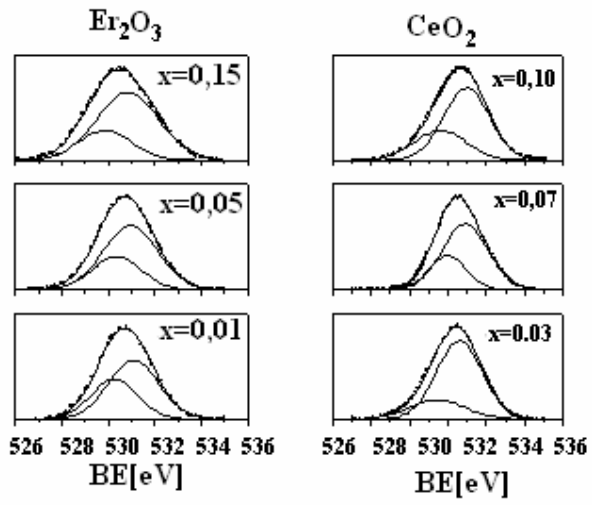

Fig. 4. High resolution O 1s spectra and the resulting peaks from the deconvolution fitting.

The erbium end cerium spectra (Er 4p, Ce 3d and Ce 4d) present a rather high signal-to-noise ratio due to the low atomic concentration of Er_2O_3 and CeO_2 in the studied samples.

The O 1s spectra from all studied glasses are presented in Fig. 4. In each set of O1s spectra an asymmetry was observed. These suggest the existence of two different types of oxygen sites in these glasses – the lower binding energy peak corresponds to non-bridging oxygen atoms while the higher energy peak corresponds to bridging oxygen atoms (table 2).

4. Discussion

The asymmetry that appears in Pb 4f and Bi 4f spectra is an indicative of the presence of PbO_n and BiO_n units in $xRE(1-x)[3Bi_2O_3{\cdot}PbO]$ glasses systems, were RE = Er_2O_3 or CeO_2. As can be observed from table 1 the position of the photoelectron peaks are shifted relatived to that arising from [7] Pb 4f at 136.9 eV for $4f_{7/2}$ and 141.76 eV for $4f_{5/2}$. The same effect occur in case of Bi 4f which are observed at 157 eV for $4f_{7/2}$ and 162.31 eV for $4f_{5/2}$. The evolution of the values obtained for BE, FWHM and spin-orbit splitting are in good agreement with the results reported for the other lead and bismuth oxide compounds [7-9]. As can be seen in table 2 by increasing the erbium content of the samples increase the number of bonding oxigens while by increasing the cerium content of the samples increases the number of the non-bonding oxygens.

Dimitrov and Komatsu [10] proposed a simple oxide clasification on the basis of correlation between electronic polarizabilities of the ions and their BE determined by XPS. So-called:

(i) semicovalent oxides with O1s binding energy in the 530.5 ÷ 533.5 eV range;

(ii) normal ionic oxides with O1s binding energy at ≈ 530 ± 0.4 eV;

(iii) very ionic oxides with O1s binding energy in the 529.5 ÷ 528.0 eV range.

According to this clasification and taking into account the values of the binding energies for the Os1 oxygens that range between 529.46 and 531.09 eV our glass systems could be considered as ionic compounds (see table2).

5. Conclusion

The XPS spectra for Pb 4f, Bi 4f and O 1s core levels of $xRE(1-x)[3Bi_2O_3{\cdot}PbO]$ glasses systems, where RE = Er_2O_3 or CeO_2 have been studied. The compositional evolution of the XPS data show that increasing of the rare earth content of the samples leads to changes in the chemical environment of the Bi and Pb ions. Thus, the XPS data show that the studied glass systems are build up from PbO_n and BiO_n units. The increases of the rare earth content of the samples modify the binding oxygen/non-binding oxygen ratio of the samples. According to the values obtained for the binding energies of the Os1 oxygens the glass systems investigated in this work could be considered predominantly as ionic compounds.

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