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Effect of oxide dopant on the structure of fluorozirconate glasses studied by X-ray photoelectron spectroscopy

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The effect of oxide dopant on the structure of $62ZrF_4$–$30BaF_2$–$8LaF_3$ (mol %) glass by equimolar substitution of BaO for BaF_2 was studied by X-ray photoelectron spectroscopy (XPS). The XPS spectra of La 3d, Ba 3d, F 1s, O 1s and Zr 3d were measured. From the deconvoluted results for the XPS spectra of elements in the glass, it was proposed that the oxide ions added to the glass mainly bond to Zr^{4+} and replace the bridging fluoride ions resulting in the formation of the F–Zr–O bond. Further analyses indicated that the oxide ions mainly play a non-bridging role instead of a bridging role in the glass structure.

1. Introduction

Fluoride glasses based on ZrF_4 have attracted considerable attention because of their broad infrared (IR) transmission range (~0.3 to ~7 μm) and their potential for very low loss optical transmission ($< 10^{-2}$ dB km^{-1}). A variety of studies [1, 2] have shown that oxide impurities can affect the IR edge and transparency. Hu Hefeng *et al.* [2] studied the effect of oxide impurity on the physical properties of $62ZrF_4$–$30BaF_2$–$8LaF_3$ (mol %) glass by equimolar substitution of BaO for BaF_2. They found that the introduction of BaO into the glass not only decreased the IR transparency at ~6 μm, shifted the transmission cut-off wavelength to higher frequencies and caused an additional absorption shoulder at 1350 cm^{-1}, but also increased the glass transition temperature, T_g, the crystallization temperature, T_c, and the viscosity of the melt. They attributed these results to the formation of F–Zr–O bands in the glass. However, the bonding states of O^{2-}, F^- and Zr^{4+} ions in the glass are not clearly understood, so in order to correlate the glass structure to the physical properties, it is necessary to study the structural role of oxide ions in the glass.

X-ray photoelectron spectroscopy (XPS) has proven to be a very powerful structural probe in studies of oxide glasses [3, 4] and oxyfluoride glasses [5–7] and holds much promise for studies of fluoride glasses [8, 9]. In the present work, we studied the F 1s, O 1s, Zr 3d, La 3d, and Ba 3d XPS spectra to obtain a better understanding of the bonding state and structural effect of oxide ions in fluorozirconate glasses.

2. Experimental procedure

The glass compositions can be expressed by the general formula $62ZrF_4$–$(30 - x)BaF_2$–$8LaF_3$–xBaO ($x = 0, 0.5, 1, 2, 3, 4, 5$). The batches (10 g) were heated in a covered platinum crucible to about 800–900 °C depending on the glass composition, and held isothermally for 20 min. The melts were cast on to a preheated stainless steel plate and pressed by another stainless steel plate. After annealing near T_g for 20 min, the sample glass was cooled to room temperature at a rate of 2 °C min^{-1}. It was found that only a small amount of barium oxide could be incorporated into the glass with $x \leqslant 5$ and that serious crystallization could easily take place when the content of barium oxide in the glass was more than 5 mol %.

Surfaces of the prepared glasses were investigated utilizing X-ray photoelectron spectroscopy (XPS). The glass samples prepared were cut into small plates with the dimensions of 15 mm × 15 mm × 1 mm. They were polished and cleaned by acetone and methanol before they were installed in the vacuum chamber. The base pressure of the chamber during experiments was maintained 3 to 4×10^{-9} torr (1 torr = 133.322 Pa). The XPS spectra of La 3d, Ba 3d, F 1s, O 1s and Zr 3d were measured and recorded by a Perkin–Elmer 560 surface analysis system. The AlK_α, operated at 300 W, was used as the X-ray source, and the passing energy of 25 eV was used to provide 0.5 eV resolution. Most surface charging during the experiment was eliminated by use of a low-energy electron gun as a neutralizer. The values of element binding energy, and drifting due to the surface-charging effect, were calibrated by the use of the C 1s reference at 284.6 eV [10]. The binding energy of the elements was determined at the centre of the corresponding XPS peaks after the deconvolution of the spectrum. The experimental

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uncertainty of the XPS binding energy was about ± 0.10 eV.

3. Results and discussion

All of the XPS spectra of the elements recorded for glasses $62ZrF_4$–$(30 - x)BaF_2$–$8LaF_3$–$xBaO$ were deconvoluted by using a curve-fitting software which is similar to that reported by Nelson [11]. There were no split peaks or shoulders observed in the XPS peaks of F 1s, La $3d_{5/2}$ and Ba $3d_{5/2}$, although the binding energy shifts were found. However, line-shape changes relative to the XPS spectra for O 1s and Zr $3d_{5/2}$ were observed.

3.1. The XPS spectra of F 1s

As reported by Almeida *et al.* [8], no splitting nor shoulder peaks were found in the XPS spectra of F 1s in the present work, although the presence of the two types of fluorine atom has been proposed in fluoride glasses [8, 12, 13]. Fig. 1 shows the dependence of binding energy of F 1s on the concentration of BaO. It was observed that the binding energy of F 1s decreased with the increase of the BaO content in the glass. This indicates that the fluoride ions are surrounded by more active metal cations, i.e. La^{3+} and Ba^{2+}, with the addition of barium oxide. From this, it was suggested that some fluorine atoms playing bridging roles in the glass are replaced by oxygen, to form non-bridging fluorine ions, and bond to La^{3+} and Ba^{2+} cations. This result can be easily understood in the view of the ionicity of the M–F bond (here M = Ba, La and Zr). According to the calculation of ionicity of M–F bonds for fluoride glasses [14], the ionicities of Ba–F, La–F and Zr–F bonds are 98%, 95% and 85%, respectively. That is, the negative charge of the fluoride ions surrounded by La^{3+} and Ba^{2+} ions is approximately 10%–13% more than that of fluoride ions surrounded by Zr^{4+} ions. So, the binding energy of F 1s related to the fluorine surrounded by La^{3+} or Ba^{2+} ions is lower than that of F 1s associated with the fluorine surrounded by Zr^{4+} ions. Although, theoretically, there is a difference in the effective charge between the fluorine bonded to La^{3+} or Ba^{2+} ions and Zr^{4+} ions, the difference is not large enough to create a new XPS line, and all that can be observed is the binding energy of F 1s as a whole becoming lower as more bridging fluorines are replaced by oxide ions.

3.2. The spectra of O 1s

It was observed that the XPS peaks of O 1s are obviously asymmetrical and can be deconvoluted into two peaks. The deconvolution of O 1s photoelectron lines is summarized in Table I. By comparing the deconvoluted XPS spectra of O 1s with the standard ones [15] of oxygen in metal oxide and in metal hydroxide, it is easy to assign the XPS peaks with higher binding energy to the oxygen in OH, which results from the H_2O absorption and hydrolysis of the glass surface, and to attribute the peaks with a lower binding energy to the oxygen surrounded by cations. From Table I, it can be observed that the binding energy of O 1s associated with the oxygen in hydroxides remains the same within the limit of experimental uncertainty. Fig. 2 shows the binding energy of O 1s related to the oxide ions as a function of the concentration of BaO in the glass. In this, we can see that the binding energy of oxide ions increases with the concentration of BaO in the glass. Like fluoride ions, the effective negative charge on the oxide ions bonded to Zr^{4+} cations is

TABLE I The deconvolution of O 1s photoelectron lines

Concentration of BaO, x (mol %)	Binding energy (eV)		Fraction of oxygen in M–O (%)
	"M–OH line"	"M–O line"	
0	531.52	–	–
0.5	531.60	530.14	36.0
1	531.49	530.24	44.5
2	531.60	530.37	50.3
3	531.57	530.43	54.6
4	531.54	530.48	59.5
5	531.56	530.44	63.9

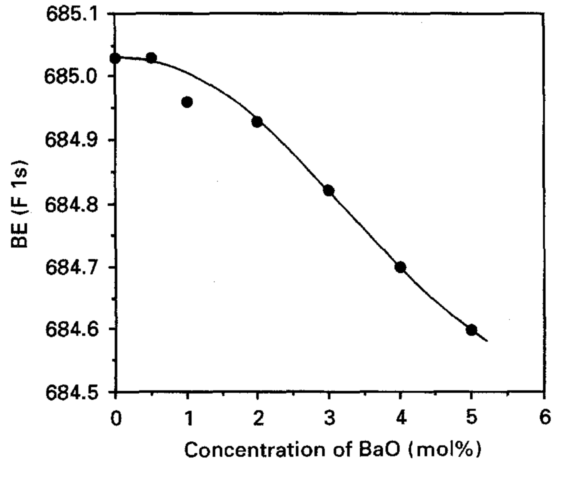

Figure 1 The binding energy (BE) of F 1s as a function of the concentration of BaO.

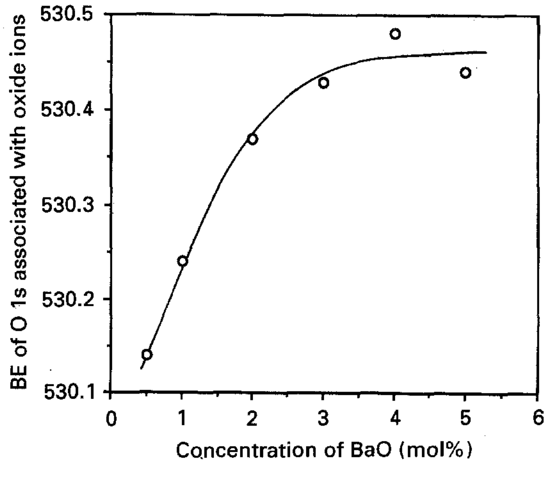

Figure 2 The binding energy of O 1s related to the oxide ions as a function of the concentration of BaO.

less than that of oxide ions bonded to La^{3+} or Ba^{2+} cations, so that the binding energy of oxide ions bonded to Zr^{4+} cations is larger than that of oxide ions bonded to La^{3+} or Ba^{2+} cations. According to this and the data listed in Table I, it can be inferred that the oxide ions added to the glass mainly bond to Zr^{4+} cations.

3.3. The XPS spectra of Zr 3d

It was observed that the Zr 3d peaks ($3d_{3/2}$ and $3d_{5/2}$) recorded for all the samples have broadened towards lower binding energy compared with standard ones [16]. This is due to the formation of new zirconium species in the glass structure. All of the Zr 3d spectra were deconvoluted in an attempt to identify the new zirconium species responsible for the Zr 3d peak broadening (as an example, Fig. 3 shows a deconvoluted Zr 3d spectra for glass: $62ZrF_4$–$27BaF_2$–$8LaF_3$–3BaO). The deconvolution was accomplished using a computer algorithm which varied the relative intensity and energy of two identical Zr 3d spectra until a "best fit" to the experimental data was obtained. During the fitting, the same intensity ratio of two corresponding lines was maintained, i.e. $I(\mathrm{Zr}\,3d_{3/2}$ for "$[ZrF_n]$ line"$)/I(\mathrm{Zr}\,3d_{3/2}$ for "$[ZrF_uO_v]$ line"$) = I(\mathrm{Zr}\,3d_{5/2}$ for "$[ZrF_n]$ line"$)/I(\mathrm{Zr}\,3d_{5/2}$ for "$[ZrF_uO_v]$ line"$)$, but no constraint was placed on the energies of the two lines. The results are summarized in Table II. It is to be emphasized that all of the Zr $3d_{5/2}$ spectra can be fitted to the sum of two lines – one at 184.22 ± 0.08 eV and the other at 182.79 ± 0.09 eV. By comparing line shapes of deconvoluted XPS spectra of Zr 3d with the standard ones of ZrF_4 and ZrO_2, we attributed these two zirconium species to zirconium fluoride ($[ZrF_n]$) and zirconium oxyfluoride ($[ZrF_uO_v]$), respectively. These results are consistent with those reported by Pantano and Brow [16]. All the above results strongly indicate that the F–Zr–O bonds are formed with the addition of oxide ions to the glass structure. From the Table II, it can be seen that a new zirconium species associated with zirconium oxyfluoride, already exists in the glass surface, even before the addition of barium oxide. If the XPS spectra of O 1s are taken into consideration, the second zirconium species can be attributed to the $[ZrF_u(OH)_v]$. Because the Zr–O and Zr–OH bonds have approximately the same chemical characteristic, the zirconium in both bonds has the same XPS spectrum.

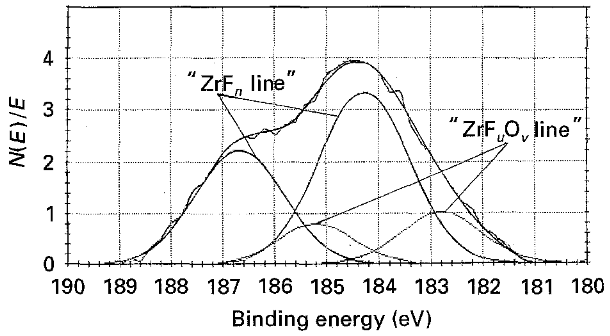

Figure 3 Deconvoluted XPS spectrum of Zr 3d for glass $62ZrF_4$–$27BaF_2$–$8LaF_3$–3BaO.

TABLE II The deconvolution of Zr 3d photoelectron lines

Concentration of BaO (mol %)	Binding energy (eV)		Fraction of $[ZrF_uO_v]$ (%)
	"$[ZrF_n]$ line"	"$[ZrF_uO_v]$ line"	
0	184.23	182.81	10.4
0.5	184.21	182.74	14.1
1	184.28	182.84	17.1
2	184.22	182.78	18.9
3	184.14	182.68	21.8
4	184.31	182.92	23.0
5	184.16	182.77	26.3

3.4. The XPS spectra of La 3d and Ba 3d

As shown in Figs 4 and 5, the binding energies of Ba $3d_{5/2}$ and La $3d_{5/2}$ remain unchanged when the concentration of BaO in the glass is less than 1 mol %, and decrease with increase of barium oxide after the BaO content in the glass exceeded 1 mol %. No split

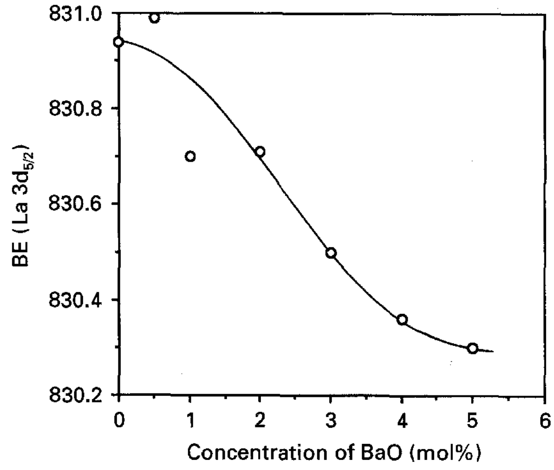

Figure 4 The binding energy of La $3d_{5/2}$ as a function of concentration of BaO in the glass.

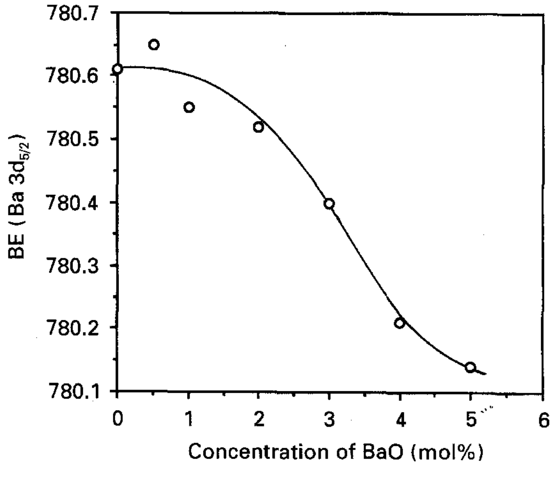

Figure 5 The binding energy of Ba $3d_{5/2}$ as a function of concentration of BaO in the glass.

nor shoulder peaks were observed. This seems to indicate that oxygen participated in the coordination with the La^{3+} and Ba^{2+} cations, in other words, some fluorine in the polyhedra $[LaF_n]$ and $[BaF_m]$ were replaced by oxygen to form $[LaF_{n-x}O_x]$ and $[BaF_{m-y}O_y]$. Because the electronegativity of oxygen is less than that of fluorine, the ionicities of La–O and Ba–O bonds are less than those of La–F and Ba–F bonds. Hence the effective charges on the lanthanum and barium will decrease with their ligand polyhedra changing from $[MF_n]$ to $[MF_{n-x}O_x]$, so their binding energies decrease. Theoretically, the change in chemical environment of an element will create new XPS lines in its XPS spectrum. In the case of La^{3+} and Ba^{2+} cations, $[MF_n]$ could not be distinguished from $[MF_{n-x}O_x]$ in their XPS spectra. These results are not unexpected because of the strong electronegativity of both F^- and O^{2-} and the very active metal characteristic of both La^{3+} and Ba^{2+} cations, as well as a small ratio of O/F. In other words, the change in binding energy associated with the effective charge difference between La^{3+} or Ba^{2+} in $[MF_n]$ and $[MF_{n-x}O_x]$, is not large enough to create a new XPS line and all that can be observed is the binding energies of Ba $3d_{5/2}$ and La $3d_{5/2}$ as a whole becoming lower as more fluorine in $[MF_n]$ is replaced by oxygen.

4. Conclusion

From the experimental results and the discussion above, it can be proposed that the oxide ions added to the glass mainly bond to Zr^{4+} and replace the bridging fluoride ions, resulting in the formation of an F–Zr–O bond. However, from the dependence of binding energies of Ba $3d_{5/2}$ and La $3d_{5/2}$ on the concentration of barium oxide in the glass, it can be concluded that the oxide ions added to the glass structure mainly play a non-bridging role instead of a bridging role in the glass structure. That is, the introduction of oxide ions to the fluorozirconate glasses results in a decrease in the degree of structural polymerization. Perhaps this is why only a small amount of oxides can be incorporated into the fluorozirconate glasses and the crystallization can easily take place with the addition of oxide dopant.

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