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Study of fluorine losses in oxyfluoride glasses

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Abstract

Glasses in $PbGeO_3$–PbF_2–CdF_2 and GeO_2–PbO–PbF_2–CdF_2 systems were studied and the fluorine losses during synthesis were investigated. Samples were characterized by differential scanning calorimetry (DSC), X-ray diffraction, Fourier transform infrared spectroscopy (FTIR) and Raman scattering spectroscopy. The use of stoichiometric germanate glass, $PbGeO_3$, instead of introducing individual oxides (GeO_2 + PbO) lead to decreasing fluorine losses, as detected by a fluorine ion selective electrode. The main structural features obtained from vibrational spectroscopy could be described by a metagermanate basic structure permeating fluorine rich regions.

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1. Introduction

GeO_2 and SiO_2 based glasses provide the reference models for most oxide glasses with the non-periodic association of $[MO_4]$ tetrahedral units ($M = Si, Ge$) giving a simple and clear picture for the vitreous network. In multicomponent glasses, large cations are accommodated in this network, which enhances disordering and decreases the connectivity and the overall strength of the network [1].

The addition of fluoride ions has been observed to lower melting temperatures, to contribute to the elimination OH^- groups, to decrease refractive index and to provide fluorine ion conductivity in silica and germanate glasses [2–4]. From a structural point of view, network connectivity decreases as fluoride anions can be considered mainly as non-bridging [2]. However, it may also lead to silicon/germanium loss through formation of gaseous metallic fluorides [5–7]. Moreover, fluorides may act as nucleating agents promoting melt crystallization and leading to less stable glasses [8].

From the point of view of optical applications very interesting materials have been proposed in the last decade involving oxyfluoride mixed systems. Wang and Ohwaki proposed a mixed lead fluorogermanate glass from which a glass ceramic could be obtained displaying transparency comparable to the mother glass [9]. Tick and co-workers extended the work to some SiO_2–Al_2O_3 based compositions [10] and, during the last several years, different authors have been working with somewhat related rare-earth-doped systems [11–21]. In all these papers, the exceptional optical properties of these new composite materials have been evaluated where the rare-earth containing β-PbF_2 crystalline phase is often obtained at the nanometric scale. Tick and co-workers have prepared optical fibers from these materials and were able to evaluate and discuss their transparency properties according to current theories [19].

As mentioned above, fluorine loss may occur in the preparation procedure and that is, in fact, a serious

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drawback in working with these mixed systems. Stoichiometry and therefore, physical and chemical properties are hardly reproducible. Concerning germanate based systems some authors [6,22,23] studying binary fluorogermanate systems (GeO_2–RF_x), have identified that different germanium fluorides evaporate (GeF, GeF_2 and GeF_4). Shelby and Bolden [6] have shown drastic changes for such parameters such as glass transition temperature (T_g), density, and ionic conductivity as a function of melting time in the GeO_2–PbO–PbF_2 system. As proposed in [22,23] a decrease in the fluorine loss rate could be achieved by using different precursors where Ge atoms would be present in polymerized structures like metagermanates and tetragermanates.

We have been studying glasses in the system $PbGeO_3$–PbF_2–CdF_2 [3,4,14] and in this work, we present some results concerning the utilization of lead metagermanate ($PbGeO_3$), instead of PbO + GeO_2 in the starting batch for the preparations of glasses. We show that by the simple procedure proposed in [22,23] fluorine loss can be reduced.

2. Experimental procedure

High purity PbF_2 (99.99% Aldrich), CdF_2 (99.99% Aldrich), GeO_2, PbO and glassy $PbGeO_3$ (prepared from PbO and GeO_2) have been used. The reagents were mixed in agate mortar using *n*-heptane as homogenizing medium for approximately 20 min. The powders were melted in open Pt–Au crucibles at 800 °C and quenched at room temperature between two copper plates. Different melting times ranging from 5 to 30 min have been used for selected compositions aiming the observation of fluorine loss.

The fluoride ion selective electrode was used to obtain the fluorine contents in the glass samples. The samples were dissolved in diluted HNO_3 and stored in polyethylene flasks (50 mL). A TISAB III (total ionic strength adjustment buffer) solution was used in order to adjust ionic strength and minimize the undesirable fluoride coordinating ability of some contaminant agents [24]. The TISAB III solution was prepared with 57 mL of glacial acetic acid (Merck P.A.), 58.0 g of sodium chloride (Merck P.A.) and 4.0 g of *trans*-1,2-diaminocyclohexane–*N*,*N*,*N*′,*N*′-tetra-acetic acid (CDTA) in 500 mL of distilled water under constant agitation. pH was adjusted to 5.3–5.5 with NaOH 6 mol L^{-1} and the volume was completed to 1 L. The solution was stored in polyethylene flasks in refrigerator. Calibration curves were obtained with standard PbF_2–CdF_2 solutions prepared from the dissolution of fluorides in acidic solution (HNO_3). Potenciometric measurements were performed with a fluoride ion selective electrode and a reference electrode (saturated calomel electrode). Measurements were made after immersing the electrodes in approximately 50 mL of solution in a 100 mL beaker, swirling the solution for 5 s, then leaving to stand for 20 s. Each millivolt (mV) measurement was the average of ten readings taken at 1 s intervals. The electrodes were rinsed with a jet of de-ionized water, then soaked in a beaker of water for 20 s, then dabbed dry with a low-lint tissue between each measurement. Thermal analysis (differential scanning calorimetry-TA Instruments-mod 3100) were performed for powdered samples in a cover aluminum pans with heating rates of 10 °C/min. Infrared absorption spectra were obtained using a PERKIN ELMER 2000 SERIES FTIR. Pellets made from powdered samples and KBr were used and spectra have been obtained in the range from 2000 to 400 cm^{-1}. Raman scattering were obtained with Renishaw Micro-Raman apparatus from powdered samples with He–Ne laser excitation (6345 Å). X-ray powder diffractograms were obtained with a D-5000 Siemens diffractometer with the Cu K_α filtered line at 0.02°/s scanning rate.

3. Results

Table 1 shows the result for fluorine ions concentration in samples obtained by melting at 800 °C for 30 min. Results are shown for samples prepared from glassy $PbGeO_3$ and the same compositions prepared from PbO + GeO_2.

Although fluorine losses have been in fact observed for all samples, the results clearly show that the utilization of $PbGeO_3$ instead of PbO + GeO_2 leads to improved fluorine retention in the final material. That observation is in agreement with literature proposals [22,23]. Fig. 1 shows the results for fluorine retention as a function of samples

Table 1
Results obtained from fluorine analyses on oxyfluoride glasses melted at 800 °C for 30 min

Samples (molar %)	Theoretical molar of [*F*] (×10^{-3})	Experimental molar of [*F*] (×10^{-3}) (±3%)	%*F* kept I: sample after melting
$60PbGeO_3$–$40PbF_2$	2.00	1.70	85
$30GeO_2$–30PbO–$40PbF_2$	2.00	1.40	70
$60PbGeO_3$–$30PbF_2$–$10CdF_2$	2.00	1.56	78
$30GeO_2$–30PbO–$30PbF_2$–$10CdF_2$	2.00	0.90	45
$60PbGeO_3$–$20PbF_2$–$20CdF_2$	2.00	1.44	72
$30GeO_2$–30PbO–$20PbF_2$–$20CdF_2$	2.00	1.00	50
$60PbGeO_3$–$10PbF_2$–$30CdF_2$	2.00	1.44	72
$30GeO_2$–30PbO–$10PbF_2$–$30CdF_2$	2.00	1.12	56
$60PbGeO_3$–$40CdF_2$	2.00	1.70	87
$30GeO_2$–30PbO–$40CdF_2$	2.00	1.46	73