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Silica doped bismuth lead oxyfluoride glass ionic conductors

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ABSTRACT

Doping of bismuth lead oxyfluorides by silica (30 at.%) makes it possible to stabilize a large vitreous domain. The presented study relates to the stability of the vitreous phase and the variation of conductivity versus temperature, as well as composition. DTA heating analyses evidenced the temperature of vitreous transition followed by the material recrystallization. The crystallized phase was identified by high temperature Guinier Lenné pattern. The best conductivity, about 3×10^{-3} Scm^{-1} at 220 °C, was obtained for the fluorine richest material.

1. Introduction

Many works were published on O^{2-} anion conductors, with good conductivities at 500–600 °C [1–5]. Oxyfluorides, F^- ion conductors, have the same level of performance around 300 °C [6]. Previous studies on ionic conductivity in bismuth oxyfluoride crystallized derivatives have shown the interest of these phases as fluorine conductors with good σ values at low temperatures [7,8]. Effectively, σ range is about 10^{-2}–10^{-3} Scm^{-1} at 200 °C. The best σ values have been reached for a large domain of hexagonal phase noted H and located in the middle of the Bi_2O_3–PbO–PbF_2 diagram.

After this work, the substitution of PbO by CdO has allowed to evidence a vitreous domain in the Bi_2O_3–CdO–PbF_2 system [9,10]. The glasses also present attractive performances ($\sigma=5\times10^{-4}$ Scm^{-1} at 200 °C for $Bi_{0.4}Cd_{0.8}Pb_{0.8}O_{1.4}F_{1.6}$). In this diagram, two synthesis types have been used: the first one in gold sealed tubes with a synthesis time of several hours in a horizontal furnace, the second very fast one, in silica tubes as described for the PbO–PbF_2 system [11]. The second method has allowed to extend the vitreous domain by introduction of SiO_2 in the basis system. The interest of this work has been to obtain glasses with good anionic conductivity when many studies on glasses have shown cationic conductivities [12].

Other tests [13] have been carried out in the Bi_2O_3–PbO–PbF_2 and Bi_2O_3–PbO–CdF_2 systems by using the method of synthesis described by Govinda Rao et al. [11]; they proved to be good fluoride conductors ($\sigma_{200\,°C}=4\times10^{-3}$ Scm^{-1}) but the SiO_2 content was not controlled by this method. So, it has been necessary to find another synthesis method.

An interesting work has been related by Goldammer et al. [14]. Effectively, they have introduced SiO_2 in the mixture PbO–PbF_2 and they have found glasses in the system SiO_2–PbO–PbF_2 with fluoride conductivity.

In conclusion, complete studies have been realized on crystallized bismuth lead oxyfluorides and on vitreous bismuth lead cadmium oxyfluorides; for the two diagrams, the synthesis has been realized in gold tubes. The conductivity is good and is due to fluorine ion. Effectively, σ fluctuates from 5×10^{-4} to10^{-2} Scm^{-1} at 200 °C. Another type of synthesis in silica tube has allowed to evidence vitreous lead bismuth oxyfluorides, the compound formulation including also silica from the tube. Some conductivity tests have shown good σ values ($\sigma=4\times10^{-3}$ Scm^{-1} at 200 °C) but the silica concentration was not known.

As a result, we have estimated that it would be attractive to complete this study by using another synthesis. We have doped the bismuth lead oxyfluorides with a constant silica concentration. We used sealed tubes, so the composition is well known. DTA and high temperature X-ray diffraction have been performed before running the conductivity experiments. Finally, the conductivity was compared with those of the literature.

2. Experimental

The materials were prepared starting from the reagents Bi_2O_3, PbO, PbF_2 and SiO_2. Bi_2O_3 and PbO were first heated at 600 °C. For each investigated composition, the mixture of the reagents in the molar

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Table 1
Molar concentrations of glasses and their treatment temperatures.

Glass number	$BiO_{1.5}$	PbO	PbF_2	SiO_2	Treatment temperature (°C)
1	0.461	0.250	0.058	0.231	700
2		0.185	0.123		
3		0.154	0.154		
4	0.308	0.369	0.092		725
5		0.277	0.185		
6		0.231	0.231		
7	0.154	0.492	0.123		700
8		0.369	0.246		
9		0.308	0.308		

proportions (approximately 1 g) was achieved by weighing, and then intimately crushed out in an agate mortar. The doping concentration (30 at.%), determined from some preliminary glass preparations, resulted in a final $30/(100+30)=0.231$ Si atom concentration within the samples; besides this common value, Table 1 gathers the bismuth and lead atom concentrations of the various prepared mixtures. The synthesis is made in a gold tube. Each tube (5 mm in diameter and 40–50 mm in length) is initially sealed at one end to form its bottom, before introducing the mixture. Then it is closed at its upper end by pinching and folding. Thus, it is weighed and introduced into a welded silica tube. The sizes of the silica tube are: 10 mm in diameter and approximately 150 mm in length. After reducing the pressure, each silica tube is sealed with the gas–oxygen blowtorch with a length of approximately 100 mm.

The tubes are introduced per series of mixtures corresponding to a given bismuth oxide concentration, into a vertical furnace, which has been heated to a determined temperature, for reaction and fusion of the mixtures. After 15 min reaction, they are soaked with water. After opening each silica tube, each gold tube is weighed in order to make sure that there is no weight loss. Successive tests and failures thus led us to retain the temperatures of treatments described in Table 1.

The gold tubes are opened with a cutter and then unrolled in order to extract, without deterioration, each massive material of cylindrical form obtained after fusion. According to the type of study carried out then, the material is crushed (diffraction of X-rays; thermal study by DTA) or surfaced to obtain cylindrical samples for conductivity measurements.

T_g (vitreous transition temperature) and T_c (recrystallization temperature) have been determined by D.T.A. using a heating rate of 10 °C/mn (92-1600 Setaram analyzer), under air gas flow. Loss weight has been simultaneously studied.

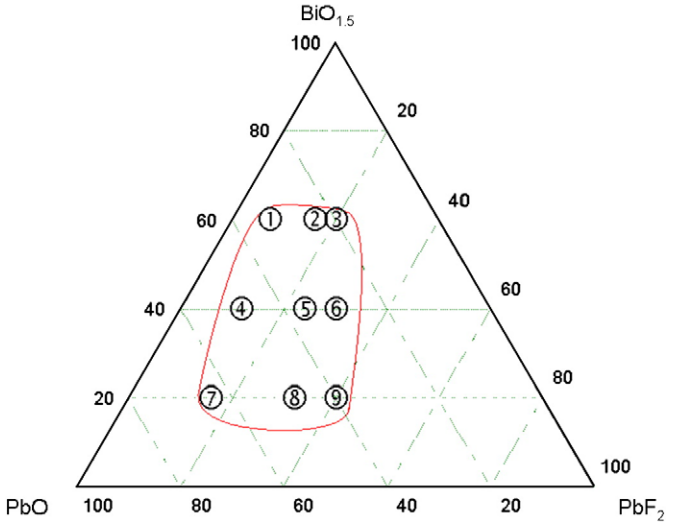

Fig. 1. Oxyfluoride glass domain for Bi–Pb–Si mixtures with 23.1% Si cationic concentration.

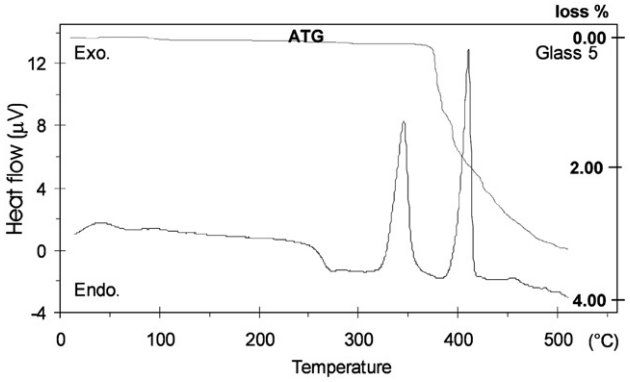

Fig. 2. DTA and TGA of glass 5 ($=Bi_{0.308}Pb_{0.461}Si_{0.231}O_{1.201}F_{0.370}$).

The structure type of the recrystallized phase and the stability in air of the different phases have been examined by high temperature X-ray diffraction using a Guinier Lenné camera under static air.

Conductivity measurements have been performed on polished blocks using the impedance spectroscopy with a Schlumberger frequency response analyzer (type Solartron SI 1255), gold electrodes have been deposited on each sample face by sputtering. All the measurements were performed under air atmosphere in the temperature range of 100–(T_g-10) °C.

3. Results and discussion

3.1. Synthesis–Phase limits — Characterizations

Fig. 1 shows the limits of the vitreous domain. The numbers correspond to sample compositions previously described in Table 1. The vitreous domain is logically nearer PbO–$BiO_{1.5}$ binary than the H phase located in the Bi_2O_3–PbO–PbF_2 diagram line and synthesized in gold tubes [7,8]. Our synthesis conditions have not allowed to obtain glasses on the PbO–PbF_2 line.

Thermal analysis of each sample has shown three sample modifications. As an example, we present (Fig. 2) the DTA curve corresponding to a central position within the evidenced glass domain. The first modification is revealed by an endothermal shift at 240 °C for $Bi_{0.308}Pb_{0.461}Si_{0.231}O_{1.201}F_{0.370}$, in the DTA curve, characteristic of the vitreous transition (T_g). The existence of this transition proves that the phase is vitreous. The second modification is evidenced by an exothermal peak characteristic of the glass recrystallization ($T_c=320$ °C). The exothermal peak with onset at 385 °C corresponds to the phase decomposition. The T.G. analysis put in evidence that this temperature corresponded to the beginning of the fluorine loss (Fig. 2).

Table 2 summarizes T_g and T_c for the studied glasses. It is not evident to conclude on these values because they strongly depend on the speed of the quench. So, T_g decreases when the Fluorine concentration increases. Govinda Rao et al. have observed the same phenomena for the glasses based on PbO and PbF_2 [11].

Table 2
T_g and T_c for the studied glasses.

Glass number	Composition	T_g (°C)	T_c (°C)
1	$Bi_{0.461}Pb_{0.308}Si_{0.231}O_{1.4035}F_{0.116}$	270	374
2	$Bi_{0.461}Pb_{0.308}Si_{0.231}O_{1.3385}F_{0.246}$	258	320
3	$Bi_{0.461}Pb_{0.308}Si_{0.231}O_{1.3075}F_{0.308}$	250	320
4	$Bi_{0.308}Pb_{0.461}Si_{0.231}O_{1.293}F_{0.184}$	260	350
5	$Bi_{0.308}Pb_{0.461}Si_{0.231}O_{1.201}F_{0.370}$	240	320
6	$Bi_{0.308}Pb_{0.461}Si_{0.231}O_{1.155}F_{0.461}$	258	320
7	$Bi_{0.154}Pb_{0.615}Si_{0.231}O_{1.185}F_{0.246}$	260	325
8	$Bi_{0.154}Pb_{0.615}Si_{0.231}O_{1.062}F_{0.492}$	228	324
9	$Bi_{0.154}Pb_{0.615}Si_{0.231}O_{1.001}F_{0.616}$	214	320