CHLORINE EVOLUTION DURING THE FUSION OF CHLOROFLUOROINDATE GLASSES

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Samples with a composition of $40InF_3–20ZnF_2–5MCl–xBaF_2–ySrF_2$, where M=Na, Li and $x+y$=35 mol%, were prepared. The thermal properties related to the Ba/Sr ratio and to the remaining chlorine content in the glasses were studied. Thermal stability is improved with the addition of chlorine. However, chlorine concentration is regulated by the sublimation of indium fluorides which takes place at about 600°C. Indium fluorides are formed during glass fusion. The mechanisms of chlorine sublimation were studied.

Keywords: fusion process, intermediate reactions, sublimated compounds

Introduction

Fluoride glasses have been studied since the middle of the seventies because of their potential application in optical telecommunications [1, 2]. The special spectroscopic properties of fluoride glasses, such as low refraction index, extended optical transmission window and high lifetime in the excited states of rare earth ions in fluoride host, are determined by the specific characteristics of fluorine ion, such as high electronegativity, low polarizability, weak metal–fluor ionic bonding and small metal–fluor distances. Due to the extended transparency in the IR range, fluoride glass fibers present lower theoretical optical losses compared to the silica fibers [3]. So the first proposed application of the fluoride glass fibers was as long-haul telecommunication fibers. Unfortunately, the promised ultra-low-loss level for fluoride fiber has never been achieved experimentally, mainly due to the fusion preparation method, where the required high purity level for optical fibers was not produced. Besides their application as passive optical fibers, fluoride glasses can also be used in active optical devices. In comparison with silica glasses, they are better hosts for rare earth ions, which are responsible for the luminescent emission, since the low phonon energy of fluoride glasses admits longer lifetimes in metastable state. Fluoride glasses allow very broad range of lasing wavelengths: it covers the 0.35–3.5 µm interval, whereas silica glasses lase in the region of 0.6–2 µm [4]. So, fluoride glasses are excellent for optical fiber lasers and optical fiber amplifiers [5–8], replacing electronic regenerators in optical telecommunication, as well as in special devices which convert infrared beam to visible light [9–15]. Lasing effect occurs at many different wavelengths for rare earth doped fluoride glasses, including the three telecommunications windows at 0.8, 1.3 and 1.55 µm, depending on the rare earth doping [16–19]. The challenge is to enhance lasing efficiency, which can be achieved either by obtaining better fluoride glass compositions or by using alternative preparation methods, such as sol–gel [20] to provide samples with better purity and homogeneity. The present paper reports about glasses in chlorofluoroindate system. The addition of chlorides to fluoride glasses extended the infrared transmission up to 10 µm [19], reducing rare earth emission losses and focuses attention to this mixed-halide system [5, 21–24]. The chlorine content influences the physical and optical glass characteristics, but upon fusion sublimation takes place, where the evolved compound is reported as $InCl_3$ [25]. Further researches indicated that the quantity of the remaining chlorine depended on the sample composition [26]. The aim of the present work is to study the process of fusion, to determine the sublimation temperatures, the composition of the sublimated compounds, the influence of the remaining chlorine on the glass samples and the thermal characteristics of the obtained glasses.

Materials and methods

Samples with the following composition $40InF_3$ $–20ZnF_2–5MCl–xBaF_2–ySrF_2$, where M=Na, Li and $x+y$=35 mol%, have been prepared. The initial compounds were BaF_2, InF_3 and SrF_2 Fluortran-grade (fiber

optic grade), from BDH-Merck, ZnF_2 – 99% purity – from Aldrich, NaCl and LiCl – 99% purity – from Synth and In_2O_3 – 99% purity – from Merck. Indium oxide was fluorinated in air with the excess of ammonium bifluoride, at 380°C for 30 min in a Pt crucible, according to the following reaction:

$$In_2O_3+6NH_4F{\cdot}HF{\rightarrow}2InF_3+6NH_4F+3H_2O \quad (1)$$

After then, this material was submitted to another heat treatment for 30 min at 500°C, to eliminate reaction residues.

Two different series of samples were prepared, as it can be seen in the Table 1.

For series A five batches with various BaF_2/SrF_2 ratios, without NaCl and with fluorinated In_2O_3 were treated at 900°C for 90 min in air in Pt crucible. The batches were cooled down spontaneously out of the furnace and then were milled. Each composition was divided into two parts. A first part of them was melted again at 850°C for 30 min in dry box under N_2, with the addition of NaCl in the last 3 min of the experiment, in order to reduce chlorine sublimation (series A-remelted). In case of the other part, NaCl was just added without any further heating (series A-powder). For series A-powder combined thermogravimetry – FTIR spectroscopy was done using a Netzsch TG-209 coupled to a Bruker FTIR-Vector 22 FTIR apparatus, to follow the reactions that occurred during the fusion of glass. The applied experimental conditions were: dynamic nitrogen atmosphere and 10 K min^{-1} heating rate up to 900°C. The effect of chlorine inclusion, the intermediate reactions and the sublimation could be followed at any temperature.

FTIR was performed on the A1-remelted sample and on A1-powder.

The glasses of series B were prepared with similar compositions, containing LiCl, however commercial InF_3 was used to avoid the N–H residues of the fluorination process. Since the interest was on chlorine sublimation, quantification of remaining chloride ions on these glasses has been performed. The batches were melted at 850°C for 30 min in Pt crucible, in a dry box under N_2 atmosphere. LiCl was also added in the last 3 min of the experiment. Samples were poured in brass mold and annealed at 240°C. Glass transition temperatures were determined using a Shimadzu DSC-50 equipment. Quanti-

fication of remaining chloride ions of these glass samples was performed by using of ion selective electrode.

Results

Infrared spectra of A1 samples (A1-powder and A1-remelted sample) containing 5% of NaCl, 10% of BaF_2 and 25% of SrF_2 are presented in Fig. 1.
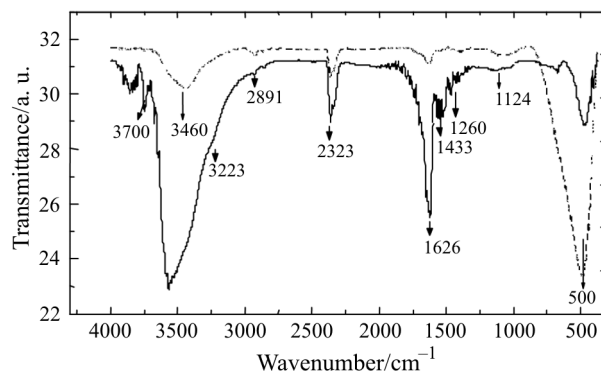

Fig. 1 Infrared spectra of samples containing 5% NaCl, 10% BaF_2 and 25% SrF_2; — – A1-powder (without any heat treatment) and --- – A1-remelted sample

The same absorption frequencies, with different relative intensities were observed in both samples. The assignments of bands are listed in Table 2.

The band around 497 cm^{-1}, exhibiting the highest absorption of the sample of the second series, corresponds to $[InF_6]^{3-}$ which belongs to the pre-crystalline structure in the glasses containing indium fluoride [27]. The other lines correspond to O–H and N–H bonds associated to the reaction atmosphere and to the residues of indium fluorination process. These lines were stronger on the A1-powder because the O–H and N–H groups were reduced under the previous heating of the A1-remelted sample. Even after heat treatments at 500°C for 30 min and at 850°C for 30 min small amount of ammonium residue was observed, although its intensity was reduced compared to the In–F absorption line. Consequently, ammonium residue elimination during fluorination by $NH_4F{\cdot}HF$ requires high temperature and time to be completed.

Table 1 Compositions of samples (in mol%) with different contents of BaF_2 and SrF_2. Series A are not glasses *vs.* series B

Sample	InF_3	ZnF_2	BaF_2	SrF_2	NaCl	Sample	InF_3	ZnF_2	BaF_2	SrF_2	LiCl
A1	40	20	10	25	5	B1	40	20	10	25	5
A2	40	20	15	20	5	B2	40	20	15	20	5
A3	40	20	20	15	5	B3	40	20	20	15	5
A4	40	20	25	10	5	B4	40	20	25	10	5
A5	40	20	30	5	5	B5	40	20	30	5	5

Table 2 Absorption frequencies taken from Fig. 1

Absorption/cm^{-1}	Assignment
3100–3600	H_2O band
3223	Characteristic frequency of N–H bond or coupling of H_2O molecules
2891	N–H bond
2323	N–H bond
1626	Amine group or fundamental vibration mode of H_2O
1433	N–H bond
1260	Frequencies of amine vibration
1124	NH_3^+ cations
500	Cluster $[InF_6]^{3-}$

A1-powder, containing 5% NaCl, 10% BaF_2 and 25% SrF_2 (series A) was studied by simultaneous TG-FTIR, in order to follow the reaction mechanism of chlorine inclusion and sublimation. The corresponding three-dimensional FTIR spectrum can be seen in Fig. 2. FTIR patterns for all other samples are practically identical to this one.
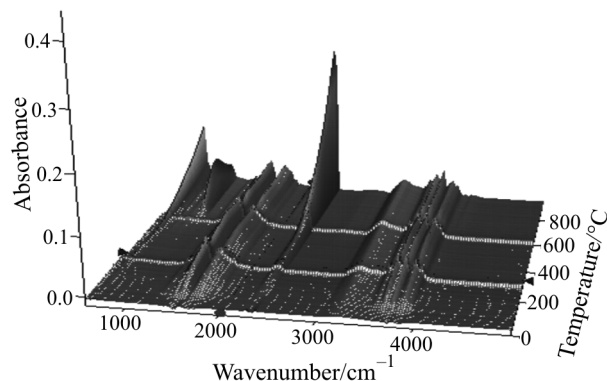
Fig. 2 FTIR spectra of gases evolved from A1-powder sample containing 5% NaCl, 10% BaF_2 and 25% SrF_2 (without any heat treatment)

The absorption band around 500 cm^{-1} corresponds to In–F bonding. Its presence above 600°C is unusual, since InF_3 melts at 1170°C. Consequently, the outcoming gas with In–F bonding should be an indium fluorochloride compound e.g. InF_2Cl, or a mixed metal–indium fluorochloride.

TG curves of the A-powder (series A), in which NaCl was just mixed, containing different proportion of BaF_2/SrF_2 are collected in Fig. 3. Mass loss steps can be seen between 100–800°C, in a wide temperature range. However, the numerical mass loss values strongly depend on the BaF_2/SrF_2 ratio. Mass losses started at 400 and at 800°C, for samples containing 10 to 20% BaF_2, and the process has begun approxi-
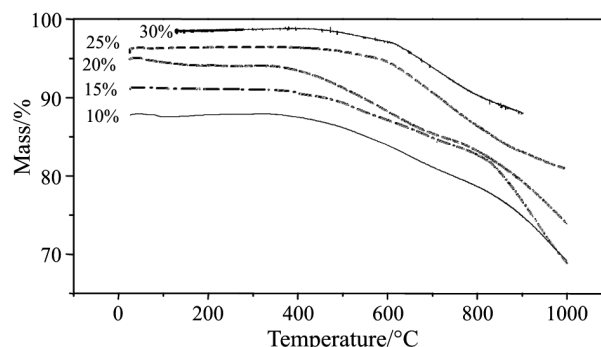
Fig. 3 TG curves of samples containing different amount of BaF_2

mately at 600°C for the ones containing of 25 and 30% BaF_2. The glass composition influences the chlorine sublimation, the elimination of the fluorination residue and the temperature of these events.

The remaining chlorine content of glasses with LiCl (series B) support this observation. Samples containing 5% LiCl were prepared with different amounts of BaF_2/SrF_2. The glass transition temperatures of these glasses are in the 253–263°C temperature range.
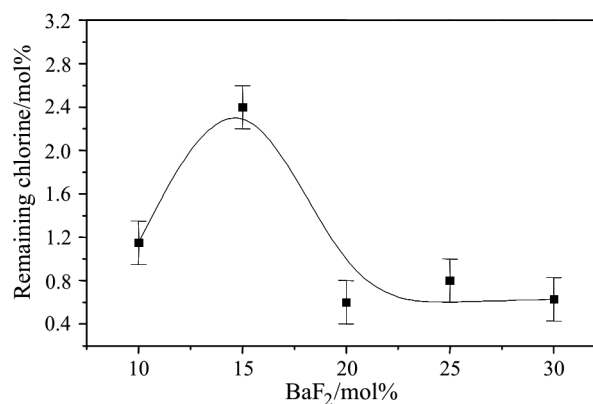
Fig. 4 Remaining chlorine content in glasses containing various quantities of BaF_2 and SrF_2

The chlorine content was determined by using ion selective electrodes. The results are indicated in Fig. 4. The remaining chlorine content corresponding to 15% of BaF_2 is almost three times higher than the chlorine content of sample with 30% BaF_2.

Discussion

The obtained results can be explained by the occurrence of intermediate reactions during heating and fusion, associated to the formation of volatile compounds at the given preparation temperatures. The sublimation of $InCl_3$ has been already reported, however, according to the present results, sublimation of other complex phases can be also observed. IR absorption at 500 cm^{-1} is asso-

ciated to In–F bonding; where indium assumes coordination number 6, suggesting that more complexes than binary gaseous molecules are being produced. The first hypothesis is the formation, for low concentration of NaCl compared to $InCl_3$, of $Na_3InCl_{6-x}F_x$. For $x=0$ the vapor pressure is higher than zero above 290°C, $lg(P/10^5\ Pa)=8.1479-4599/(T/K)$, (where the pressure is in bar and temperature is in Kelvin). Due to the low bonding energy of chlorides the volatility of this compound should be higher. For LiCl glasses Li_3InF_6, with melting temperature of 600°C, and most probably $Li_3InCl_{6-x}F_x$, can be formed during fusion. It was observed that lithium–indium fluorochloride is more volatile than the fluoride. The formation of these compounds depends on the reaction balance in the presence of a medium rich of other metal cations that compete with indium to form intermediate compounds. Another compound, which may have sublimate, is InF_xCl_{3-x} when $x<3$. So far, the amount of indium sublimated is higher than it was predicted when only $InCl_3$ was sublimated. Since different compounds sublimate at different temperatures and with different amounts, the homogeneity of chlorofluoride glass samples must be low, spoiling its optical properties.

Conclusions

Fluorination of oxides using $NH_4F\cdot HF$ is not appropriate to obtain good quality raw material for fluoride glasses with satisfactory optical and thermal properties. Residues of N–H compounds are observed after heat treatment at 500 and even at 850°C, affecting the final quality of the glasses, since they can influence the nucleation that induces crystallization.

TG and FTIR curves showed that chlorofluoride system phases such as $M_3InCl_{6-x}F_x$ and M_3InF_6 where M=Li, Na and InF_xCl_{3-x}, with $x<3$, tend to sublime during glass fusion.

The remaining chlorine content of chlorofluoride glasses depends on the composition and was the highest at 15% of BaF_2 content.

Acknowledgements

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