Journal of Molecular Structure 1001 (2011) 78–82

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc

^{19}F MAS-NMR studies of strontium oxyfluoride aluminosilicate glass

M. Środa [a,*], Z. Olejniczak [b]

[a] AGH – University of Science and Technology, Faculty of Materials Science and Ceramics, al. Mickiewicza 30, 30-059 Kraków, Poland
[b] Institute of Nuclear Physics, Polish Academy of Sciences, Radzikowskiego 152, 31-342 Kraków, Poland

ARTICLE INFO

Article history:
Received 3 March 2011
Received in revised form 16 June 2011
Accepted 17 June 2011
Available online 30 June 2011

Keywords:
Oxyfluoride glass
SrO
^{19}F MAS-NMR
Glass–ceramics
LaF_3
Aluminosilicate glass

ABSTRACT

Local environment of fluorine atoms in the lanthanum oxyfluoride aluminosilicate glasses and glass–ceramics modified by SrO was studied by solid state ^{19}F MAS-NMR spectroscopy and X-ray diffraction. The effect of strontium concentration on the formation of crystalline LaF_3 phase was determined, as a function of heat treatment conditions. In all glasses studied, the F–Me(n) (where Me = Sr, La), but no Na–F species were observed. The presence of F–La,Sr(n) units, in which fluorine is coordinated by both lanthanum and strontium, was detected in the glass with higher content of SrO. Supplementary XRD analysis of this series confirmed that an increase of strontium contents leads to the formation of $Sr_{0.69}La_{0.31}F_{2.31}$ and $LaSr_2F_7$, instead of the pure LaF_3 only.

1. Introduction

Oxyfluoride glasses are intensively studied for their potential applications in optoelectronic devices as low-loss optical fibers [1] and optical amplifier materials [2]. An appropriate heat treatment induces the fluoride crystalline phase in the oxide glassy matrix, generating a low phonon structure for optically active ions, i.e. rare earth elements. The process of cerammization strongly depends on the glass composition, which affects the stability of amorphous structure as well as the type and order of the formed crystals. One of the promising low phonon phase is LaF_3, and its crystallization can be induced in alumino-silicate [3] and boro-silicate glassy matrix [4]. A low phonon phase in the glassy matrix plays a role of the host for optically active lanthanides to increase the efficiency of luminescence. For this structural configuration the probability of non-radiative relaxation of excited states is lower, so that the photon creation is enhanced.

The properties of Sr in the acidic silicate glasses resemble those of its two neighbors in the periodic table, i.e. Ca and Ba. Because of similar effective radius, Sr is sometimes compared with Pb^{2+}, despite their different polarizabilities. In optical glasses, Ca and Ba are often partially replaced by Sr, which leads to lower melting temperature and easier refining [5]. The substitution of CaO by SrO in alumino-silicate glass increases its density and decreases viscosity, owing to its greater polarizability. The effect of strontium substitution for calcium in the SiO_2–Al_2O_3–P_2O_5–CaO–CaF_2 system was investigated by Hill et al. [6]. It was found to induce radio-opacity and affect the thermal stability by modifying the nucleation and crystallization behavior of the glass that is often used for biomedical application. On the other hand, to our knowledge, the effect of strontium on the structure and properties of oxyfluoride aluminosilicate glasses that can be used as a material for transparent glass–ceramic has not been previously studied.

Recently, the influence of alkaline and alkaline earth oxides on the structure of alumino-silicate glasses with LaF_3 was analyzed by DTA, XRD, FT-IR and Raman spectroscopy [7,8]. Their thermal stability, and the formation of crystalline phases were determined. The effect of BaO was studied by the Dajneka group using ^{19}F MAS-NMR method [9]. The modifiers were found to affect the kinetics of the LaF_3 formation during the heat treatment, leading to significant changes in the micro- and nano-morphology of the materials.

The latter studies showed that both the modifiers and aluminum readily coordinate with the F^- ions in the glass structure [10–12]. This may prevent the formation of LaF_3 and/or cause simultaneous formation of new $La_xMe_{x-1}F_y$ phases (where Me is the alkaline earth metal) during cerammization [7,13]. For LaF_3-doped sodium alumina-silicate, the process of cerammization was found to induce the $NaLaF_4$ formation [14,15]. The DTA and FTIR studies showed that the alkaline earth ions (Mg, Ca, Ba) reduced the depolymerization of the oxyfluoride network, contrary to their effect in the pure silicate network [7,8]. In the present work, we use the ^{19}F MAS-NMR spectroscopy to study the effect of SrO on the position of F^- ions in the network and on the formation of LaF_3 during the controlled cerammization process.

---

* Corresponding author.
E-mail address: msroda@agh.edu.pl (M. Środa).

0022-2860/$ - see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.molstruc.2011.06.021

Table 1
Nominal composition of the prepared oxyfluoride aluminosilicate glasses.

Glass no.	Composition (mol%)						$\frac{Al_2O_3}{Na_2O + Na_2F_2 + SrO + 3La_2F_6}$
	SiO_2	Al_2O_3	SrO	Na_2O	Na_2F_2	La_2F_6	
0.4Sr	53.5	15	22.5	3	3	3	0.4
0.6Sr	66	15	10	3	3	3	0.6
0.8Sr	72.25	15	3.75	3	3	3	0.8

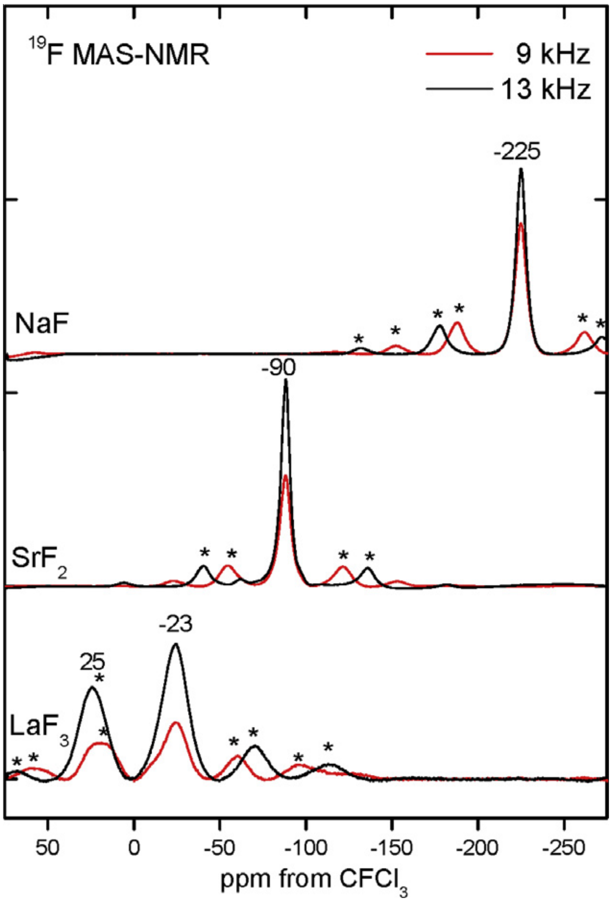

Fig. 1. ^{19}F MAS-NMR spectra of polycrystalline NaF, SrF_2 and LaF_3 at two spinning speeds: 9 and 13 kHz.

2. Experimental

The compositions of glasses studied are listed in the Table 1. They were designed to determine the effect of the charge of the ion modifiers (Na^+, Sr^{2+}, La^{3+}) on the framework structure of the aluminosilicate glass. As the quantitative measure, the ratio: $Al_2O_3/(Na_2O + Na_2F_2 + SrO + 3La_2F_6)$ was chosen, which represents the relation between the content of Al^{3+} ion and the value of positive charge introduced by modifying ions in the glass structure. This ratio was varied from 0.4 to 0.8 by substituting SrO for SiO_2, with the concentration of all other components kept constant. Batches were prepared by mixing appropriate quantities of chemically pure reagents: SiO_2, Al_2O_3, Na_2CO_3, NaF and LaF_3. The mixture in 20 g portions was placed in platinum crucible in an electric furnace and melted at 1450 °C in the air atmosphere. During melting the crucible was covered to minimize the fluorine loss. The molten glass was poured out onto a stainless steel plate forming a layer of ca. 3 mm thickness. The obtained glasses were transparent with a small degree of opalescence for glass with the highest content of SrO (0.4Sr sample), which could be eliminated by faster cooling.

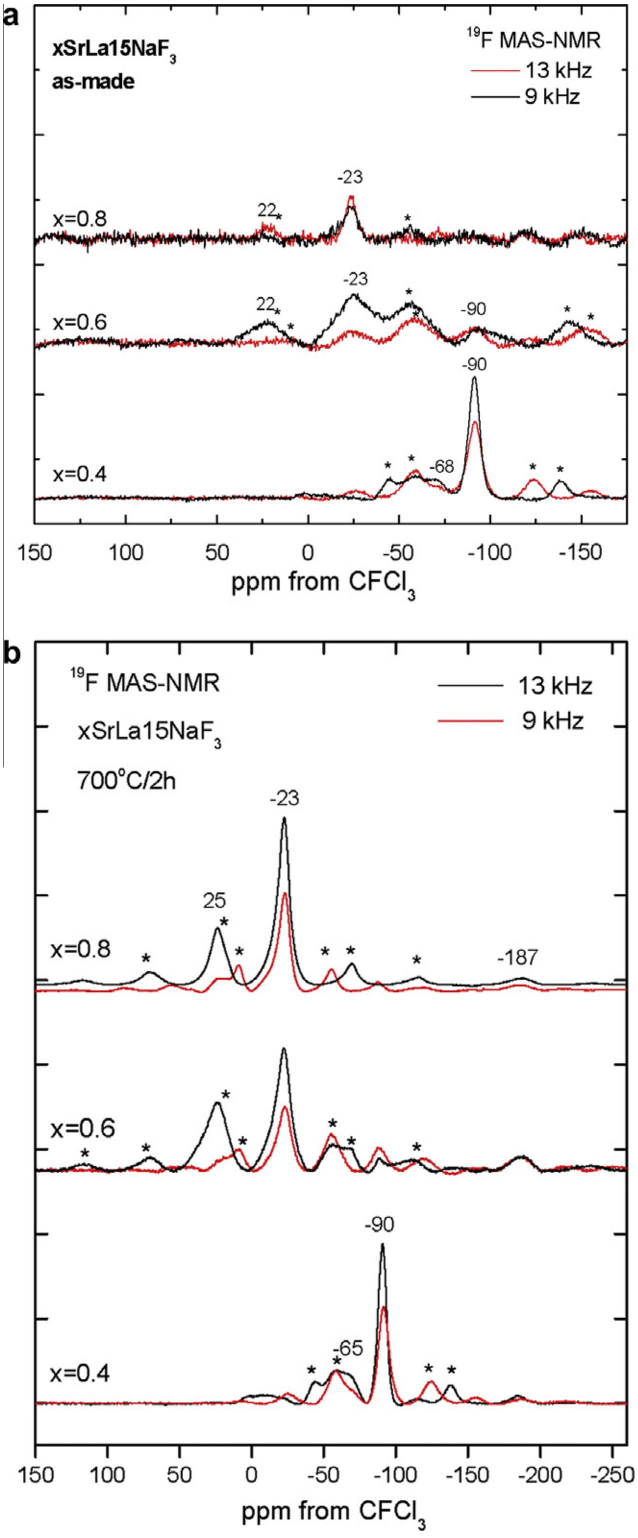

Fig. 2. ^{19}F MAS-NMR spectra of Sr-oxyfluoride glass as-made (a) and after 700 °C/2 h treatment (b).

High resolution, solid state ^{19}F Magic-Angle-Spinning Nuclear Magnetic Resonance (MAS-NMR) spectra were measured on a Tecmag APOLLO pulse NMR spectrometer at the magnetic field of 7.05 Tesla produced by the Magnex wide-bore superconducting magnet. The resonance frequency for ^{19}F was 282.7 MHz. A Bruker HP-WB high-speed MAS probe equipped with the 4 mm zirconia

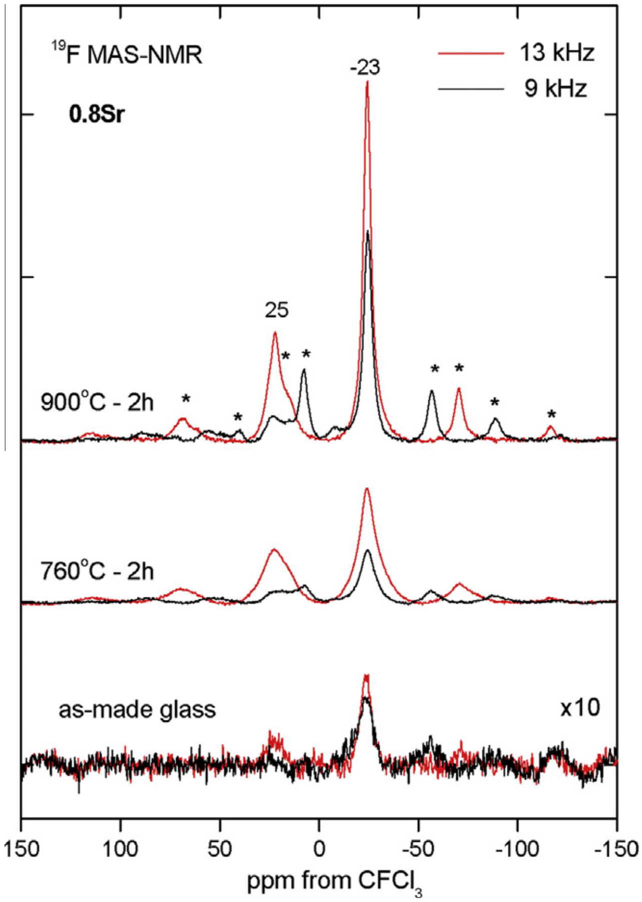

Fig. 3. ^{19}F MAS-NMR spectra of 0.8Sr glass after heat treatment at 760 °C and 990 °C for 2 h.

rotor and KEL-F cap was used to record the MAS spectra at the spinning speed varying from 9 to 13 kHz. Each spectrum was measured at least twice using different spinning speeds, in order to identify central bands in the spectrum. The spectra were measured using a single 2 μs radio-frequency pulse, corresponding to π/2 flipping angle. The acquisition delay used in accumulation was 2 s, and 256 scans were acquired. The frequency scale in ppm was referenced to the ^{19}F resonance of 1 M solution of NaF, which is located at −120 ppm from $CFCl_3$ [16].

The Bruker HP-WB MAS probe that was used in the measurements exhibits a significant fluorine background, which becomes dominant in the case of samples containing small amounts of the element. Therefore it was necessary to eliminate it, by measuring the signal from the empty rotor and subtracting it digitally.

Powder X-ray diffraction (XRD) was measured on a X'Pert Philips using Cu Kα radiation. The crystallite size was calculated from the Scherrer equation: the value of the shape factor, *K*, was taken to be 0.9 and α-Al_2O_3 was used as an internal standard.

3. Results and discussion

The ^{19}F MAS-NMR spectra of model crystalline SrF_2, NaF and LaF_3 samples measured at two spinning speeds are shown in Fig. 1. The spinning sidebands are marked by stars and they are separated by 31.8 and 46.0 ppm, for the spinning speeds equal to 9 and 13 kHz, respectively. The chemical shift observed in these model compounds moves towards more positive values with the decrease of ionicity (*i*): F–Na 83.3%, F–Sr 75.6%, F–La 67.8% [17], i.e. with the increase of the fluorine–cation bond strength.

A single central band at −225 ppm observed in the NaF spectrum corresponds to the fluorine atom surrounded by six sodium ions F–Na(6) [18]. The peak at the same position was also reported by Zeng and Stebbins in the Na–silicate glass [16]. It should be noted that no such line was found in any of glass or glass–ceramics samples studied in this work. It means that in oxyfluoride aluminosilicate glasses modified by alkaline earth oxides the fluorine ions do not make bonds similar to that existing in NaF.

The ^{19}F MAS-NMR spectrum of SrF_2 exhibits a single central band at −90 ppm. This is close to −84 ppm reported by Miller [19], who assigned it to the fluorine anion interacting with four strontium ions: F–Sr(4). Two central bands at +25 and −23 ppm are observed in the spectrum of crystalline LaF_3. They originate from fluorine ions interacting with the local structure of the first coordination sphere F–La(3), and with three near and one more distant lanthanum neighbors F–La(3 + 1), respectively [20]. In fact, the central band at +25 ppm is a superposition of two lines at +26 and +19 ppm, which were identified in experiments performed at higher magnetic field of 11.7 Tesla [9]. An additional broadening

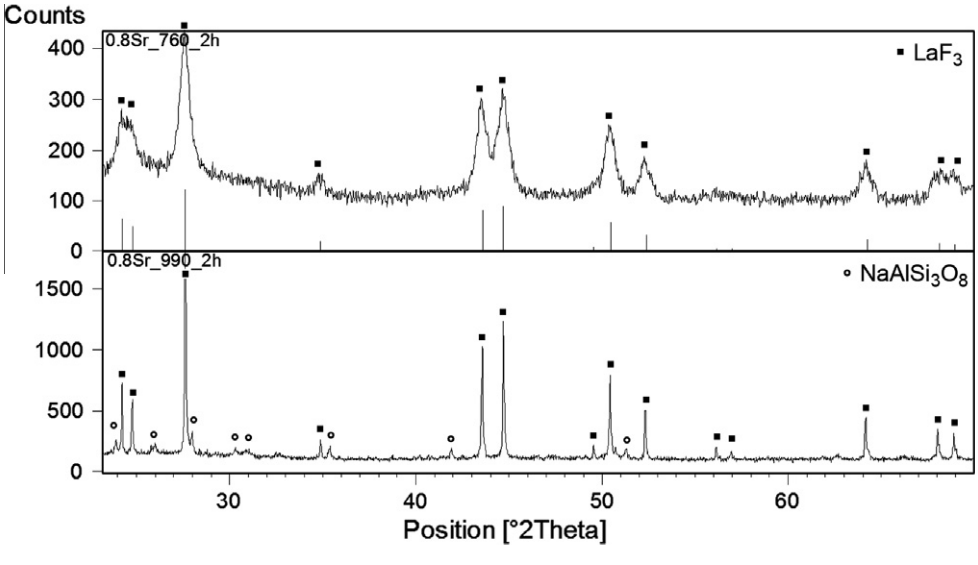

Fig. 4. XRD analysis of low strontium content glass (0.8Sr) after heat treatment at 760 °C (top) and 990 °C (bottom).

Table 2
LaF_3 crystallite sizes of the 0.8Sr glass after heat treatment.

Temperature of heat treatment, time 2 h (°C)	Average crystallite size (nm)
760	12
900	180
990	176

of this band that is visible on Fig. 1 is caused by a partial overlap of the spinning sideband.

The ^{19}F MAS-NMR spectra of as-made glasses measured at 9 and 13 kHz spinning speeds are shown in Fig. 2a. In the sample containing the smallest amount of strontium (0.8Sr) two central bands were found, at −23 and +22 ppm, the second partially overlapping with the spinning sideband belonging to the first. They originate from fluorine ions interacting with the local structure of the first coordination sphere F–La(3), and with three near and one more

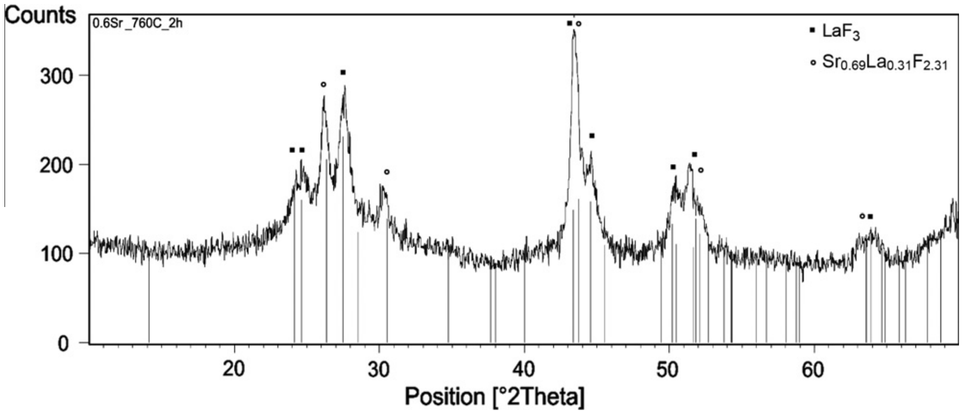

Fig. 5. XRD analysis of 0.6Sr glass after heat treatment at 760 °C.

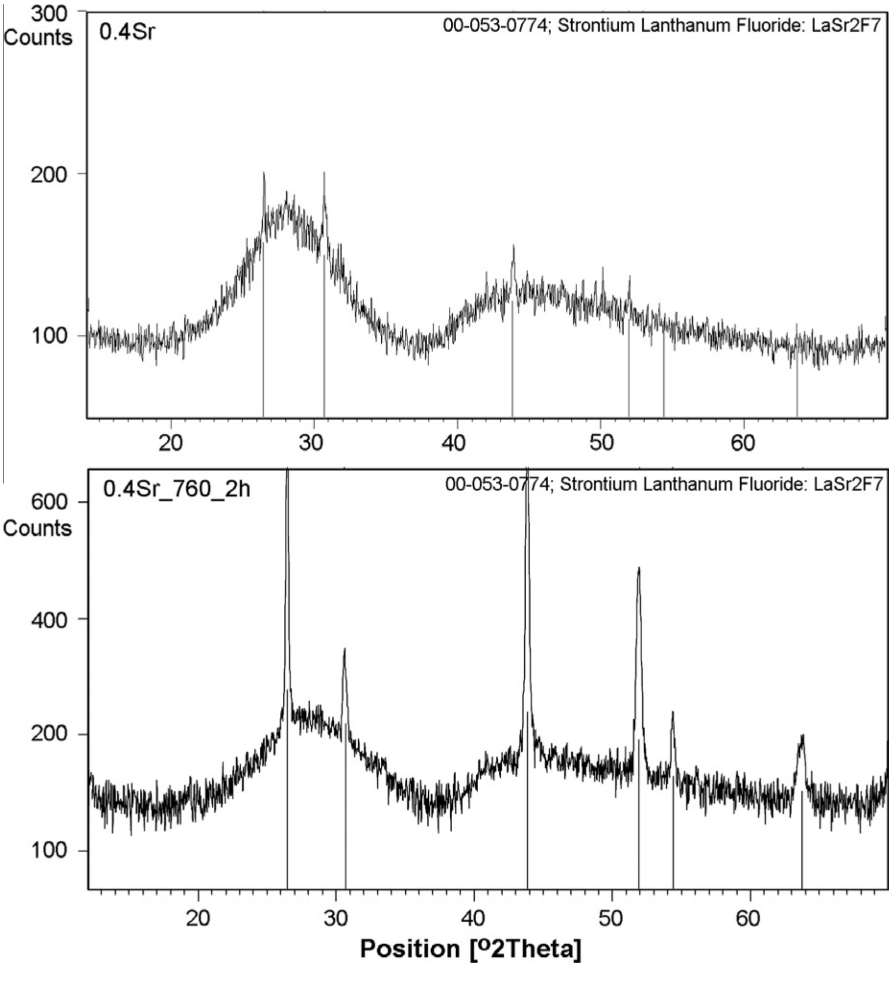

Fig. 6. XRD analysis of high strontium content glass (0.4Sr): as-made (top) and after heat treatment at 760 °C (bottom).

distant lanthanum neighbors F–La(3 + 1), respectively [20]. With the increase of strontium concentration (sample 0.6Sr) these lines become more pronounced and wider, but they almost completely disappear in the 0.4Sr sample, having the highest strontium concentration. This is the evidence of decreasing number of fluorine ions surrounded by lanthanum atoms. At the same time, new central bands appear already in the spectrum of 0.6Sr sample at −65 and −90 ppm, the latter becoming dominant in the case of 0.4Sr sample. The observed changes in the NMR spectrum with the increase of strontium content result from the increasing coordination of fluorine ions by Sr^{2+} ions. The line at −90 ppm can be assigned to the local structure of F–Sr(4) type, and its formation is accompanied by the decrease of the number of fluorine atoms that are close to La^{3+} ions. Using similar arguments, we can assign the line at −65 ppm to the local structure of F–Sr$(4-n)$La(n) type, where fluorine is coordinated by lanthanum and strontium ions simultaneously. The result show that the increase of strontium content causes significant changes occurring in the fluoride sub-network of the glass. Comparing to other bivalent modifiers, i.e. Mg, Ca, Ba used in oxyfluoride glasses [10], Sr has the highest affinity to fluorine ions. Therefore it will strongly compete with lanthanum for fluorine.

The ^{19}F MAS-NMR spectra of glasses that were heat-treated at 700 °C for 2 h are shown in Fig. 2b. The positions of central bands are very similar to that found in the original glasses, but the peaks amplitudes are bigger while their FWHM widths much smaller. This is the effect of cerammization process, which causes progressive ordering of the structure around the fluorine ions. In the case of the 0.4Sr sample, the process already began while the melt was undercooled, which can be seen in Fig. 2a. For the samples containing smaller amount of Sr (0.6Sr and 0.8Sr), the thermal treatment caused a significant intensity increase of +25 and −23 ppm lines, corresponding to crystalline LaF_3 phase. For larger Sr content (0.4Sr), the pure crystalline LaF_3 phase is not observed. Instead, the mixed structures of La–F–Sr type and the Sr–F bonds are formed, as manifested by the lines at −65 and −90 ppm, respectively. Such effect was not seen in the glass samples containing other modifiers, like MgO and CaO [10]. The origin of a weak central band at −187 ppm that is present in the NMR spectra of all heat-treated samples is not known at the moment.

The ^{19}F MAS-NMR spectra of the 0.8Sr sample heat-treated for 2 h at various temperatures are presented in Fig. 3. They clearly show a further intensity increase of the lines corresponding to the LaF_3 phase (+25 and −23 ppm) with the increasing cerammization temperature.

In order to confirm the NMR results, X-ray diffraction measurements were carried out on heat-treated glass samples. In the sample containing the smallest amount of SrO (0.8Sr) heat-treated at 900 °C, only the crystalline LaF_3 phase (reference code (RC): 01-82-0691) was detected. When the cerammization temperature was increased to 990 °C, an additional albite phase ($NaAlSi_3O_8$, RC: 01-071-1156) appeared (Fig. 4). The LaF_3 crystallite sizes in this sample for increasing cerammization temperature are presented in the Table 2, as determined by the Scherrer method [21].

The XRD analysis carried out on the 0.6Sr sample heat-treated at the same temperature range detected two crystalline phases: LaF_3 and $Sr_{0.69}La_{0.31}F_{2.31}$ (RC: 01-078-1144) (Fig. 5). In the sample with the highest strontium content (0.4Sr) only the crystalline $LaSr_2F_7$ phase (RC: 00-053-0774) was found (Fig. 6). These results are in good agreement with the changes observed in the NMR spectra.

The above results suggest that the central band observed in the range from −68 to −65 ppm in the ^{19}F MAS-NMR spectrum originates from the local structure of F–[Sr$(4-n)$,La(n)] type, in which fluorine anions coordinate with both lanthanum and strontium cations.

4. Conclusions

The ^{19}F MAS-NMR studies demonstrate the strong influence of SrO on the position and coordination of fluorine atoms in the glass framework. It causes significant changes in the first crystallization step: LaF_3 only, LaF_3 and $Sr_{0.69}La_{0.31}F_{2.31}$, and $LaSr_2F_7$ only fluoride phases are formed for 0.8Sr, 0.6Sr, and 0.4Sr glasses, respectively. Furthermore, the NMR results unambiguously exclude the occurrence of fluorine–sodium bonds in the oxyfluoride aluminosilicate glasses containing LaF_3 and modified by both Na_2O and SrO. Instead, the fluorine atoms prefer the bonding with lanthanum and strontium. The mixed strontium–lanthanum fluorides are formed in the cerammization process, when the SrO concentration increases. This is manifested by the appearance of the new central band in the ^{19}F MAS-NMR spectrum at about −65 ppm. The above results show that the addition of strontium affects strongly the LaF_3 crystallization kinetics and the structure of the oxyfluoride glass. This way the process of forming the nanocrystalline low-phonon-energy phase can be controlled to a larger extent.

Acknowledgements

The work was supported by AGH – University of Science and Technology, Faculty of Material Engineering and Ceramics, Grant No. 11.11.160.365/2011.

References

[1] P.A. Tick, N.F. Borrelli, I.M. Reaney, Opt. Mater. 15 (1) (2000) 81–91.
[2] P.A. Tick, N.F. Borrelli, L.K. Cornelius, M.A. Newhouse, J. Appl. Phys. 78 (11) (1995) 6367–6374.
[3] M. Dejneka, in: Proceedings of the XVIII International Congress on Glass, C9-1, 1998.
[4] M. Rozanski, M. Środa, Cz. Koepke, in: Proceedings of SPIE, The International Society for Optical Engineering, vol. 7120, 2008, pp. 89–333.
[5] M.B. Volf, Chemical Approach to Glass, Glass Science and Technology, vol. 7, Elsevier, 1984.
[6] R.G. Hill, A. Stamboulis, R.V. Law, A. Clifford, M.R. Towler, C. Crowley, J. Non-Cryst. Solids 336 (2004) 223–229.
[7] M. Środa, J. Therm. Anal. Calorim. 97 (2009) 281–287.
[8] M. Środa, Cz. Paluszkiewicz, Vib. Spectrosc. 48 (2008) 246–250.
[9] R.E. Youngman, M.J. Dejneka, J. Am. Ceram. Soc. 85 (2002) 1077–1082.
[10] M. Środa, Z. Olejniczak, J. Non-Cryst. Solids 357 (2011) 1696–1700.
[11] R.G. Hill, R.V. Law, M.D. O'Donnell, J. Hawes, N.L. Bubb, D.J. Wood, C.A. Miller, M. Mirsaneh, I. Reaney, J. Eur. Ceram. Soc. 29 (2009) 2185–2191.
[12] T.J. Kiczenski, J.F. Stebins, J. Non-Cryst. Solids 306 (2002) 160–168.
[13] M. Środa, J. Therm. Anal. Calorim. 97 (2009) 239–243.
[14] N. Hemono, G. Pierre, F. Munoz, A. de Pablos-Martin, M.J. Pascual, A. Duran, J. Eur. Ceram. Soc. 29 (2009) 2915–2920.
[15] L. Delevoye, L. Montagne, J. Non-Cryst. Solids 357 (2011) 1463–1468.
[16] Q. Zeng, J.F. Stebbins, Am. Mineral. 85 (2000) 863–867.
[17] E. Görlich, Nature 192 (1961) 133–135.
[18] F. Wang, C.P. Grey, Chem. Mater. 9 (1997) 1068–1070.
[19] J.M. Miller, Prog. Nucl. Mag. Reson. 28 (1996) 255–281.
[20] J.F. Stebbins, Q. Zeng, J. Non-Cryst. Solids 262 (2000) 1–5.
[21] J.I. Langford, A.J.C. Wilson, J. Appl. Cryst. 11 (1978) 102–113.