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

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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.

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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

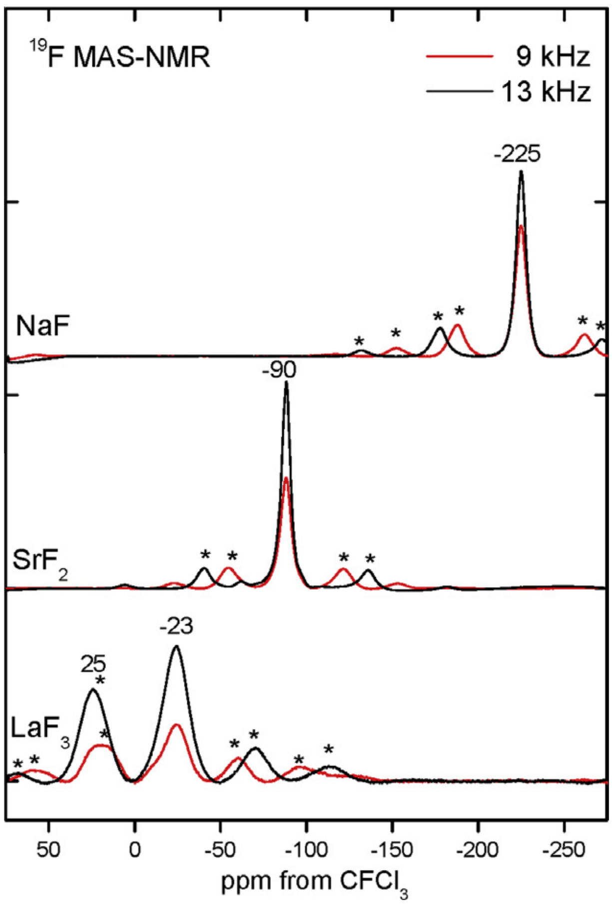

Fig. 1. ^{19}F MAS-NMR spectra of polycrystalline NaF, SrF_2 and LaF_3 at two spinning speeds: 9 and 13 kHz.

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.

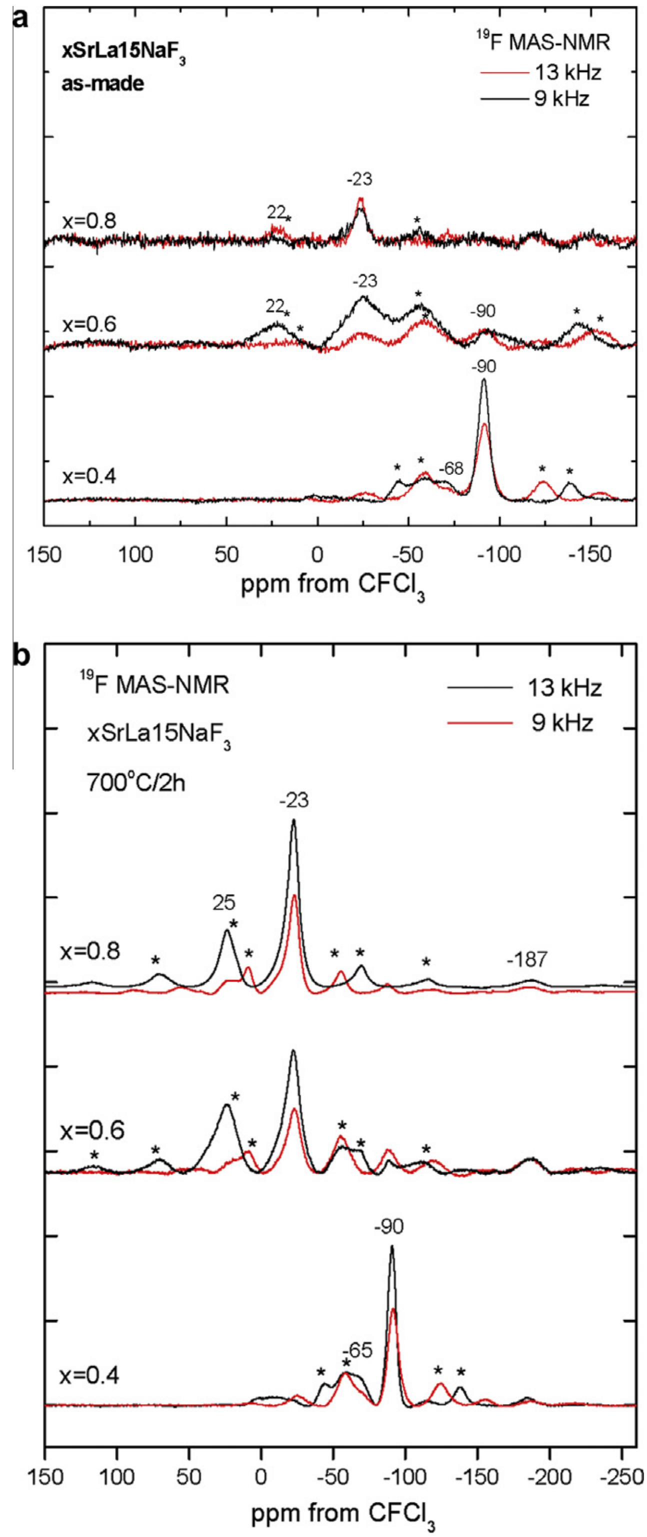

Fig. 2. ^{19}F MAS-NMR spectra of Sr-oxyfluoride glass as-made (a) and after 700 °C/2 h treatment (b).

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