



# Effect of alkaline earth oxides on ceramization of LaF<sub>3</sub> in aluminosilicate glass: <sup>19</sup>F MAS-NMR study

Marcin Środa<sup>a,\*</sup>, Zbigniew Olejniczak<sup>b</sup>

<sup>a</sup> AGH-University of Science and Technology, Faculty of Materials Science and Ceramics, Kraków, Poland, al. Mickiewicza 30, 30-059 Kraków, Poland

<sup>b</sup> Institute of Nuclear Physics, Polish Academy of Sciences, Radzikowskiego 152, 31-342 Krakow, Poland

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## ABSTRACT

Local environment of fluorine atoms in the lanthanum oxyfluoride aluminosilicate glasses and glass-ceramics modified by alkaline earth oxides, i.e. MgO, CaO and BaO, was studied by solid state <sup>19</sup>F MAS-NMR spectroscopy. The effect of the type and concentration of the modifier on the formation of crystalline LaF<sub>3</sub> phase was determined, as a function of heat treatment conditions. In all series of glasses studied, the F–Me(n), but no Na–F species were observed. The presence of F–La,Ba(n) units, in which fluorine is coordinated both by lanthanum and barium, was detected in the Ba-glass. Supplementary XRD analysis of this series confirmed that an increase of barium contents leads to the formation of Ba<sub>0.3</sub>La<sub>0.7</sub>O<sub>0.7</sub>F<sub>1.3</sub>, instead of pure LaF<sub>3</sub> only.

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## 1. Introduction

Glasses with the mixed cation sub-framework have long been used in various commercial applications. Recently, some unconventional non-oxide glass compositions with interesting optical properties were developed. For this purpose, the fluoride glasses are the most promising for their wide range of optical transmittance and low phonon energy. A well known example is the ZBLAN glass [1]. Unfortunately, the halide glasses are characterized by poor chemical and thermal resistivity, as well as low mechanical durability. Still, the mixed-anion framework glasses are intensively studied. The oxyfluoride glass can be an excellent blank material for obtaining transparent glass-ceramics host for rare earths ions in the optical devices exhibiting the luminescence effects. The fluoride nanocrystallites dispersed in the glassy matrix should possess a phonon energy as low as possible, to accept optically active ions easily, and to prevent their non-radiative decay after excitation. The above criteria can be fulfilled by one of the following phases: LaF<sub>3</sub>, Pb<sub>1-x</sub>Cd<sub>x</sub>F<sub>2</sub>, or GdF<sub>3</sub> [2,3]. Therefore, the first challenge in designing the optical glass-ceramics is to find such composition, in which the formation of appropriate fluorides in the first step of crystallization can be carefully controlled by time-temperature treatment, retaining at the same time the transparency of the material [4]. The second process is the insertion of optically active cations into the structure of fluoride crystallites.

The influence of alkaline and alkaline earth oxides on the thermal stability, formation of crystalline phases and the structure of the aluminosilicate glasses with LaF<sub>3</sub> was analyzed recently by DTA, XRD, FT-IR and Raman spectroscopy [5,6]. These studies did not provide any detailed information on the fluorine coordination. Therefore the solid state <sup>19</sup>F MAS-NMR was applied in the present work to determine the role of alkaline earth ions in the formation of fluorine compounds in the glass network and in the generation of crystalline LaF<sub>3</sub> during the controlled ceramization process.

Previous <sup>19</sup>F NMR studies of both crystalline compounds and glasses were performed by Kiczinski et al. [7], Hill et al. [8], and by Youngman and Dejneka [9]. A compilation of chemical shifts corresponding to various local fluorine structures in [7] included the F–Me(n), Al–F–Me(n) and Si–F–Me(n) environments (Me = Mg, Ca, Ba, La) that are relevant for the present study. The studies of oxyfluoride glass and glass-ceramics [9] detected the nanocrystalline LaF<sub>3</sub> phase and identified additional sites corresponding to Si–F and Al–F bonds. Their relative amounts depended on the type and concentration of the modifier, as well as the conditions of heat treatment. In the most recent <sup>19</sup>F MAS-NMR study of fluorine containing glass-ceramics [8], the chemical shifts corresponding to crystalline F–Mg(n) and F–Ca(n) species were determined. This information was helpful in the interpretation of NMR spectra obtained in the present work.

## 2. Experimental

Two physical parameters of the alkaline earth oxide glass modifiers can affect the framework structure of the aluminosilicate glass: the

\* Corresponding author.

E-mail address: [msroda@agh.edu.pl](mailto:msroda@agh.edu.pl) (M. Środa).

atomic number of the alkaline earth element introduced, and the change of relative charge of all ion modifiers ( $\text{Na}^+$ ,  $\text{Me}^{2+}$ , and  $\text{La}^{3+}$ ), with respect to the charge of  $\text{Al}^{3+}$  ions that are present in the network. Thus, we use a ratio:  $\text{Al}_2\text{O}_3/(\text{Na}_2\text{O} + \text{MeO} + 3\text{La}_2\text{F}_6)$  that was proposed previously [5,6], as a quantitative measure of relation between the content of  $\text{Al}^{3+}$  ions and the value of positive charge introduced by modifying ions. Accordingly, six series of glasses were prepared, with the corresponding substitution of MgO, CaO and BaO and the ratios equal to 0.4 and 0.6. In this range, the crystallization of fluoride in the glass matrix could be controlled by a careful choice of temperature and time of heat treatment. The required composition was achieved by changing the contents of MeO (Me = Mg, Ca, Ba) at the cost of  $\text{SiO}_2$ , keeping the contents of all other components constant.

Batches were prepared by mixing appropriate quantities of chemically pure reagents:  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{CaCO}_3$ ,  $\text{BaCO}_3$ , MgO, NaF and  $\text{LaF}_3$ . The mixtures in 20 g batches were melted in a covered platinum crucible placed in an electric furnace, at the temperature of 1450 °C, in the air atmosphere. The molten material was then poured out on a stainless steel plate, forming about 3 mm thick layer of glass. The glass compositions are listed in Table 1. In addition to the three series described above, in which the fluorine content was enhanced by the application of NaF, one glass without NaF was prepared, and its composition is given in the last row of Table 1.

The obtained glass was broken into smaller pieces that were heat treated at various temperatures for 1 h, in order to induce the ceramization and crystallization processes. Finally, the samples were grounded in a mortar to obtain a fine powder that was necessary for the MAS-NMR experiments.

High resolution, solid state  $^{19}\text{F}$  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. A Bruker HP-WB high-speed MAS probe equipped with the 4 mm zirconia rotor and KEL-F cap was used to record the MAS spectra at the spinning speed varying from 9 to 14 kHz (digitally controlled to  $\pm 1$  Hz). Each spectrum was measured at least twice using different spinning speeds, in order to identify central bands in the spectrum. The spectra were measured at 289.9 MHz, using a single 2  $\mu\text{s}$  radio-frequency (rf) pulse, corresponding to  $\pi/2$  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  $^{19}\text{F}$  resonance of 1 M solution of NaF, which is located at  $-120 \pm 0.5$  ppm from  $\text{CFCl}_3$  [10]. Due to significant differences of observed linewidths for the spectral components corresponding to crystalline and glassy phases, the reported line positions have uncertainties of about  $\pm 1$  ppm and  $\pm 5$  ppm, respectively.

The  $T_1$  relaxation times for the investigated samples were not measured, because it was not the purpose of this research. However, they were estimated by measuring the NMR spectra at two different delays and were found to be shorter than 0.5 s. Moreover, the relative intensities of various lines in the NMR spectra measured at different delays were the same. This indicated that the relaxation times for all spectral components were identical.

The Bruker HP-WB MAS probe that was used in the measurements exhibits a significant fluorine background, which becomes dominant

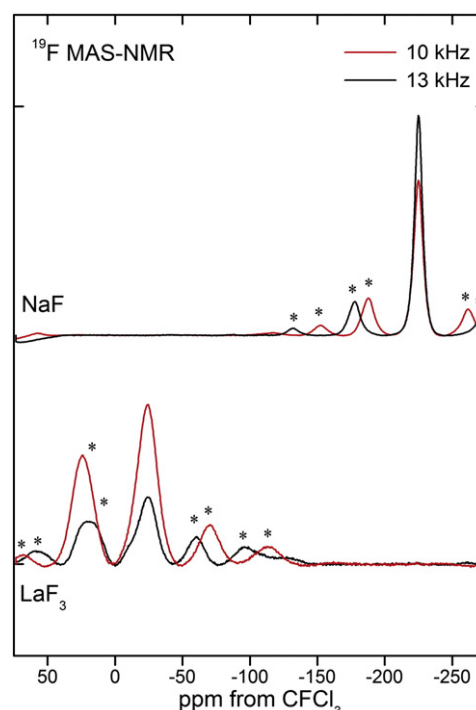


Fig. 1.  $^{19}\text{F}$  MAS-NMR spectra of polycrystalline NaF and  $\text{LaF}_3$  at two spinning speeds: 10 and 13 kHz.

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.

### 3. Results

In order to facilitate the interpretation of  $^{19}\text{F}$  MAS-NMR spectra of glasses, some model, crystalline samples were measured first. The spectra of crystalline NaF and  $\text{LaF}_3$  shown in Fig. 1 are helpful in identifying similar species in glass and glass-ceramic samples. The experiments are performed at two spinning speeds: 10 and 13 kHz, so that the central bands (CB) and the spinning sidebands (SS) could be easily identified. The distance between the spinning sidebands, which are marked by asterisks in the figure, is equal to 35.5 ppm and 46.0 ppm, for the spinning speeds of 10 and 13 kHz, respectively.

A single peak at  $-225$  ppm observed in the NaF spectrum corresponds to the fluorine atom surrounded by six sodium ions  $\text{F}-\text{Na}(6)$  [12]. The peak at the same position was also reported by Zeng and Stebbins in the Na-silicate glass [10]. It should be noted that no such line was found in any of glass or glass-ceramic samples studied. 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.

Two central bands at  $+25$  and  $-23$  ppm are observed in the spectrum of crystalline  $\text{LaF}_3$ . They originate from fluorine ions interacting with the local structure of the first coordination sphere

Table 1  
Nominal composition of the oxyfluoride aluminosilicate glasses.

Glass no. (Me = Mg, Ca, Ba)	Composition (mol%)						$\frac{\text{Al}_2\text{O}_3}{\text{Na}_2\text{O} + \text{MeO} + 3\text{La}_2\text{F}_6}$
	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	MeO (Me = Mg, Ca, Ba)	$\text{Na}_2\text{O}$	$\text{Na}_2\text{F}_2$	$\text{LaF}_3$	
0.4MeF	53.5	15	22.5	3	3	3	0.4
0.6MeF	66	15	10	3	3	3	0.6
0.4Ca	53.5	15	22.5	6	–	3	0.4

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