Influence of alkaline earth oxides on thermal stability of oxyfluoride glass

Marcin Środa

Abstract A new type of glass from the Na_2O–MeO–Al_2O_3–SiO_2–LaF_3 system where MeO = MgO, CaO, BaO and SrO has been studied. The aim of the investigation was to determine, by means of thermal techniques (DTA and DSC), the influence of alkaline earth ions additions on its thermal stability and the ability of LaF_3 phase to crystallization. The effect of LaF_3 crystallization was analyzed in connection with glass composition expressed by the $Al_2O_3/(MeO + Na_2O + 3La_2F_6)$ ratio varying from 0.4 to 0.8 for the alkaline earth admixtures. The compositions of the glasses have been designed so as to make it possible to define the effect of the charge of the ion modifiers (Na^+, Me^{2+}, La^{3+}) on the alumina position in the framework of the glass. Two series of glasses were obtained with a different F^- content. The formation of LaF_3 depends directly on the strength of the network and can be control by the Al_2O_3/modifiers ratio as well as the content of fluorine ions. Generally, it can be stated that transparent glass-ceramic with nanocrystallization of LaF_3 can be obtained for $Al_2O_3/(Na_2O + MeO + 3La_2F_6) \leq 0.6$ in the examined glasses. The more the ionicity of the alkaline earth ions the greater the tendency for the crystallization of Me_2LaF_7 and MeF_2. In the glass structure the substitution of oxygen ions by F^- ions facilitated the crystallization of LaF_3. Simultaneously, it influenced the thermal stability of the aluminosilicate network and induced the crystallization of appropriate silicates during the heat treatment.

Introduction

Transparent glass-ceramics become alternative materials for the optoelectronic crystallize systems. They have been developed for optical amplifiers, solid state laser and up-conversion devices, etc. [1–9].

The advantage of glass-ceramics is the easiness of the melting and forming (drawing) of glass which next should be heat treated. It can be obtained with a nanocrystalline phase which gives it special optoelectronic properties. For this purpose the oxyfluoride glassy system are developed for gaining luminescence in the silicate matrix [10, 11].

Oxyfluoride glass-ceramics combine the advantages of oxide glass, i.e. high mechanical strength, chemical resistance, good thermal stability and fluoride glass, i.e. low phonon environment for the rare earth ions (RE) and a higher tendency to crystallization. The efficiency of luminescence strongly depends on the incorporation of RE into the low phonon crystallites immersed in the glassy matrix [12].

To my knowledge the effect of the alkaline earth ions on the thermal stability of oxyfluoride aluminosilicate glass has not been studied yet. Thus, the paper presents the effect of modifiers, which induce depolymerisation of the glassy network on the process of nanocrystallization of LaF_3 and the thermal stability of network-mixed oxyfluoride glass.

M. Środa (✉)
Faculty of Material Science and Ceramics, AGH—University of Science and Technology, Mickiewicza Ave. 30, 30-059 Kraków, Poland
e-mail: msroda@agh.edu.pl

Experimental

The compositions of the glasses have been designed so as to make it possible to define the effect of the charge of the

ion modifiers (Na$^+$, Me^{2+}, La^{3+}) on the alumina coordination in the framework of the glass. Thus, the ratio Al$_2$O$_3$/(Na$_2$O + MeO + 3La$_2$F$_6$) has been accepted for all series of melts.

Glasses were prepared in the Na$_2$O–MeO–Al$_2$O$_3$–SiO$_2$–LaF$_3$ system where Me = Mg, Ca, Sr and Ba, respectively. Two series for each alkaline earth oxide with a lower and higher content of fluoride were obtained. The glass compositions are listed in Table 1.

Batches were prepared by mixing chemically pure reagents: SiO$_2$, Al$_2$O$_3$, Na$_2$CO$_3$, NaF and LaF$_3$. Alkaline earth oxides were introduced by the appropriate carbonate. Glasses have been obtained by melting 20 g batches in a covered platinum crucible in an electric furnace at a temperature of 1450 °C in air atmosphere. Each molten glass was poured out onto a stainless plate forming a layer of ca. 3 mm thickness.

The ability of the obtained glasses to crystallize was determined by DTA/DSC measurements conducted on the Perkin Elmer DTA-7 System operating in heat flux DSC mode. The samples of 60 mg in mass were heated in platinum crucibles at a rate of 10 °C min^{-1} in dry nitrogen atmosphere to the temperature of 1000 °C. The glass transition temperature T_g was determined from the inflection point on the enthalpy curve; the jump-like changes of the specific heat ΔC_p accompanying the glass transition and the enthalpy of crystallization (ΔH_{cryst}) of the glass were calculated using the 7 Series Perkin Elmer Thermal Analysis Software Library. The ability of glasses to crystallize was measured by the values of the maximum crystallization temperature ($T_{max\ cryst}$), the enthalpy of crystallization (ΔH_{cryst}) and the values of the thermal stability parameter of glasses ($\Delta T = T_{max\ cryst} - T_g$). Glasses revealing the effect of crystallization were selected for further thermal treatment.

The kind and the size of the formed crystallites were examined by XRD (Philips X'Pert Diffractometer) and SEM (FEI Nova200 NanoSEM) methods.

Results

Mg-glass

All Mg-glasses have been transparent and no opalescence was observed after melting. The thermal stability varied with the MgO content (Fig. 1a). The more MgO in the melts, the lower the transformation temperature (T_g) and the stronger the tendency to crystallize was observed. The specific heat (ΔC_p) accompanying the glass transition diminished with the increase of MgO in the melt (Table 2).
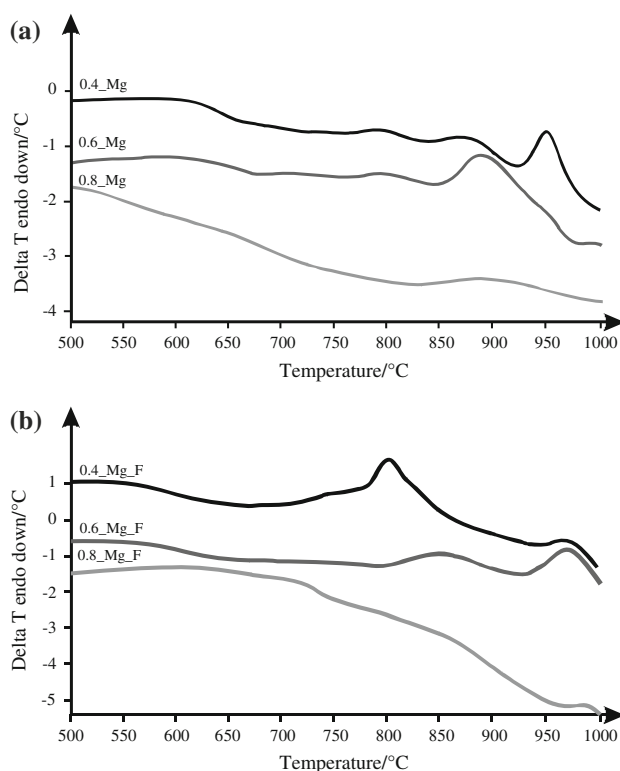

Fig. 1 DTA curves of Mg-oxyfluoride aluminosilicate glass: Mg-glasses (a) and Mg_F-glasses (b)

Table 1 Composition of prepared oxyfluoride alumino-silicate glasses (MeO = MgO, CaO, SrO and BaO)

Glass		Ratio Al$_2$O$_3$/(MeO + Na$_2$O + 3La$_2$F$_6$)	Composition (mol%)					
			SiO$_2$	MeO	Al$_2$O$_3$	Na$_2$O	Na$_2$F$_2$	La$_2$F$_6$
Series I	0.4_Me	0.4	53.5	22.5	15.0	6.0	–	3.0
	0.6_Me	0.6	66.0	10.0	15.0	6.0	–	3.0
	0.8_Me	0.8	72.25	3.75	15.0	6.0	–	3.0
Series II	0.4_Me_F	0.4	53.5	22.5	15.0	3.0	3.0	3.0
	0.6_Me_F	0.6	66.0	10.0	15.0	6.0	3.0	3.0
	0.8_Me_F	0.8	72.25	3.75	15.0	6.0	3.0	3.0

Table 2 Thermal characteristics of Mg-oxyfluoride glasses

Sample		$T_g/°C$	$\Delta C_p/J\ g^{-1}\ °C^{-1}$	$T_{max\ crys}/°C$	$\Delta H_{crys}/J\ g^{-1}\ (T_{max\ cryst}/°C)$	$\Delta T = T_{max\ cryst} - T_g/°C$
Series I (glass)	0.4_Mg	641	0.243	793, 873, 953	9.5, 6.1, 39.9	152
	0.6_Mg	656	0.290	796, 892, 960	4.5, 71.7[a]	140
	0.8_Mg	686	0.429	–	–	–
Series II (glass)	0.4_Mg_F	582	0.801	708, 755, 802, 968	29.0, 66.8, 243.4, 35.6	126
	0.6_Mg_F	596	0.486	715, 860, 973	8.6, 69.2, 75.8	119
	0.8_Mg_F	648	0.284	721, 988	3.6, 9.2	73

[a] Two stages of crystallization have been combined into one exothermal effect

There was no evidence of crystallization, confirmed by XRD, even after heat treatment at 920 °C during 1 h for 0.8_Mg glass. Formation of LaF_3 was observed for 0.6_Mg glass after heating at 820 °C for 12 h. The glass revealed the formation of $Na_2Al_2O_4$ and albite $Na(AlSi_3O_8)$ after ceramization at 920 °C for 1 h. The increase of MgO content (0.4_Mg glass) shifted the peak of the $Na_2Al_2O_4$ crystallization to a lower temperature and diminished the ΔH. At the same time the peak of the $Na(AlSi_3O_8)$ crystallization become more visible. Values of ΔH indicate that the increase of MgO content from 10 to 22.5 mol% influences the higher tendency to crystallize the fluoride phase and the silicate matrix. In this case, there was no crystallization of Mg-compounds.

Increasing fluorine (series II) revealed the diminishing T_g and $T_{max\ cryst}$ temperatures. Additional exothermal peak at maximum ~ 800 °C was observed for 0.4_Mg_F glass on DTA curve which derives from the formation of Na_2MgSiO_4. The replacement of a part of oxygen by fluorine induced the lowering of the thermal stability which is calculated as $\Delta T = T_{max\ cryst} - T_g$ (Table 2).

Ca-glass

The Ca-glasses are characterized by a higher transformation temperature than Mg-glasses but the course of the change for T_g and ΔC_p are similar for both glasses

(Table 3). The crystallization of LaF_3 for the first stage is observed for glass 0.8_Ca and 0.6_Ca on the DTA curves (Fig. 2). With the increase of CaO in the glass structure the process of the formation of $CaSiO_3$ became more visible at the temperature 1000 °C. $Ca_2Al(AlSiO_7)$ and $La_{4.67}(SiO_4)_3O$ appeared at the additional stage of crystallization in the range 880–950 °C for the 0.4_Ca sample. The introduction of the higher content of F^- ions (series II) shifted the maximum of exothermic peak to the lower temperature. A new peak of crystallization was observed at the temperature 710 °C for 0.4_Ca_F glass. The XRD investigation confirmed the crystallization of $(Ca,La)F_2$ besides the formation of LaF_3. It indicates that with the increase of Ca^{2+} content the tendency for CaF_2 crystallization becomes stronger.

Sr-glass

Sr-glasses of series I was transparent. Replacement of a part of oxygen ions by fluorine induced the effect of opalescence in the glass. XRD study showed the formation of $LaSr_2F_7$ in the 0.4_Sr_F melt. The crystallization of $Sr_{0.69}La_{0.31}F_{2.31}$ and LaF_3 was observed for 0.6_Sr_F glass. The loss of fluorine ions by the network connected with the fluorides crystallization influences the increase of the transformation temperature with the increase of SrO content for series II (Table 4, Fig. 3).

Table 3 Thermal characteristics of Ca-oxyfluoride glasses

Sample		$T_g/°C$	$\Delta C_p/J\ g^{-1}\ °C^{-1}$	$T_{max\ crys}/°C$	$\Delta H_{crys}/J\ g^{-1}\ (T_{max\ cryst}/°C)$	$\Delta T = T_{max\ cryst} - T_g/°C$
Series I (glass)	0.4_Ca	678	0.424	818, 883, 905	21.5, 375.9[a]	140
	0.6_Ca	706	0.778	742, 934, 1010	14.9, 256.4[a]	36
	0.8_Ca	–[b]	–	762, 1008	12.8, 115.2	–
Series II (glass)	0.4_Ca_F	624	0.523	710, 807, 944	39.0, 80.9, 112.1	86
	0.6_Ca_F	688	0.483	755, 848, 952	6.8, 79.0, 115.6	67
	0.8_Ca_F	709	0.342	802, 1057	4.6, 20.7	93

[a] Two stages of crystallization have been combined into one exothermal effect

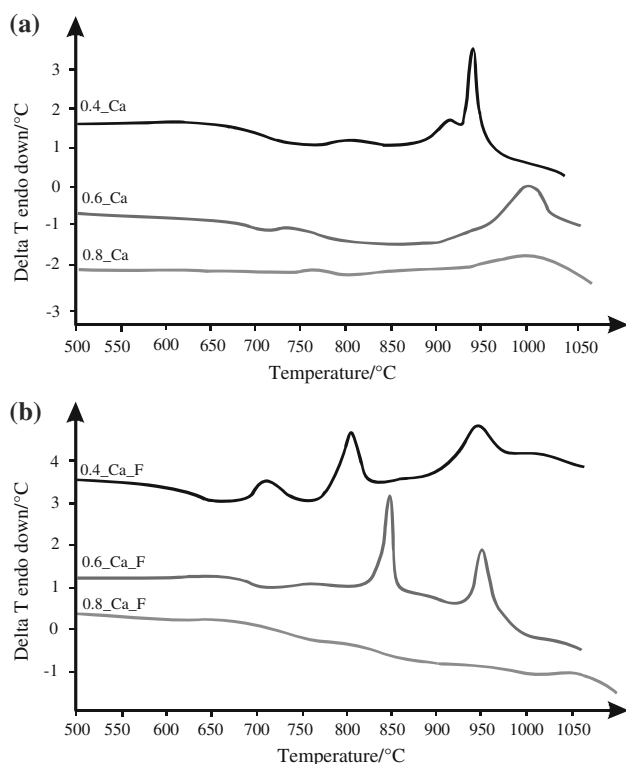[b] The effect of transformation was connected with the crystallization of LaF_3

Fig. 2 DTA curves of Mg-oxyfluoride aluminosilicate glass: Ca-glasses (a) and Ca_F-glasses (b)

Fig. 3 DTA curves of Sr-oxyfluoride aluminosilicate glass: Sr-glasses (a) and Sr_F-glasses (b)

Lanthanum fluorine is the only phase which forms up to a temperature of 900 °C for the 0.8_Sr sample. An additional exothermal peak was observed at the range 950–1000 °C derived from $NaAlSi_3O_8$. The increase of Sr content in the glass induced crystallization $Sr_{0.69}La_{0.31}F_{2.3}$ together with LaF_3 at 700 °C. Additional peaks of $La_2Si_2O_7$ and $La_{10}(SiO_4)_6O_3$ crystallization appeared on the DTA curve at the range 820–870 °C and 880–920 °C, respectively. It has been observed that crystallization of $La_{10}(SiO_4)_6O_3$ became stronger and appeared at lower temperature with the increase of SrO.

The introduction of the additional amount of F^- ions (series II) diminished the thermal stability of the glass which was manifested by the spontaneous crystallization of fluorides. The more 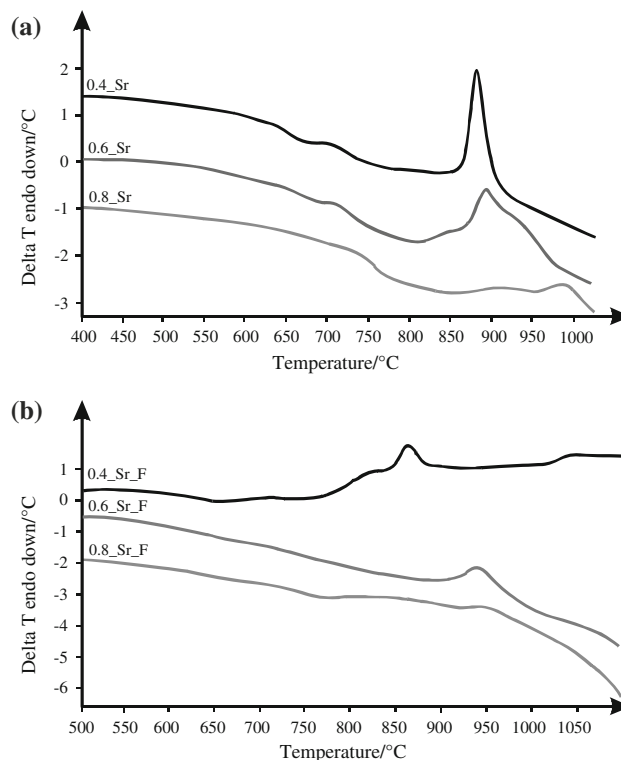SrO in the structure of the melts the stronger ceramization was observed. The crystallization of fluorides induced a reverse of the course of change for T_g and ΔT compared to series I and the higher values of ΔT.

Ba-glass

The thermal stability of Ba-glasses showed the similarity to Sr-glasses but exothermic effects observed on DTA curves gave higher values of ΔH (Fig. 4). The introduction of F^- to the glass (series II) induced greater opalescence than in Sr-glass. The loss of transparency during quenching was connected with the crystallization of LaF_3. Ba_2LaF_7 as the second phase was confirmed by the XRD study for the 0.4_Ba_F glass. The more Ba was added to the glass the lower T_g temperature was measured. Simultaneously,

Table 4 Thermal characteristics of Sr-oxyfluoride glasses

Sample		$T_g/°C$	$\Delta C_p/J\ g^{-1}\ °C^{-1}$	$T_{max\ crys}/°C$	$\Delta H_{crys}/J\ g^{-1}\ (T_{max\ cryst}/°C)$	$\Delta T = T_{max\ cryst} - T_g/°C$
Series I (glass)	0.4_Sr	646	0.442	708, 883	20.1, 153.0	62
	0.6_Sr	653	0.237	718, 850, 894, 935	15.7, 215.6[a]	65
	0.8_Sr	657	0.420	740, 907, 986	25.2, 11.5, 15.6	83
Series II (glass ceramics)	0.4_Sr_F	625	0.4261	714, 830, 866, 905	9.7, 261.1[a]	89
	0.6_Sr_F	605	0.499	705, 887, 943	7.4, 2.1, 92.9	100
	0.8_Sr_F	590	1.052	700, 841, 945	5.9, 37.2, 13.3	110

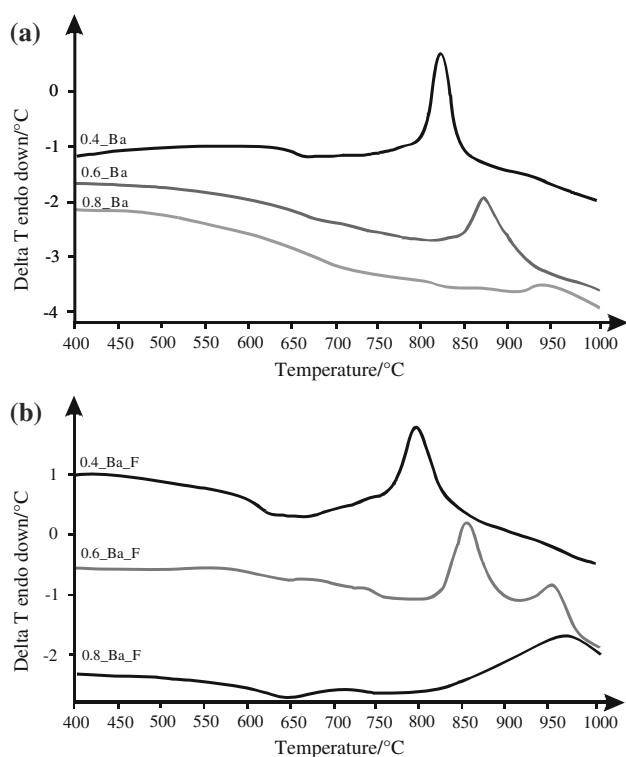[a] Multi-stage of crystallization has been combined into one exothermal effect

Fig. 4 DTA curves of Ba-oxyfluoride aluminosilicate glass: Ba-glasses (a) and Ba_F-glasses (b)

former or/and a modifier forming octahedral [AlO_6]. The position of aluminium in the network depends on the formers/modifiers ratio. When the ratio is less than 1 it can replace Si^{4+} in the network in accordance with the scheme: $Me^+[Al^{3+}O_4]^{4-} \leftrightarrow [Si^{4+}O_4]^{4-}$ [13]. Thus, it can play a significant part in the strength of the network.

The obtained melts were characteristic of the ratio $Al_2O_3/(Na_2O + MeO + 3La_2F_6) < 1$. It indicates that a quantity of electrons supplied by modifiers is enough to provide an electrical charge balance of Al^{3+} in tetrahedral coordination.

Oxyfluoride Me-glasses based on an identical aluminosilicate matrix reveal the effects of crystallization fluorides at the first stage of crystallization near the T_g temperature and the second multi-stage crystallization of the silicate.

The ability of LaF_3 to crystallize increased with the weakening of the field strength of modifiers which is expressed by Dietzel's equation [14]: $F = z/r^2$ where z—number of charges, r—internuclear distance in a sequence Mg ($F = 0.47$) < Ca (0.36) < Sr (0.32) < Ba (0.27). The bond strength of Sr^{2+} and Ba^{2+} in the network of the glass is weak enough and the ions participate in the formation of the alkaline earth fluorides at the first stage of crystallization at lower temperatures.

There is no such effect observed in the Mg- and Ca-glasses (except 0.4_Ca_F sample) whose modifiers have the similar bond strength to La^{3+} ion ($F = 0.52$).

The content of alkaline earth ions in the glass has great influence on the ceramization of LaF_3. When MeO content increases T_g decreases and ΔH of crystallization increases. This phenomenon is connected with the depolymerization of the aluminosilicate network.

The replacement of O^{2-} ions by F^- in the network induces the same course of the T_g change like in the instance of the increase of MeO content. The weak strength of the bonds in the network or/and the more depolymerization of the network, the greater the tendency of the glass for the crystallization of fluorides is observed. For optoelectronic purpose the lanthanium-alkaline earth fluorides possess higher phonon energy than LaF_3. One can expect that the admixtures of lanthanide ions incorporated into lanthanium-alkaline earth fluorides will have a lower

the main peak of crystallization shifted towards lower temperatures (Table 5). LaF_3 as the only phase crystallizes at the control process of the heat treatment at the range 750–760 °C for 0.8_Sr and 0.6_Sr glasses. $NaLa_9(SiO_4)_6O_2$ and $BaAl_2Si_2O_8$ phases appeared at 900 °C in 0.6_Ba glass. An additional amount of BaO (0.4_Ba glass) forced the formation of $Ba_{0.3}La_{0.7}O_{0.7}F_{1.3}$ and BaF_2 instead of LaF_3 and the crystallization of $NaLa_9(SiO_4)_6O_2$ was replaced by $Ba_4La_6O(SiO_4)_6$.

Discussion

Generally, alumina ions occupy two different position 4- and 6-coordination in the network of the glass. They can substitute Si^{4+} in tetrahedron and play the role of the glass

Table 5 Thermal characteristics of Ba-oxyfluoride glasses

Sample		T_g/°C	ΔC_p/J g^{-1} °C^{-1}	$T_{max\ crys}$/°C	ΔH_{crys}/J g^{-1} ($T_{max\ cryst}$/°C)	$\Delta T = T_{max\ cryst} - T_g$/°C
Series I (glass)	0.4_Ba	650	0.526	740, 823	139.9[a]	90
	0.6_Ba	658	0.160	752, 845, 872	163.6[a]	94
	0.8_Ba	696	2.744	760, 943	28.4	64
Series II (glass ceramics)	0.4_Ba_F	609	0.356	706, 748, 794	103.3[a]	97
	0.6_Ba_F	620	0.126	740, 852, 950	14.2, 125.6, 30.9	120
	0.8_Ba_F	623	0.139	711, 984	13.3, 254.5	88

[a] Multi-stage of crystallization has been combined into one exothermal effect

luminescence efficiency due to the increase of the non-radiation relaxation from the excited levels of the lanthanide.

Concept of crystallization

The crystallization of the alkaline earth containing oxy-fluoride glasses is the multistage process with three well distinguished steps (Table 6). Crystallization starts near the T_g transformation and LaF_3 is formed as the first compound (Fig. 5a). It is accompanied by composed La- and Me-fluorides formation. The next step (850–950 °C) consists of the formation of La- and/or Me-silicates, by the reaction of the oxides with the network SiO_2. At the third stage of crystallization (950–1050 °C) Na-aluminosilicate (albite) is formed (Fig. 5b). CaO containing glass is an exception and instead of albite, silicate–pseudo wollastonite appears. Chemical composition and structure of these compounds indicate that they are formed by the components of elements of the glass structure network.

The chemical composition and the order of the formation of crystal phases whose temperature increases from the transformation temperature to the liquid state of glass correspond to the concept of the structural mechanism of multistage glass crystallization by Stoch [15, 16]. According to it, at the glass transformation temperature, the crystallization is a process of rebuilding the middle range organization domains in amorphous structure. The

Table 6 Crystallization of oxyfluoride glass

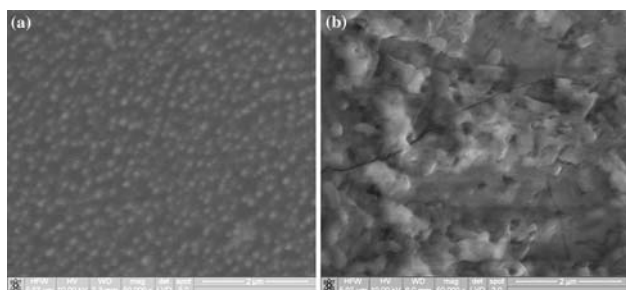| Sample	Proces of crystallization		
	I Stage	II Stage	III Stage
0.4_Mg	LaF_3 ($\leq$820 °C)	$Na_2Al_2O_4$ (880 °C)	$Na(AlSi_3O_8)$ (960 °C)
0.6_Mg	LaF_3 ($\leq$820 °C)	$Na_2Al_2O_4$ (900 °C)	$Na(AlSi_3O_8)$ (950 °C)
0.8_Mg	–	–	–
0.4_Mg_F	LaF_3 (750 °C)	Na_2MgSiO_4 (800 °C) $Na_2Al_2O_4$ (880 °C)	$Na(AlSi_3O_8)$ (980 °C)
0.6_Mg_F	LaF_3 (750 °C)	$Na_2Al_2O_4$ (880 °C)	$Na(AlSi_3O_8)$ (980 °C)
0.8_Mg_F	LaF_3 (750 °C)	$Na_2Al_2O_4$ (880 °C)	$Na(AlSi_3O_8)$ (980 °C)
0.4_Ca	LaF_3 ($\leq$800 °C)	$Ca_2Al(AlSiO_7)$ $La_{4.67}(SiO_4)_3O$ (900–950 °C)	$CaSiO_3$ (1000 °C)
0.6_Ca	LaF_3 ($\leq$800 °C)	$Ca_2Al(AlSiO_7)$ $La_{4.67}(SiO_4)_3O$ (900–950 °C)	$CaSiO_3$ (1000 °C)
0.8_Ca	LaF_3 ($\leq$800 °C)	–	–
0.4_Ca_F	LaF_3, $(Ca,La)F_2$ (710 °C)	$CaLa_4(SiO_4)_3O$ (800 °C)	$CaSiO_3$ (960 °C)
0.6_Ca_F	LaF_3 ($\leq$800 °C)	$Ca_3La_6(SiO_4)_6$ $La_2Si_2O_7$ (850 °C)	$CaSiO_3$ (960 °C)
0.8_Ca_F	LaF_3 ($\leq$800 °C)	–	$CaSiO_3$ (1050 °C)
0.4_Sr	LaF_3, $Sr_{0.69}La_{0.31}F_{2.3}$ ($\leq$750 °C)	$La_{10}(SiO_4)_6O_3$ (880–920 °C)	–
0.6_Sr	LaF_3, $Sr_{0.69}La_{0.31}F_{2.3}$ ($\leq$750 °C)	$La_2Si_2O_7$ (820–870 °C) $La_{10}(SiO_4)_6O_3$ (880–920 °C)	$NaAlSi_3O_8$ (950 °C)
0.8_Sr	LaF_3 ($\leq$900 °C)	–	$NaAlSi_3O_8$ (950–1000 °C)
0.4_Sr_F (glass-ceramics)	$LaSr_2F_7$ (700 °C)	Spontaneous crystallization during quenching $La_{10}(SiO_4)_6O_3$, $NaAlSi_3O_8$	
0.6_Sr_F (glass-ceramics)	$Sr_{0.69}La_{0.31}F_{2.31}$, LaF_3 (700 °C)		
0.8_Sr_F (glass-ceramics)	LaF_3 ($\leq$800 °C)		
0.4_Ba	$Ba_{0.3}La_{0.7}O_{0.7}F_{1.3}$, BaF_2	$Ba_4La_6O(SiO_4)_6$ (830 °C)	–
0.6_Ba	LaF_3 (750 °C)	$NaLa_9(SiO_4)_6O_2$ (880 °C)	–
0.8_Ba	LaF_3 (750 °C)	–	$NaAlSi_3O_8$ (950 °C)
0.4_Ba_F (glass-ceramics)	LaF_3, Ba_2LaF_7	Spontaneous crystallization during quenching $Ba_4La_6O(SiO_4)_6$, $NaLa_9(SiO_4)_6O_2$, $NaAlSi_3O_8$	
0.6_Ba_F (glass-ceramics)	LaF_3, Ba_2LaF_7		
0.8_Ba_F (glass-ceramics)	LaF_3, Ba_2LaF_7		

Fig. 5 SEM of Ba-glass after a proces of the crystallization: the first stage of crystallization (**a**), the third stage of crystallization (**b**)

rebuilding or reorganization of the primary glass structure needs the breaking of part of the chemical bonds to make components free enough to form the structure of new compounds. Due to this components weakly bond with the network, in this case La-fluorides, are formed as the first.

When the temperature and mobility of components increase and network depolymerization modifiers interact with silica, what is manifested is the formation of Me- and La-silicates. The rest of the silicate network crystallizes, forming Na-aluminosilicate (albite) and in CaO containing glass, pseudowollastonite.

The chemical affinity of components is governed by the composition of newly forming crystal phases. In oxide glasses it has the character of acid–base interactions. The chemical affinity of SiO_2 as the most acidic component to another components, increases with their basicity indicated by the ionicity of cation–oxygen bond, and it increases in the order Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}. The diminishing temperature of the second step of crystallization, and the formation of Me- and La-silicates occur in the same order.

Conclusions

The aim of the investigation was to work out the glass composition in the system $Na_2O–MeO–Al_2O_3–SiO_2–LaF_3$ for the best effect of the crystallization of LaF_3. Nanocrystallization of LaF_3 for the good transparency of oxyfluoride glass-ceramics can be obtained for all Me-glasses but the effect of ceramization is different for each alkaline earth ion. The formation of LaF_3 depends directly on the strength of the network and can be controlled by the Al_2O_3/modifiers ratio as well as the content of fluorine ions. Generally, it can be stated that transparent glass-ceramic with nanocrystallization of LaF_3 can be obtained for $Al_2O_3/(Na_2O + MeO + 3La_2F_6) \leq 0.6$ in the examined glasses. The more ionicity of the alkaline earth ions the greater the tendency of the crystallization of Me_2LaF_7 and MeF_2. It corresponds to the FTIR spectroscopy study which showed that alkaline earth ions diminished the depolymerisation of the oxyfluoride network (contrary to the silicate network) [17].

The formation of the alkaline earth fluorides results from a higher affinity of fluorine to Me^{2+} ions compared to oxygen affinity and the formation of Me-F(n) species in the structure. This phenomenon is responsible for the crystallization of MeF_2 during the thermal treatment.

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