



Structural evolution of Ni environment in lithium, magnesium and zinc aluminosilicate glasses and glass-ceramics



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ABSTRACT

Three glasses in the $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ (LAS), $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ (MAS) and $\text{ZnO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ (ZAS) systems were investigated to obtain spinel-based transparent glass-ceramics doped with TiO_2 to induce internal nucleation and with NiO to provide optically active ion. The sequence of phase transformations of initial glasses during heat-treatments was studied by *in situ* X-ray absorption spectroscopy, X-ray diffraction and room temperature optical spectroscopy.

For all glasses, there is a change of Ni^{2+} coordination with the increase of the heat-treatment temperature. The $^{15}\text{Ni}^{2+}$ sites in the parent glass disappear and new distorted $^{16}\text{Ni}^{2+}$ sites are formed within aluminotitanate and (Ni, or Ni,Mg, or Ni,Zn) aluminate amorphous regions. The local environment around Ni^{2+} then evolves from distorted octahedra to regular octahedra due to the nickel-doped spinel crystallization. In LAS glass-ceramics only, Ni^{2+} incorporates at elevated temperature octahedral and tetrahedral sites in crystals of β -quartz solid solution, whose content increases with time and temperature of heat treatment accompanied by a continuous decomposition or dissolution of spinel. In MAS and ZAS glass-ceramics, Ni-doped spinel exist in the whole temperature range of applied heat-treatments.

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1. Introduction

There is an upsurge of interest in recent years to develop new materials in the field of telecommunication and information technology. Particular attention has been devoted to glass-ceramics doped with optically active ions for their potentially enhanced optical properties [1]. Interest in glass-ceramics for optical applications comes from the advantage to combine properties of both glasses and crystals. These materials keep the easier and low cost manufacturing of glasses, while the crystalline phases embedded in the glass matrix offer optically active environment for transition elements. This offers the possibility to obtain glass-ceramic materials with a large range of compositions and with higher doping concentrations than single crystals. Transition metals (TM) and among them Ni^{2+} ions are effective emission centers [2–15]. Such ions can be optically active and, in the same time, they can have a strong influence on the crystallization processes [16–20].

Transparent glass-ceramics were widely investigated in aluminosilicate systems ($\text{SiO}_2-\text{Al}_2\text{O}_3-\text{Li}_2\text{O}-\text{ZnO}-\text{MgO}$) as they can nucleate nanocrystalline spinels (10–50 nm in size) that are known to concentrate Ni^{2+} ions [1,8,11,20–26]. It was demonstrated that Ni^{2+} ions located in octahedral sites in spinel structure have a wide IR luminescence in

the 1.1–1.6 μm region drawing attention for tunable laser sources, broadband amplifiers, solar collectors and phosphors [5,7,11,25–29]. These spinels in aluminosilicate glass-ceramics are mainly solid solutions in the ternary MgAl_2O_4 (spinel)– ZnAl_2O_4 (gahnite)– NiAl_2O_4 . Spinel has the general formula $\{\text{A}_{1-\delta}\text{B}_\delta\}\{\text{B}_{2-\delta}\text{A}_\delta\}\text{O}_4$, where the brackets represent octahedral and the braces tetrahedral sites occupied by A^{2+} and B^{3+} ions. The cation site distribution is described by the inversion parameter δ giving the two extreme cases, normal spinel ($\delta = 0$) and inverse spinel ($\delta = 1$).

As the luminescence originates from electronic transitions in the partly filled $3d$ orbitals, the spectral characteristics are directly related to the local Ni^{2+} environment. For instance, as mentioned above, Ni^{2+} has to enter octahedral sites, $^{16}\text{Ni}^{2+}$, to give rise to efficient luminescent properties [30,31]. In glass-ceramics, the Ni^{2+} local environment strongly depends upon the glass composition, the nucleating agents, the heat treatment that can promote amorphous–amorphous separation, compositional heterogeneities or specific crystalline phases. A difficulty in the interpretation of glass-ceramics behavior resides in the availability of various environments for Ni^{2+} : ions can be localized in the residual glass (with a potential different coordination compared to the initial glass due to changes in composition of the remaining glassy part), in one or several different crystalline environments and at the glass/crystal interface. In order to better control and optimize the desired properties, it is highly desirable to understand the Ni^{2+} site

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distribution and the factors that may influence it. An indirect possibility to verify the introduction of the desired cations within specific crystals is by analyzing the lattice parameters obtained by X-ray diffraction that are sensitive to substitution of cations with different sizes [27,32]. However, chemically selective methods (optical absorption, X-ray absorption) have the advantage to give directly an unambiguous information on the cationic site [33–36].

In this paper, three aluminosilicate systems are considered, $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ (LAS), $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ (MAS) and $\text{ZnO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ (ZAS) doped with TiO_2 to induce internal nucleation and with NiO to bring active optical ions. Although the luminescence properties have been widely investigated in such systems, a comprehensive and detailed understanding of the Ni^{2+} environment as a function of the chemical composition and heat treatment remains elusive. In order to better understand the effect of all the heat-treatment processes, especially around the optically active Ni^{2+} ions, we have combined different techniques: *in situ* high temperature (HT) X-ray diffraction (XRD) gives the crystallization sequence while optical absorption and *in situ* HT X-ray absorption spectroscopy (XAS) allow the determination of the Ni^{2+} environment and its evolution with time and temperature. The crystallization sequences are strongly different considering different glass matrices. We compare the influence of the glass matrix on the crystallization sequence and on the evolution of Ni environment.

2. Experimental section

2.1. Sample preparation

Lithium ($64\text{SiO}_2-24\text{Al}_2\text{O}_3-12\text{Li}_2\text{O}$), magnesium ($60\text{SiO}_2-20\text{Al}_2\text{O}_3-20\text{MgO}$) and zinc ($50\text{SiO}_2-25\text{Al}_2\text{O}_3-25\text{ZnO}$) aluminosilicate glasses were prepared with the addition of NiO and TiO_2 . Glasses were melted at 1580°C for 3 h with stirring, poured onto a cold plate and annealed at $640-680^\circ\text{C}$. The exact glass compositions are listed in Table 1. All precursor glasses are transparent with a brown coloration and amorphous according to X-ray diffraction.

2.2. Optical spectroscopy

Ultra-violet (UV)–visible–Near Infrared (NIR) optical absorption spectra of polished samples were acquired in transmission mode on a Perkin Elmer Lambda 1050 spectrometer in the range $2000-250\text{ nm}$ or $5000-40,000\text{ cm}^{-1}$. Absorbance spectra were normalized to thickness and NiO concentration.

2.3. X-ray diffraction

X-ray diffraction (XRD) patterns were collected *in situ* at high temperature using a PANalytical X'Pert PRO diffractometer with nickel-filtered $\text{Cu K}\alpha$ radiation and an Anton Paar HTK 1200 furnace. Data were acquired over an angular range $24^\circ \leq 2\theta \leq 60^\circ$ and with an acquisition time of 30 min on the glass at room temperature to check the amorphicity and on the glass-ceramic following preliminary studies [20,22,37]. The measurements were carried out on coarsely crushed powders to limit surface crystallization. The crystalline phases are determined with X-Pert High Score Plus software.

Table 1
Nominal glass composition (in mol%).

	SiO_2	Al_2O_3	MgO	Li_2O	ZnO	NiO	TiO_2
LAS-1.7Ni	59.41	22.27	–	11.13	–	1.62	5.57
LAS-3Ni	58.73	22.02	–	11.0	–	2.75	5.5
MAS	52.17	17.4	17.4	–	–	4.33	8.7
ZAS	45.05	22.52	–	–	22.52	1.8	8.11

2.4. X-ray absorption spectroscopy (XAS)

The Ni K-edge XAS spectra were obtained on the SAMBA beamline at SOLEIL synchrotron using a Si(111) crystal monochromator. Data were collected in transmission geometry on polished slabs for the glass and glass-ceramic samples and on powdered pellets for the crystalline references. Energy calibration is determined with a metallic Ni foil. The *in situ* temperature measurements are realized in a Linkam heating stage. Quick-XAS spectra mode allows acquisition time of about 1 s and data were averaged over 60 scans. Spectra of crystal references with different Ni^{2+} coordination sites were recorded for comparison (four-fold coordination $^{14}\text{Ni}^{2+}$: NiCr_2O_4 ; five-fold coordination $^{15}\text{Ni}^{2+}$: KNiPO_4 ; six-fold coordination $^{16}\text{Ni}^{2+}$: NiO and NiAl_2O_4 spinel).

Standard XAS analysis was performed using the Athena software [38]: an averaged XAS spectrum is normalized to the absorption edge height and the background is removed using the automatic background subtraction routine AUTOBK. The background is interpolated over several eV intervals below and above the pre-edge using an arctan function and pre-edge information is derived by fitting a pseudo-Voigt function using the program Fityk [39]. Error bars are determined from a statistical analysis of the fitted values over a region where the pre-edge intensity does not vary.

3. Results

3.1. Precursor glasses

Fig. 1 shows the Ni K-edge XANES (X-ray Absorption Near Edge Structure) spectra of different aluminosilicate glasses compared to that of KNiPO_4 crystalline reference characteristic of $^{15}\text{Ni}^{2+}$. The spectrum for the MAS glass has been studied in detail in another paper [40]. Very small differences can be observed between all these spectra. The main edge at 8350 eV (peak B) does not change in position but its intensity is more intense for the MAS glass and less intense for the ZAS and LAS glasses. A lower intensity could be due to less distorted sites or a lesser amount of $^{14}\text{Ni}^{2+}$ sites. There is also a shift towards low energies of the first EXAFS (Extended X-ray Absorption Fine Structure) oscillation near 8400 eV of the LAS and ZAS glasses compared to the MAS glass. This indicates that the former glasses have larger Ni–O distances, in agreement with less $^{14}\text{Ni}^{2+}$ sites.

The pre-edge at $\sim 8334\text{ eV}$ (peak A) comes from transitions to partly filled $3d$ levels. Its intensity is higher for tetrahedral symmetry (Td) with strong p–d hybridizations and lower for octahedral symmetry (Oh) in which the transitions are dipole-forbidden [41]. Consequently, the pre-edge intensity can be related directly to average local coordination [42,43], as confirmed for crystalline references (Table 2): higher intensity means lower average coordination number. The variation in peak position is small and not significant. The pre-edge analysis for the glasses (Table 2) confirms the trend observed on the XANES region: the lower pre-edge intensity for the LAS and ZAS glasses indicates fewer $^{14}\text{Ni}^{2+}$ sites than for the MAS glass; the increase of the NiO concentration in LAS glass does not influence the Ni^{2+} environment.

Optical spectra for the glasses (Fig. 2) are very similar to each other and to previously studied Ni-doped silicate and aluminosilicate glasses [43]. They are dominated by the band at $\sim 22,900\text{ cm}^{-1}$ which is assigned to fivefold coordinated Ni^{2+} in trigonal bipyramid, as well as the bands at $18,450\text{ cm}^{-1}$, $11,500\text{ cm}^{-1}$ and 5920 cm^{-1} . They correspond to transitions from the ground state $^3E'(F)$ to excited ones $^3A'_2(P)$, $^3E'(P)$, $^3A'_2(F) + ^3A''_{1(2)}(F)$ and $^3E''(F)$ [43]. Weak bands corresponding to four-fold coordinated $^{14}\text{Ni}^{2+}$ ions, at $13,720\text{ cm}^{-1}$ and $\sim 16,200\text{ cm}^{-1}$ (associated with transitions from the ground state $^3T_1(F)$ to excited ones $^1E(D)$ and $^3T_1(P)$ [43]) are present in smaller amount than ^{15}Ni sites. The detailed interpretation of such absorption spectra can be found in previous investigations [7,43]. Based on those results, we suggest that absorption of precursor glasses is predominately determined by five-coordinated $^{15}\text{Ni}^{2+}$ ions located in the amorphous glass matrix.

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