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Effect of alkali and alkaline-earth cations on the neodymium environment in a rare-earth rich aluminoborosilicate glass

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Abstract

The local structure around neodymium in an aluminoborosilicate glass bearing 3.6 mol% Nd_2O_3 is studied by optical absorption spectroscopy and EXAFS at the Nd L_{III}- and K-edges. The influence of the nature of alkalis ($M^+ = Li^+$, Na^+, K^+, Rb^+, Cs^+) and alkaline-earths ($M^{2+} = Mg^{2+}$, Ca^{2+}, Sr^{2+}, Ba^{2+}) on the coordination sphere of Nd^{3+} ions in the glass is particularly investigated. The Nd^{3+} sites are well-defined with Nd—O mean distances of 2.46 ± 0.03 Å, whatever the alkali and alkaline-earth ion type except Li^+ and Mg^{2+}, for which glasses exhibit slightly more disordered Nd sites and longer Nd—O distances (2.49 ± 0.03 Å). Using bond valence considerations, a model is proposed for the Nd site, and consists in 7–8 non-bridging oxygens (NBO), every NBO being charge compensated by 2–3 alkalis and alkaline-earths. The Nd—O mean distance is adjusted according to the mean field strength of these cations, to avoid overbonding of the NBO's. A glass series with varying Ca^{2+}/Na^+ concentration ratio shows that Nd^{3+} cations are able to maintain this average coordination site even at high alkaline-earth content.

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1. Introduction

A rare-earth rich aluminoborosilicate glass (about 10 wt% or 3.6 mol% RE_2O_3) has been designed for the immobilization of concentrated high-level nuclear waste (HLW) [1,2]. For the purpose of structural study, the composition of this glass has been restricted to seven oxides and is the following: (mol%) 61.81 SiO_2–3.05 Al_2O_3–8.94 B_2O_3–14.41 Na_2O–6.33 CaO–1.90 ZrO_2–3.56 RE_2O_3 (RE = Nd). Part of the rare-earth oxide simulates all the lanthanides and actinides occurring in HLW. The other part helps to incorporate the high amount of HLW and ensure good chemical durability and high glass transformation temperature. The present work is part of an extensive study of the structure and thermal stability of this multicomponent glass [1–3] and focuses on the structural position of the rare-earth cation. A first glass series with increasing amount of RE_2O_3 has put in evidence the modifying role of the RE^{3+} ion in this glass [2]. Moreover, the optical absorption and X-ray absorption spectra of RE^{3+} (RE = Nd) resemble the spectra of RE^{3+} in simple alkali silicate glasses, while they are dissimilar to the spectra of alkali borates or rare-earth aluminate glasses. This fact is not surprising as the network is dominated by SiO_4 tetrahedral units (72%), and is suspected to homogeneously incorporate smaller amounts of AlO_4^- units (7%), and BO_4^-, BO_3, BO_3^- units (21%) [4]. At last, no Nd—Nd clustering at distances less than 4 Å could be detected from Nd L_{III}-edge EXAFS in these studies [2].

Then, a structural model has emerged for the rare-earth cation in this glass, in which RE^{3+} enters a

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coordination sphere with several non-bridging oxygens (NBO, which are bonded to one network former and to several non-framework cations such as alkali or alkaline-earths) mainly connected to silicate units, and is surrounded by other modifying cations for its charge compensation. In the seven-oxide glass, these cations are Na^+ and Ca^{2+}, but a great variety of neighboring cations must be assumed in the nuclear glass with complete composition. The RE^{3+}, modifying cations and NBO's probably form depolymerized regions throughout the network, according to widely accepted models of glass structure [5,6], though their extent is matter of debate. To improve this model, we now investigate how the distribution of sites of the rare-earth ion may be dependent on the nature of the surrounding alkali and alkaline-earth ions. This investigation aims to explore the variety of RE^{3+} sites in the nuclear glass and reveal possible links to its chemical stability. Secondly, we expect to get a better insight into the details of the distribution of sites for RE^{3+} in the seven-oxide glass, *i.e.* the range of oxygen coordination, the mean parameters and distortion of the coordination sphere, and the identity of nearest neighbors.

Three glass series are studied: (1) A glass series with a varying R ratio, $R = 100 \times [CaO]/([CaO] \times [Na_2O])$; (2) A glass series with $R = 30$, $M^{2+} = Ca^{2+}$ and $M^+ = Li^+$, Na^+, K^+, Rb^+ or Cs^+; (3) A glass series with $R = 30$, $M^+ = Na^+$ and $M^{2+} = Mg^{2+}$, Ca^{2+}, Sr^{2+} or Ba^{2+}. The cation field strength is defined as z/r^2, where z is the charge of the cation and r its mean distance to oxygens. The three series cover a reasonably wide range of mean field strength (MFS) for the M^+ and M^{2+} cationic group, from 0.17 to 0.32, as estimated from expected cation-oxygen distances [7] (Table 1). Then, the features of the RE^{3+} environment will be discussed in term of the mean field strength of the cationic neighbours.

2. Experimental

Three series of glasses have been prepared with the reference composition given in the introduction and RE = Nd. The first series has a varying $R = 100 \times [CaO]/([CaO] + [Na_2O])$ ratio, with $R = 0$, 15, 30, 50, 70, 85. The corresponding glasses are referred to as «CaNaR». The two other series differ in the nature of the M^+ alkali ion («M^+» glasses), or of the M^{2+} alkaline-earth ion («M^{2+}» glasses), and have $R = 30$ as in the seven-oxide reference glass. The oxide powders were melted at 1300 °C for 3 h, then heated at 1400 °C for 15 min and quenched in water. The glass frit was ground and melted again at 1300 °C for 2 h to ensure good homogeneity. The melt was finally cast into glass cylinders of 1.4 cm diameter, which were annealed at $T_g + 20$ °C for 2 h, then cut and polished to get ~1 mm thick plates for the optical absorption study. For all the glasses, composition was checked by chemical analysis (ICP-AES) and/or electron probe microanalysis (EPMA), and corresponds within 2 mol% to the nominal composition.

Optical absorption spectroscopy was performed in transmission mode at $T \approx 10$ K, because at this temperature, only the lowest Stark level of the $^4I_{9/2}$ ground state of Nd^{3+} is populated. Spectra were collected on the 400–950 nm range with a double-beam CARY-5E spectrophotometer, using a spectral band width SBW of 0.6 nm (instrumental resolution function is thus $25\ cm^{-1}$ at 500 nm), a data interval DI of 0.2 nm and 1 s acquisition time.

X-ray absorption spectroscopy (XAS) has been carried out at the synchrotron HASYLAB (Hamburg, Germany), on the E4 beamline for the Nd L_{III}-edge (6212 eV in these glasses) and on the high-energy X1 beamline for the Nd K-edge (43 592 eV in these glasses). Appropriate quantities of glass powder to get about 1 order of magnitude of

Table 1
Position of the $^4I_{9/2} \rightarrow {}^2P_{1/2}$ optical absorption band and best-fit EXAFS parameters of the Nd—O coordination shell

Glass sample	MFS ($Å^{-2}$)	$^4I_{9/2} \rightarrow {}^2P_{1/2}$ band center ($\pm 4\ cm^{-1}$) at 10 K	XAS exp.: Edge and Temperature	dNd—O (Å)	σ^2 ($Å^2$)	3^d cum. ($\times 10^{-4}\ Å^3$)	4^{th} cum. ($\times 10^{-5}\ Å^4$)
CaNa0	0.17	23 212	L_{III}, 6 K	2.447 ± 0.010	0.027 ± 0.001	14 ± 5	60 ± 15
CaNa15	0.20	23 216	L_{III}, 6 K	2.456	0.0285	15	64
CaNa30	0.22	23 222	L_{III}, 6 K	2.462	0.028	15	60
CaNa50	0.26	23 228	L_{III}, 6 K	2.473	0.028	16	58
CaNa70	0.30	23 230	L_{III}, 6 K	2.483	0.028	15.5	54
CaNa85	0.32	23 233	L_{III}, 6 K	2.484	0.029	15	56
Li	0.28	23 238	K, 77 K	2.48 ± 0.015	0.011 ± 0.0025	14 ± 4	0
Na (=CaNa30)	0.22	23 222	K, 77 K	2.46	0.011	12	0
K	0.19	23 215	K, 77 K	2.46	0.010	12	0
Rb	0.18	23 211	K, 77 K	2.46	0.010	13	0
Cs	0.17	23 206	L_{III}, 77 K	2.45 ± 0.02	0.029 ± 0.003	18 ± 8	60 ± 20
Mg	0.27	23 234	L_{III}, 77 K	2.50	0.028	20	50
Ca (=CaNa30)	0.22	23 222	L_{III}, 77 K	2.46	0.028	13	65
Sr	0.20	23 222	L_{III}, 77 K	2.465	0.027	17	50
Ba	0.19	23 217	L_{III}, 77 K	2.47	0.027	17	50

The MFS is the mean field strength of the alkali and alkaline-earths cations, taking into account their relative proportions in the glass and expected M—O distances from addition of ionic radii [7]. The worst statistical error obtained over the series of spectra acquired and analysed in rigorously identical conditions, is indicated (three series).