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Influence of lanthanum on borosilicate glass structure: A multinuclear MAS and MQMAS NMR investigation

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ABSTRACT

The physical and chemical properties of silicate glasses containing rare-earth elements (REEs), either as dopants or at higher concentrations, are sensitive to the REE structural and chemical environment. An unambiguous role of REEs in the glass structure still remains difficult to define because many configurations may exist and are strongly composition-dependent. The structural configuration of lanthanum and its interactions with sodium and calcium are examined here in borosilicate glasses. The impact of lanthanum and calcium substituted for sodium on the boron speciation is investigated by ^{11}B MAS NMR. The resulting ^{29}Si MAS NMR spectra and their interpretations are discussed. A quantitative approach of ^{17}O MQMAS NMR data with the reconstruction of ^{17}O NMR parameter distributions provides an overview of lanthanum distribution and its interactions with the other cations in the vitreous network. No clustering of lanthanum atoms is observed; they are uniformly distributed in the glass structure, surrounded by about 6 non-bridging oxygen atoms and mixed with sodium and calcium atoms to the detriment of the number of BO_4 groups. These data provide a better understanding of the addition of rare earths in the glass and of the conditions favorable to their uniform distribution in soda-lime borosilicate glass matrices.

1. Introduction

Glasses doped with rare-earth elements (REEs) are of great interest for applications in many fields, including optical fibers, amplifiers, laser waveguides and magneto-optical devices [1]. Other applications lead to higher REE concentrations, such as borosilicate glasses for high-level radioactive waste produced by reprocessing spent fuel. REEs are found as fission products in the glass packages and may also be used as surrogates for minor actinides [2]. The precise role of REEs in the glass structure, however, has not been clearly defined because many configurations may exist and are strongly composition-dependent. The structural configuration of the rare earth element, its local environment, and its distribution in the vitreous matrix may influence its properties, such as chemical durability (and long term performance [2–4]) or its physical properties [5]. Although the REEs in silicate glasses are expected to break up the network and decrease the viscosity [6], it has been pointed out that they may increase the hardness of the glass [7]. They could act as "intermediate" cations between a depolymerization role resembling network modifiers and a stabilization role of anionic species due to their high field strength (defined as the ratio of the cation charge to the square of the cation-oxygen bond length) resembling network formers (Si, Al, B).

These trivalent ions result in a more negatively charged local environment and may lead to major structural changes compared to alkalis. Whereas sodium silicate glasses have an extended domain without phase separation [8], the rare-earth silicate glass domain is more limited. REE ions have limited solubility in silicate glass and may form clusters [9,10]. Fluorescence line narrowing (FLN) was used in europium-doped silicate glass to reveal Eu^{3+} clustering [11]. Phase separation in sodium-aluminoborosilicate glasses was attributed to gadolinium cations partitioning to the borate-rich environments [12], constituted of Gd-metaborate species [13]. The addition of a network former with a charge deficit such as $[AlO_4]^-$ may facilitate the dispersion of REE within the glass by using a fraction of them as charge compensators [14,15].

In alkali silicate glasses, Schaller et al. [16] using ^{29}Si MAS NMR estimated an increase in polymerization when one lanthanum atom was substituted for three sodium atoms. It was thus suggested that several percent of oxygen atoms formed so-called free oxide ions (O^{2-}) that is not bound to any silicon atoms but instead associated with La^{3+} ions only. Such free oxides were mainly observed in molecular dynamics (MD) simulations [14,17]. These species are expected in highly depolymerized low-silica compositions such as "sub-orthosilicate" glasses ($SiO_2 < 33$ mol%) in which they have been inferred from ^{29}Si 2D MAS NMR [18] and detected by ^{17}O NMR [19]. The authors showed that

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in alkaline-earth silicate glasses the formation of Q^1 favors the formation of O^{2-} ions bound only to Mg^{2+} and Ca^{2+} cations. However, O^{2-} species have not been observed by ^{17}O NMR in glass with higher silica content [20]. Conversely, a high proportion of O^{2-} (>5%) was suggested by oxygen 1s XPS in sodium and potassium silicate glasses but from indirect determination of the number of bridging oxygen atoms [21,22]. Recent ^{17}O MAS NMR measurements did not detect, however, these species in potassium silicate glasses [23].

The local environment of REE was also probed by Raman spectroscopy [6,16,13], X-ray absorption spectroscopy (XAS) and neutron diffraction [24–27] with no evidence of clustering in sodium silicate glasses [28,25,27] as well as in more complex glasses [29]. MD simulation indicated a dependence of glass chemical composition on europium or erbium coordination with a coordination number varying from around 4 to 5 in silicate glass to around 6 in sodium silicate glass [30,14,15,31,32]. A coordination number of about 6 has been experimentally confirmed by EXAFS for almost all REEs in lanthanide-bearing sodium disilicate glass [27]. Simulations usually report a significant decrease of REE clustering in sodium silicate glasses that breaks up clusters forming RE–O–(Si,Na) units. The increase in the number of nonbridging oxygens (NBOs) leads to a more homogeneous REE distribution in the glass structure [30,33]. The REE coordination has been found higher in complex soda-lime aluminoborosilicate glasses investigated by EXAFS, with coordination numbers between 6 and 8 [2,3,34,35].

In this work, the effect of lanthanum in the borosilicate glass structure (used as glass models simulating nuclear waste containment glass) was investigated as well as its interactions with lower field strength cations, sodium and calcium, using complementary experimental techniques such as ^{29}Si, ^{11}B and ^{17}O MAS and ^{17}O MQMAS NMR. Two glass series, containing lanthanum oxide or calcium oxide at the expense of sodium oxide, were used to shed light on similarities between these cations. ^{29}Si may provide information about the degree of polymerization in simple glasses [36], but mainly depends on the nature of the second-neighbor atoms [37–40]. ^{11}B MAS NMR gives information about the interactions between elements within the borosilicate network from boron speciation; the proportion and the nature of charge-compensating cations of $[BO_4]^-$ species can thus be estimated according to variations in the glass chemical composition [41,42]. Oxygen-17 constitutes a central NMR probe of the entire glass network which has been successfully applied to various borosilicate glass compositions [43–50,23]. The quantitative approach of ^{17}O MQMAS spectra constitutes a powerful tool to deeper investigate the environment of each nucleus in oxide glasses [49,51]. This approach enables the reconstruction of the three-dimensional NMR parameter distributions (quadrupolar parameters C_Q, η_Q and isotropic chemical shift δ_{iso}) for each oxygen sites, taking into account the effects of correlation among NMR parameters [52]. Model glasses with increasing complexity were thus investigated by ^{17}O NMR.

2. Experimental

2.1. Glass synthesis

Two series of borosilicate glasses were synthesized: one containing lanthanum oxide substituted for sodium oxide (0Ca*x*La series: $60SiO_2$–$20B_2O_3$–$(20 - x)Na_2O$–xLa_2O_3 where $x = 0, 1, 2, 4, 8, 10$) and the other without lanthanum but containing calcium oxide substituted for sodium oxide (*x*Ca0La series: $60SiO_2$–$20B_2O_3$–$(20 - x)Na_2O$–$xCaO$ where $x = 0, 4, 8, 10$). These glasses were produced by mixing suitable amounts of analytical grade H_3BO_3, SiO_2, Na_2CO_3, CaO, and La_2O_3 (100 g batches). The powder mixture was decarbonated for 1 h at 700 °C and melted between 1300 °C and 1450 °C for 3 h. The glasses were quenched in air and crushed before refining (second melt) for 2 h at 1300 °C or 1450 °C to ensure their homogeneity. The glass composition was verified by alkaline fusion and ICP analysis. Nanoscale glass homogeneity was checked by transmission electron spectroscopy (TEM) for the glass with higher La content.

Oxygen-17 enriched samples were synthesized from alkoxides hydrolyzed by ^{17}O-enriched water (between 70% and 90%). All the oxides of the glass were thus enriched according to the method described elsewhere [48]. The mixture was heated to 1100 °C in a furnace for 30 min in argon atmosphere. Both series were synthesized: a ternary sodium silicate glass containing lanthanum and two more complex sodium borosilicate glasses, one containing calcium and the other containing both calcium and lanthanum. The glass samples were chemically analyzed by alkaline fusion (NaOH + KNO_3 and $Li_2B_4O_7$, $5H_2O$) of glass powder, then recovered in HNO_3 for ICP-AES analysis. The analyzed molar compositions are indicated in Table 1.

2.2. NMR spectroscopy

^{11}B and ^{17}O MAS NMR spectra were collected on a Bruker Avance II 500WB NMR spectrometer (magnetic field strength 11.72 T) with a 4 mm CPMAS probe. The spinning frequency was 12.5 kHz or 14 kHz for all experiments. ^{29}Si MAS NMR spectra were collected on a Bruker Avance I 300WB spectrometer (magnetic field strength 7.02 T) with a 4 mm CPMAS probe at a spinning frequency of 10 kHz.

2.2.1. ^{29}Si MAS NMR ($I = 1/2$, $\nu_o = 59.4$, 7.02 T)

Spectra were acquired using a CPMG pulse sequence [53] by accumulating typically 32 echoes with a delay of 2–3 ms between consecutive 180° pulses. The echoes were then summed up to obtain the spectrum. A 20 s recycle delay was used (no change in the lineshape was observed for longer recycle times, as confirmed by measurements with 200 s and 1200 s). The spectra are referenced to an external sample of tetrakis(trimethylsilyl)silane for which the highest intensity peak is situated at −9.9 ppm from that of liquid TMS.

2.2.2. ^{11}B MAS NMR ($I = 3/2$, $\nu_o = 160.14$ MHz, 11.72 T)

A short pulse (tip angle π/12 with a pulse length of 1 μs) was used to ensure a quantitative spectrum [54] with a recycle delay of 2 s. Chemical shifts are referenced to an external sample of 1 M boric acid solution (19.6 ppm). The contribution of the satellite transitions (STs) to the centerband was eliminated by subtracting the same spectrum shifted by the rotation frequency. The detailed experimental parameters have been indicated elsewhere [41]. This typically yielded a correction of 2–3% on the BO_4 population.

2.2.3. ^{17}O MAS and MQMAS NMR ($I = 5/2$, $\nu_o = 67.67$ MHz, 11.72 T)

The MQMAS spectra were acquired with 64 t_1 increments of one rotation period in the first dimension and a 1 s repetition time (4500 FIDs per t_1 value). The Z-filter pulse sequence [55] was used with first and second pulse durations of 7 μs and 2.6 μs, respectively (RF field 60 kHz), and a third 90° soft pulse selective on the central transition of 5.5 μs (RF field 15 kHz) [56]. ^{17}O MAS spectra were acquired using a Hahn echo pulse sequence, with soft 90° and 180° pulses (selective on

Table 1
Analyzed glass compositions (mol%), tetrahedral boron atom (from ^{11}B MAS NMR) and calculated non-bridging oxygen populations.

Mol%	Non-enriched									^{17}O enriched		
	0Ca*x*La						*x*Ca0La			5La	12Ca	5Ca4La
	0La	1La	2La	4La	8La	10La	4Ca	8Ca	10Ca			
SiO_2	62	62	62	60	59	58	62	63	62	60	56	55
B_2O_3	18	17	18	18	19	20	18	17	18	–	18	17
Na_2O	20	20	18	18	14	12	16	12	10	35	14	20
CaO	–	–	–	–	–	–	4	8	10	–	12	5
La_2O_3	–	1	2	4	8	10	–	–	–	5	–	4
$\%B^{IV}$	71	66	62	52	41	35	64	57	53	–	57	54
$\%NBO_{th}$	8	12	13	19	27	31	8	10	10	57	16	28