



# Rare-earth silicate crystallization in borosilicate glasses: Effect on structural and chemical durability properties



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## ABSTRACT

Due to their low solubility, some elements, such as lanthanides, can lead to crystalline phases in borosilicate glass during cooling. The impact of rare earth (lanthanum and neodymium) silicate crystallization on glass structural configuration as well as on glass chemical durability was investigated in soda-lime borosilicate glasses. Partially crystallized glasses containing a single  $\text{Ca}_2\text{RE}_3(\text{SiO}_4)_6\text{O}_2$  (RE = La, Nd) phase (ranging from 1 to 36 wt.%) were synthesized by heat treating homogeneous glasses. Structural characterizations of vitreous and crystalline parts were carried out by  $^{29}\text{Si}$ ,  $^{11}\text{B}$ ,  $^{23}\text{Na}$  and  $^{17}\text{O}$  MAS and MQMAS NMR. The crystallization leads to a reorganization of the cation distribution around the rare earth elements. By keeping a part of the lanthanum and the calcium, crystallization causes a decrease in the number of NBOs in the vitreous part. A part of the sodium, initially near the lanthanum, becomes available to form Si–O–Na bonds and to convert trihedral boron into tetrahedral boron. Through the study of the alteration of different materials – homogeneous, crystallized and surrounding glasses, rare earth silicate ceramics, and separated mixtures of glass and crystals – a precise description could be made of the influence of the presence of crystals has on chemical durability. For the various alteration regimes, it was thus shown that the alteration kinetics increase proportionally to the crystal content, and that apatite-type crystals do not lead to a composition gradient on the glass–crystal interface. Although the crystals formed were more durable than the vitreous matrix, the chemical durability of partially crystallized glasses depends on the composition and structure of the surrounding glass.

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## 1. Introduction

A growing number of vitreous materials incorporate Rare Earth Elements (REEs). These elements, used to dope the materials, can improve the properties of glasses used for optical applications [1,2]. Lanthanum, an element of interest in health applications with bioglasses [3,4], could also enable a better control of the release of elements necessary for bone regeneration by making the structure of borate glasses more stable [4,5]. Vitreous matrices may also be used to confine lanthanides such as fission products from the highly radioactive waste produced by nuclear industry spent fuel recycling [6]. For new types of waste, partially crystallized vitreous matrices could be foreseen. During cooling, elements that are weakly soluble in glass like REEs, can lead to crystallizations [7,8], modifying the material's macroscopic properties (viscosity, thermal conductivity, aqueous alteration). For the disposal of highly radioactive waste packages in deep geological repositories, it is necessary to have the best possible understanding of

the long-term behavior of the containment matrices, in particular of their interactions with groundwater [9]. While the chemical durability of homogeneous matrices has been widely studied [10–13], a clear understanding of the behavior of partially crystallized vitreous matrices remains to be established.

Our recent work on the chemical durability of borosilicate glasses containing sodium molybdate crystals (obtained by a phase separation process) illustrated the role of highly crystals in aqueous solution [14]. In particular, it was shown how structural and chemical modifications of the glass surrounding the crystals evolved when the crystal content increased, and to what extent the surrounding glass controlled the leaching kinetics. The study presented here focused on the influence of crystals which are less soluble in water than the vitreous matrix and examined the apatite-structure rare earth silicates formed by crystallization during melt cooling. Soda-lime borosilicate compositions containing neodymium or lanthanum were used, as they enable the formation of just a single crystal phase in quantities which vary depending on the thermal treatment applied. This simplified system made it easier to investigate the role of crystals both in the surrounding glass structure and in its chemical durability.

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Previous studies on the role of rare earths in the structure of homogeneous borosilicate glasses [15] and their leaching behavior [16,17] contributed information regarding the local structure of pristine and altered glasses. From data obtained by Raman spectroscopy,  $^{29}\text{Si}$  and  $^{11}\text{B}$  MAS NMR,  $^{17}\text{O}$  MQMAS NMR, EXAFS at the La  $L_3$ -edge, and fluorescence line narrowing, the relationships between the local structural environment around the rare earth, the chemical composition of the glass, and its behavior during aqueous alteration were established.

These data showed that for soda-lime borosilicate glasses, lanthanum was homogeneously distributed within the vitreous structure, with no lanthanum ion clustering for contents of up to at least 10 mol%<sup>15</sup>. In these 5-oxide glasses, the rare earth was surrounded by about 6 non-bridging oxygens (NBOs), and the compensation for the additional negative charges related to the presence of an excess of NBOs came from other cations having similar ionic radii to lanthanum, i.e. sodium and/or calcium. The compensation on these sites took place at the expense of tetrahedral boron; the greater the quantity of lanthanum in the glass, the more sodium was mobilized within these structural units. Part of the boron charge compensating sodium was therefore transferred to the rare earth, and so the amount of trihedral boron increased. It is worth noting that this behavior could be different in borate glasses, where the rare earth can directly compensate for  $\text{BO}_4$  units. In this case, it was seen that variations of the sodium to lanthanum ratio only slightly modified the boron coordination [5].

To study the aqueous alteration of glass, different kinetics regimes may be examined separately: the forward dissolution rate, the rate drop, which occurs during the formation of an alteration layer on the glass surface, and the long-term rate, called the residual rate, obtained after amorphous silica saturation is reached in the solution [12]. In the forward dissolution rate regime, more direct relationships can be established between the kinetics of element release from the glass and its structure [18]. With increased lanthanum content in the glass, the forward rate decreases dramatically [19]. It appears that the lanthanum ion surrounded by about six silicon atoms in its environment [15] strengthens the silicate network against hydrolysis. As the rare earth is surrounded by ionic bonds, it is not as strongly bonded to the silicate network over the long term as other elements, like zirconium, which though having a similar coordination, make stronger covalent bonds [20–22]. In these conditions, the reorganization of the silicate network around the rare earth is possible, and the silicon can, more freely than with zirconium atoms, re-condense within the alteration layer and thus participate in its passivation. Thus the long term alteration kinetics decrease with the increase of glass rare earth content [16].

The objective of this work was to investigate structurally heterogeneous vitreous systems in order to evaluate the effects of the presence of crystalline phases on glass chemical durability. Lanthanum and neodymium are found as fission products in nuclear glasses, and can be used as surrogates for minor actinides [7,23]. Suitably-adapted heat treatments can enable an apatite-type crystalline phase to be obtained in this type of glasses [7]. By varying the thermal treatments of the vitreous materials, the influence of the crystalline phase content on glass alteration was evaluated from the  $\text{Ca}_2\text{RE}_8(\text{SiO}_4)_6\text{O}_2$  crystal compositions, with RE = La or Nd. The influence of the different parameters related to crystallization (amount of crystals, glass–crystal interface, and vitreous phase composition) on alteration, as well as the effect of the nature of the rare earth, is discussed in this paper.

## 2. Experimental

### 2.1. Glass, partially crystallized glass and ceramic synthesis

Partially crystallized glasses were developed from two homogeneous glasses (called RE-H, with H for homogeneous):  $51.5\text{SiO}_2$ –

$16.6\text{B}_2\text{O}_3$ – $16.6\text{Na}_2\text{O}$ – $7.4\text{CaO}$ – $8.0\text{RE}_2\text{O}_3$  with RE = La or Nd (in mol%). The La and Nd bearing glasses were synthesized by mixing suitable amounts of reagent-grade oxides  $\text{SiO}_2$ ,  $\text{H}_3\text{BO}_3$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{CaO}$  and  $\text{La}_2\text{O}_3$  or  $\text{Nd}_2\text{O}_3$ . The mixtures were melted in a Pt–Rh crucible at 1300 °C for 3 h. Glasses were quenched in air and crushed before a second melt for 1 h at 1300 °C to ensure homogeneity. Glass compositions were checked by alkaline fusion and Inductively Coupled Plasma–Optical Emission Spectroscopy (ICP-OES). The glass molar composition analysis results are given in Table 1 (La–H and Nd–H).

To prepare crystallized glasses, these two homogeneous glasses were crushed into powder (<20  $\mu\text{m}$ ) to create a large number of interfaces between the glass grains, and heat treated in a Pt/Au crucible at various temperatures ranging from 720 °C to 800 °C, for durations of between 15 and 30 min. These conditions were chosen after characterization of RE-H glasses by DTA experiments. Glass transition and glass crystallization temperatures were thus obtained at a rate of  $10\text{ }^\circ\text{C}\cdot\text{min}^{-1}$  ( $T_{g\text{ La-H}} = 574\text{ }^\circ\text{C}$ ,  $T_{g\text{ Nd-H}} = 579\text{ }^\circ\text{C}$ ,  $T_{c\text{ La-H}} = 880\text{ }^\circ\text{C}$  and  $T_{c\text{ Nd-H}} = 875\text{ }^\circ\text{C}$ ). The resulting crystallized glasses were called RE-C- $x$  (with C for crystallized and  $x$  the crystalline weight content). Due to the high mixing between glass and crystal, it was not possible to analyze the surrounding glass only by electron microprobe. The surrounding glassy matrix compositions were thus determined from the degree of crystallization and the chemical composition of the crystals. Glasses whose compositions reproduced the surrounding glassy matrix composition of the crystallized glasses were synthesized following the protocol used for the two homogeneous glasses (RE-H). These homogeneous glasses are called surrounding glasses, RE-S- $x$  (with S for surrounding and  $x$  the crystalline weight content). Moreover, additional surrounding glassy matrices were synthesized (see Table 1). The glass molar composition analysis results are also indicated in Table 1. A glass with a similar composition to that of the La–H glass was synthesized (La H- $^{17}\text{O}$ ) from alkoxides hydrolyzed by  $^{17}\text{O}$ -enriched water, so that all the oxides of the glass were enriched according to the method described elsewhere [21]. The mixture was melted for 25 min at 1200 °C in argon atmosphere to avoid exchange with  $^{16}\text{O}$ . After structural investigations, this glass was treated at 780 °C for 45 min in argon atmosphere to obtain a highly-crystallized glass enriched in  $^{17}\text{O}$ , called La-C- $^{17}\text{O}$ - $x$  (with C for crystallized and  $x$  the crystalline weight content).

Ceramics  $\text{Ca}_2\text{RE}_8(\text{SiO}_4)_6\text{O}_2$  were prepared with a protocol inspired by Kidari et al. [7]. To avoid any secondary phases, the reagent-grade oxides were calcined at 400 °C ( $\text{SiO}_2$ ,  $\text{CaCO}_3$ ) and 1000 °C ( $\text{Nd}_2\text{O}_3$ ,  $\text{La}_2\text{O}_3$ ) and then suitable amounts were mixed in an agate mortar. After heating for 12 h at 1500 °C, the samples were crushed into powder and sieved down to 63  $\mu\text{m}$ . The powders were then pressed into cylindrical pellets at a pressure of 1.5 bars in a 13 mm stainless steel die and sintered at 1500 °C for 100 h to obtain a densification rate greater than 92%. From these ceramics, mixtures were prepared by mixing suitable amounts of surrounding glass and ceramic to reproduce the crystal/glass proportions of the highest crystal content for each rare earth system. These mixtures were called RE-M (with M for mixtures).

**Table 1**

Composition of the vitreous part of the homogeneous and crystallized glasses in the lanthanum and neodymium series. The compositions of the homogeneous glasses (RE-H) are the results of analyses, while those of the surrounding glasses (RE-S) were calculated based on the crystal content and the composition analyses for the associated homogeneous glass. The compositions are expressed in mol% of oxides.

	La H- $^{17}\text{O}$	La H	La S-9.5	La S-26	La S- $^{17}\text{O}$ -36	Nd H	Nd S-1	Nd S-4	Nd S-15	Nd S-26
$\text{SiO}_2$	53.3	52.0	52.2	52.4	54.2	51.9	51.9	51.9	52.0	52.0
$\text{B}_2\text{O}_3$	14.2	15.8	16.7	18.3	17.9	16.6	16.7	17.0	18.1	19.2
$\text{Na}_2\text{O}$	14.5	16.9	17.8	19.6	18.3	16.7	16.8	17.1	18.2	19.3
$\text{CaO}$	9.5	7.8	7.3	6.3	7.6	7.0	7.0	6.8	6.1	5.4
$\text{La}_2\text{O}_3$	8.4	7.5	6.1	3.4	2.0	–	–	–	–	–
$\text{Nd}_2\text{O}_3$	–	–	–	–	–	7.9	7.7	7.3	5.6	4.0

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