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Mariona Tarrago, Charles Le Losq, Thibaut Robine, Solenn Reguer, Dominique Thiaudière, et al..
Redox-induced crystallisation in Ti-bearing glass-forming melts: a Ti K-edge XANES study. *Materials
Letters*, 2022, 319, pp.132296. 10.1016/j.matlet.2022.132296 . hal-03857140

HAL Id: hal-03857140

<https://hal.science/hal-03857140>

Submitted on 17 Nov 2022

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Redox-induced crystallisation in Ti-bearing glass-forming melts: a Ti K-edge XANES study

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Abstract

Ti is usually tetravalent in silicate glasses. It may be trivalent under very reduced conditions, but this remains unclear. In this study, *in situ* Ti K-edge XANES experiments were performed on four different Ti-bearing melts, equilibrated at high temperatures using a micro-furnace with controlled atmosphere. No formation of Ti³⁺ was observed, even at $fO_2 \sim 10^{-15}$ (estimated). Instead, systematic crystallization of the melts was observed. In experiments at $fO_2 \leq 10^{-12}$, the system favours Ti⁴⁺ crystallization instead of reduction to Ti³⁺ in the studied melts. Fluxing melts with reduced gas mixtures, like Ar-2% H₂, may be a novel way to induce surface crystallisation and produce ceramic-coated glass materials.

Keywords: titanium, glass, melt, crystallization, XANES, redox

Highlights

- Only Ti⁴⁺ was found at high temperature in silicate melts at fO_2 between 0.21 and 10^{-6}
- Ti-bearing melts systematically crystallize above 1500 °C under very reducing atmospheres
- Crystallisation might be preferred to reduction

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1. Introduction

Controlled crystallization gives ceramic and glass-ceramic products with enhanced strength or hardness, broadening their range of applications. Many studies focus on crystallization-related key issues such as nucleating agents, which enhance nucleation and crystallization kinetics to produce novel materials [1]. One of those agents is Titanium, Ti. TiO₂-bearing glasses and glass-ceramics have applications in several fields including biomaterials, laser materials and optical fibres [2-4]. In glasses, Ti is usually tetravalent (e.g., [5-7]). Ti³⁺ may appear under very reduced conditions, potentially relevant for the young Earth [8] or for material properties [9]. Unfortunately, the conditions for Ti⁴⁺-Ti³⁺ redox changes remain elusive.

In the present study, Ti K-edge XANES experiments are conducted on melts equilibrated at high temperature in a micro-furnace [7, 10] with a controlled atmosphere. Four compositions were studied: one synthetic analogue of the Lunar Orange glass collected during the Apollo missions (LO glass), a wollastonite composition containing 5 mol% TiO₂ (CT50.05), a Ti-bearing nepheline composition (NAT50.25.18), and the SiO₂-TiO₂ ULE glass from Corning Inc. Those compositions were selected because (i) the LO and ULE glasses represent natural and industrial Ti-rich compositions, respectively, and (ii) the CT50.05 and NAT50.25.18 are glasses with well-known structure containing different Al concentrations and also different network-modifying cations (Ca and Na).

2. Material and methods

The LO, CT50.05 and NAT50.25.18 glasses were prepared following [7]. The ULE® glass was made by Corning Inc. (Corning Code 7972). Nominal glass compositions are reported in Table 1. Unpolarized Raman spectra were recorded using a T64000 Jobin-Yvon® Raman spectrometer and a Coherent® Innova 70-C5 Ar⁺ laser operating at 514.532 nm [7, 10].

Table 1: Nominal chemical composition (mol%) of the glasses analysed in this study.

Sample	SiO ₂	Al ₂ O ₃	Na ₂ O	K ₂ O	CaO	MgO	TiO ₂	FeO _{tot}	MnO	Cr ₂ O ₃
Lunar orange	39.79	3.70	0.40	0.03	8.15	22.13	6.55	18.75	0.24	0.27
NAT50.25.18	50.00	18.75	25.00				6.25			
CT50.05	49.66				49.66		0.69			
ULE®	93.00						7.00			

In-situ Ti K-edge XANES data were collected on the DiffAbs beamline at SOLEIL synchrotron, France. A Double Crystal Monochromator equipped with two Si(111) crystals was used to tune the energy. XANES spectra were collected in fluorescence mode using a four-element detector (SDD, Vortex-ME4®, Hitachi) set at 90° from the incident beam. XANES spectra were collected between 4920 and 5200 eV, with steps of 2 eV

before 4960 eV, 0.3 eV between 4960 and 4980 eV, 0.6 eV between 4980 and 5010 eV, 1 eV between 5011 and 5100 eV, and 2 eV above 5102 eV. Energy was calibrated against the first inflection point of the Ti K-edge XAS spectrum of a Ti metal foil (Fig. 1, 4966.4 eV). Energy resolution was of 0.3 eV at the Ti K-edge. Acquired spectra were normalized using the Athena software [11].

The samples were oriented at 45° from the incident beam, in the microfurnace [7]. Temperature can be varied up to 2000 K with a precision of ± 10 K [7]. fO_2 was set by fluxing air ($fO_2 = 0.21$), N_2 ($fO_2 \sim 10^{-6}$) or Ar-2% H_2 ($fO_2 \sim 10^{-15}$). Desired temperatures are reached within seconds, and fO_2 takes ~ 5 minutes to reach equilibrium. fO_2 values are estimated from the nominal oxygen concentration in each gas.

Reference Ti K-edge XAS spectra from rutile, brookite, anatase, benitoite, fersnoite, ilmenite, Ti_4O_7 and $TiCl_3$ were also acquired (figure 1). The pre-edge on the XANES spectra is linked to the transition from 1s energy levels to 3d molecular orbitals [12-14]. Energy shifts are related to changes in Ti valence and coordination [14]. The absorption edge shifts toward higher energies when oxidizing Ti from Ti^0 to Ti^{4+} (Fig. 1). Ti^{4+} is the valence in fersnoite, ilmenite, benitoite, brookite, rutile and anatase. Ti^{3+} is present in Ti_4O_7 and $TiCl_3$.

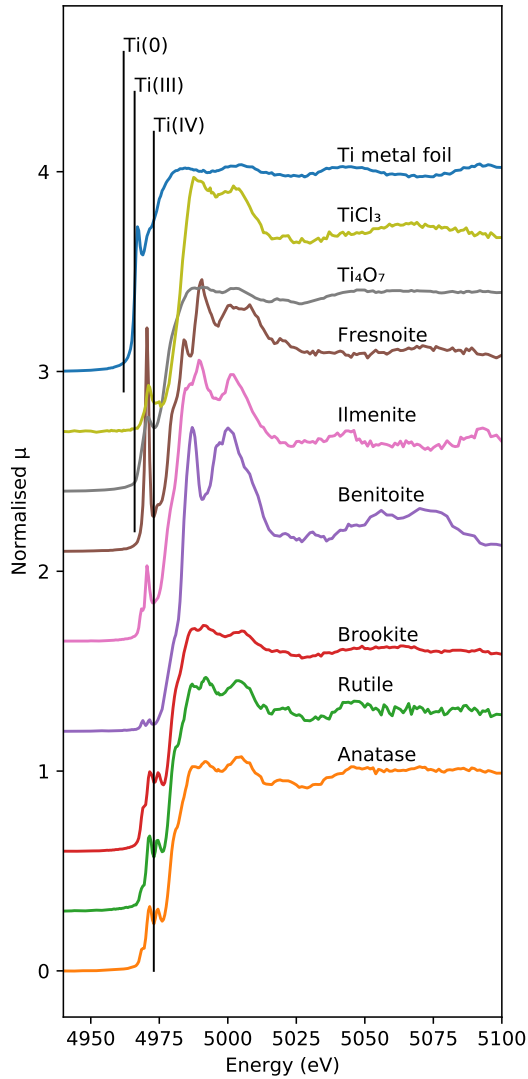


Figure 1: Ti K-edge XANES spectra of the reference materials. The vertical lines show the edge position for the 3 oxidation states of Ti.

3. Results

All Ti K-edge XANES spectra show a pre-edge peak at ~4970 eV (Fig. 2), indicating the presence of Ti⁴⁺ in all melts and glasses. The spectra of melts under air and N₂ ($fO_2 = 0.21$ and 10^{-6}) are similar to those previously reported for glasses [6,14], and are comparable between each other. The fO_2 change from 0.21 to 10^{-6} thus did not modify Ti environment, in agreement with previous findings [6, 15]. After equilibrating the melts under air and N₂ (Fig. 2), the furnace cell was flushed with Ar-2%H₂ gas for, at least, 10 min. Systematic rupture of the Pt wires happened in those conditions, ending the experiments and quenching the sample (quench rate > ~200 K/s). Therefore, only *post mortem* (PM) spectra were measured (Fig. 2); those exhibit multiple sharp oscillations, indicating that the melts crystallized as confirmed by Raman spectroscopy (Fig. 3). Indeed, Raman spectra of the starting glasses contain the characteristic broad bands of glasses including boson peak, but those of

PM Ar-2%H₂ runs show sharp, localized bands indicating crystallization. Among these crystalline phases, anatase was identified.

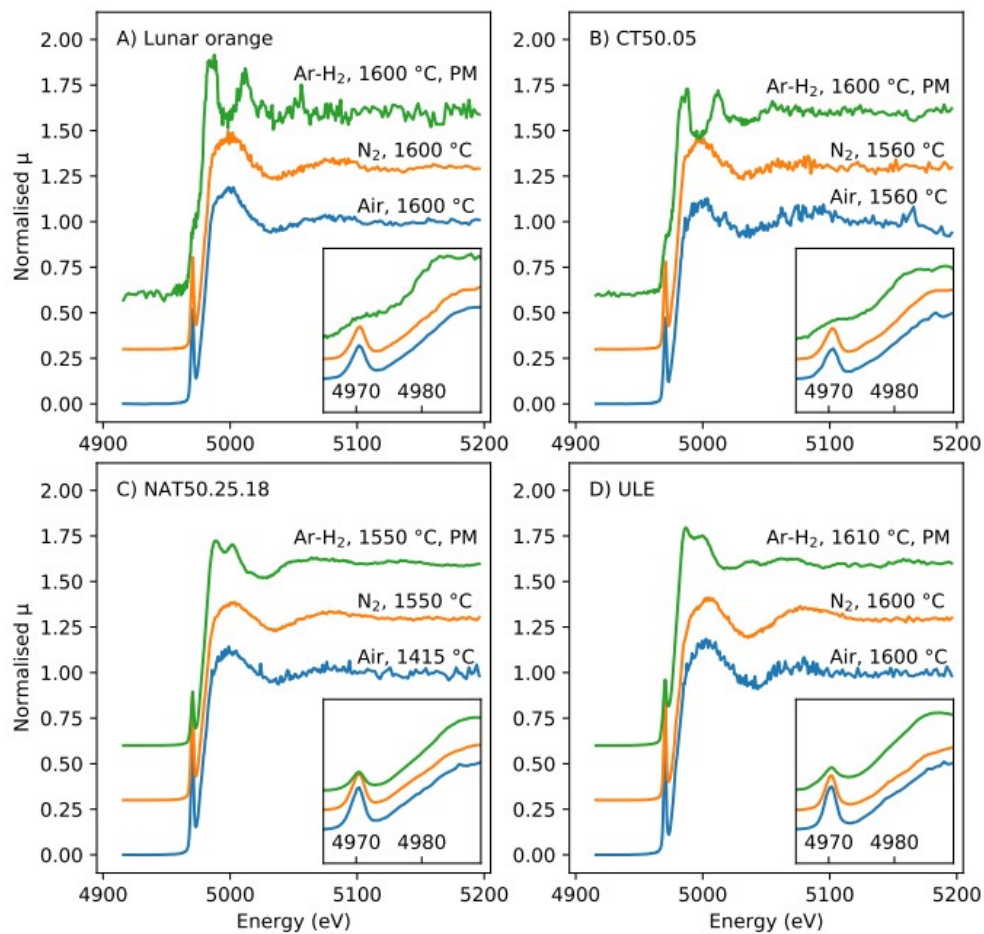


Figure 2: Example of Ti K-edge spectra collected during a given run in situ in air first and then N₂, and after Ar-H₂ fluxing (collected after the experiment, PM for Post-Mortem). The insets display a magnification of the pre-edge region.

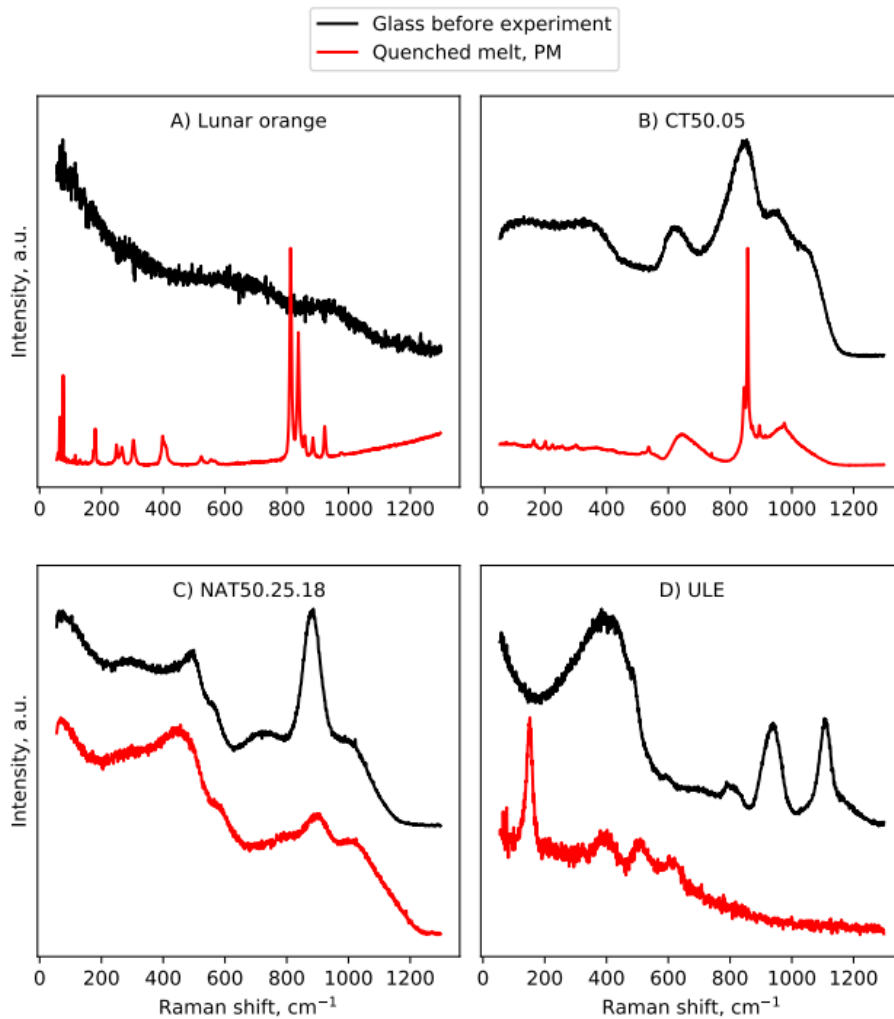


Figure 3: Raman spectra before and after the experiments shown in Figure 2.

4. Discussion

Literature evidence for Ti^{3+} in Ti-bearing silicate glasses is scarce. Ti^{4+} reduction in Ti^{3+} has been achieved using irradiation in silica and aluminoborosilicate glasses [16, 17]. $Li_2Si_4O_9$, $Na_2Si_4O_9$ and other sodium silicate glasses doped with Ti_2O_3 and fused at $fO_2 \sim 10^{-8}$ also appear to contain Ti^{3+} after quenching [9, 18]. However, those results are not consistent with other studies. For instance, glasses synthesised in CO-CO₂ furnaces at fO_2 reaching $10^{-12.9}$ only present Ti^{4+} [15]. Present results seem to agree with the latest observations: no evidence for Ti^{3+} was detected from XANES or from eventual colour changes of the glasses.

Instead, systematic crystallization of Ti-bearing phases happened at $fO_2 \sim 10^{-15}$. In another study, synthetic glasses with a composition analogous to that of lunar glasses crystallized during experimental runs at fO_2 between $10^{-12.9}$ and 10^{-15} [25]. Therefore, reducing conditions may favour Ti^{4+} precipitation in minerals. This is consistent with the influence of fO_2 on phase diagrams of Fe-bearing melts. For example, under an increasingly reducing atmosphere, the mineral assemblages in the MgO-CaO-Al₂O₃-FeO-Fe₂O₃-SiO₂ system and its associated subsystems crystallize at progressively lower temperatures, and crystal-free products become

scarcer [19]. Here, crystallization of Ti⁴⁺-bearing phases seems also to be favoured over Ti reduction in the most reduced atmosphere.

5. Conclusions

Ti K-edge XANES experiments on silicate melts at high temperature indicate that Ti⁴⁺ is dominant at fO_2 above 10^{-6} and temperatures reaching 1600 °C. Under a reduced Ar-2% H₂ atmosphere, the melts systematically crystallized Ti⁴⁺-bearing phases, and Ti³⁺ was undetected. This suggests that Ti⁴⁺ precipitation in mineral phases may be strongly preferred to reduction of Ti⁴⁺ into Ti³⁺. Reduced atmospheres may thus favour the crystallization of Ti-rich silicate melts. Such specificity could be used to produce novel glass materials coated with Ti-bearing nano-crystalline phases to enhance their mechanical properties (i.e. hardness or flexural strength). This phenomenon should be heightened in Fe-bearing systems, due to the favoured apparition of Fe-Ti oxide phases, very common in magmatic samples for instance.

Acknowledgements

We acknowledge SOLEIL (Gif sur Yvette, France) for provision of synchrotron radiation facilities (project 20191962) and PARI multidisciplinary platform at IPGP. CLL acknowledges funding from a Chaire d'Excellence IDEX19C627X/FD070/D110 from the IdEX Université de Paris ANR-18-IDEX-0001.

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