



# Chromium oxide additions in lithium disilicate glass crystallization



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## ABSTRACT

The effect of chromium oxide additions (0.05–1.00 mol% interval) on the crystallization of an original  $26\text{Li}_2\text{O} \cdot 74\text{SiO}_2$  glass (mol%) formulated in the liquid metastable immiscibility dome of the binary system has been investigated by XRD and TEM-replica electron microscopy. Results were discussed by considering the phases that can be formed in the  $\text{Li}_2\text{O}-\text{Cr}_2\text{O}_3-\text{SiO}_2$  partial equilibrium ternary diagram. From these glasses, lithium disilicate is the main crystalline phase after thermal treatments at 550–650 °C. Maximum crystallization is obtained with the lowest content addition of  $\text{Cr}_2\text{O}_3$  (0.05 mol%). Glass-in-glass phase separation was observed in these glasses coexisting with the crystallization areas.

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## 1. Introduction

In order to promote controlled crystallization in glasses for producing glass-ceramics, small additions of nucleating agents are usually added to promote crystal growth of several crystalline phases inside glasses. These include metallic elements, Pt, Ag, and Au, or non-metallic oxides,  $\text{P}_2\text{O}_5$  and  $\text{TiO}_2$ , and others from the transition elements of the periodic table [1]. Among these transition oxides,  $\text{Cr}_2\text{O}_3$  has been widely used for some time as a nucleating agent for controlling the nucleation and crystal growth in glasses such as  $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$  with  $\text{AlF}_3$  (1.5 wt%) and the addition of this oxide in 3 wt% content [2]. The addition of chromium oxide in basaltic base glass compositions ( $\text{CaO}-\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$  system) has also been usual since the last decades [3,4], giving rise to very small crystals precipitated in these types of glasses. Even wastes containing this oxide, and/or with additions of  $\text{Cr}_2\text{O}_3$ , have demonstrated the capacity of this oxide for enhancing crystal nucleation and growth in a wide range of compositions [5–9]. Not only does this oxide improve bulk crystallization, it even favors surface sintered crystallization; thus,  $\text{Cr}_2\text{O}_3$  has demonstrated its capacity for producing glass-ceramics with good properties and performance for a wide range of applications [10].

The aim of this research was to investigate several additions of  $\text{Cr}_2\text{O}_3$  (0.05–1 mol%) for the crystallization process in  $26\text{Li}_2\text{O} \cdot 74\text{SiO}_2$  glass. The evolution of crystalline phases was followed under X-ray diffraction (XRD) analysis and transmission electron microscopy (TEM)-replica observations. Results were discussed

according to the  $\text{Li}_2\text{O}-\text{Cr}_2\text{O}_3-\text{SiO}_2$  phase equilibrium diagram and by also viewing the effect of phase separation from such additions.

## 2. Experimental

The binary glass composition of 26–74 (mol%) is located inside the  $\text{Li}_2\text{O}-\text{SiO}_2$  immiscibility dome and very close to the pseudo-eutectic composition of the  $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$  in this binary system [11,12]. This composition, which is not exactly located at the stoichiometric  $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ , was selected for evaluation of the optimal  $\text{Cr}_2\text{O}_3$  addition, because this oxide is usually difficult to dilute in the original melt [13]. According to previous results [14], the composition investigated here, 26–74 (mol%), is inside the glass-in-glass phase separation dome [15] and the lithium disilicate crystallization is slow with respect to the stoichiometric composition. Melting was carried out at 1350 °C for 3 h in a platinum crucible and a Super Khantal electric furnace with  $\text{Li}_2\text{CO}_3$  as precursor of  $\text{Li}_2\text{O}$  and pure silica.  $\text{Cr}_2\text{O}_3$  additions were 0.05, 0.10, 0.30, 0.60, and 1.00 (mol%), giving rise to five respective original or mother glasses, named in Table 1 as 05, 1, 3, 6, and 10, which shows the respective weight (wt%) composition. These original glasses containing  $\text{Cr}_2\text{O}_3$  were moulded in prismatic bars, which were cut into cubes ( $10 \times 10 \times 10 \text{ mm}^3$ ), and afterwards subjected to thermal treatments at 450–700 °C intervals to promote nucleation and crystal growth with several heating times. After chemical analysis of the final glasses, it was proven that both oxides of lithium and chromium volatilize in percentages of 10.5 wt% in the case of 05 glass and 11.6 wt% for  $\text{Li}_2\text{O}$  and 13.8 wt% for  $\text{Cr}_2\text{O}_3$  in the case of 3 glass.

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**Table 1**  
Composition (wt%) and aspect of original glasses.

Name	Color	Li <sub>2</sub> O	SiO <sub>2</sub>	Cr <sub>2</sub> O <sub>3</sub>
05	Transparent green	14.92	84.93	0.15
1	Transparent green	14.90	84.81	0.29
3	Transparent green	14.81	84.32	0.87
6	Opal green	14.68	83.59	1.73
10	Opaque green	14.51	82.63	2.86

The total crystallization curves, which in this case include the nucleation and crystal growth velocities, were determined by XRD relative intensities of powdered heat treated glass samples to the maximum diffraction line (0.540 nm), which correspond to Miller index planes of (110) diffraction for the monoclinic lithium disilicate (JCPDS 72-0102 and JCPDS 40-0376 cards) [16].

**3. Results and discussion**

After XRD mineralogical analysis of the final glass-ceramics obtained by thermal treatment, the main crystalline phase was lithium disilicate (Li<sub>2</sub>O·2SiO<sub>2</sub>). Simultaneously, with this phase the silica phases crystallize as cristobalite and tridymite in those glasses containing more than 0.3 mol% of Cr<sub>2</sub>O<sub>3</sub>. From compositions between 0.6% and 1% addition of chromium oxide, lithium chromate crystallizes (Li<sub>2</sub>O·Cr<sub>2</sub>O<sub>3</sub>), which even already appears in the original glass with the higher Cr<sub>2</sub>O<sub>3</sub> content. In the glass with 1.0 mol%, Cr<sub>2</sub>O<sub>3</sub> spinel cubic crystals precipitated in the glassy matrix were also detected, which correspond to some content of this addition non fully dissolved in the lithium silicate melt [14]. Only in glasses with lower content of chromium addition does the lithium disilicate crystallization volume increase notably; while for higher additions of this oxide, the crystallization decreases, also favoring the precipitation of some silica crystalline phases, such as cristobalite and tridymite, at lower heating temperatures. In any case, for higher additions of Cr<sub>2</sub>O<sub>3</sub>, lithium chromate is formed, even from the original or mother glass (Table 2).

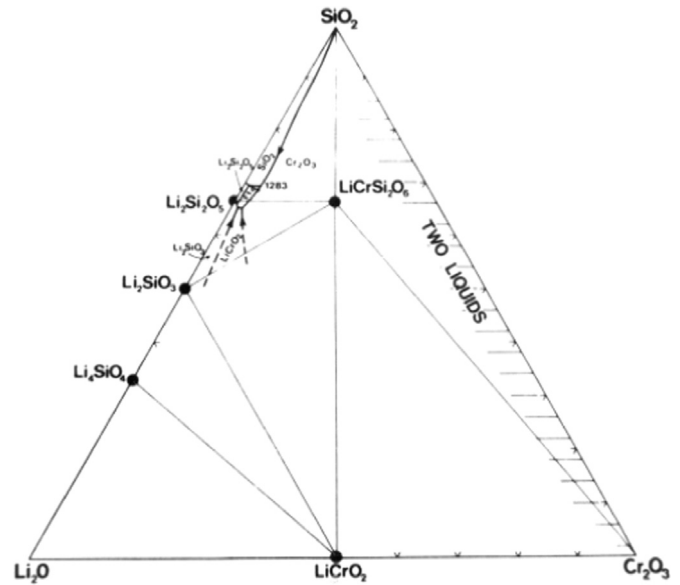
The lithium disilicate phase as main crystalline phase and the formation of lithium chromate as minor phase are in agreement with the Li<sub>2</sub>O-Cr<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> phase equilibrium diagram determined by Izquierdo and West [17] (Fig. 1). Even more, the formation of a chromium spodumene 1:1:4 could be a possibility. However, in the compositions tested here, this crystalline phase was not detected.

Fig. 2a shows the relative crystallization of lithium disilicate showing the left part of the usual crystallization behaviour curves because heating experiments for determination of these curves were performed up to 700 °C. The effect of chromium oxide additions up until the 0.6 mol% composition can be clearly seen. It is more evident that the minimum Cr<sub>2</sub>O<sub>3</sub> content gives rise to the maximum growth curve for this crystalline phase and at 650 °C of heating. Fig. 2b depicts the variation of maximum crystallization at 650 °C depending on the chromium oxide addition, with this effect more evident at lower nucleating agent contents.

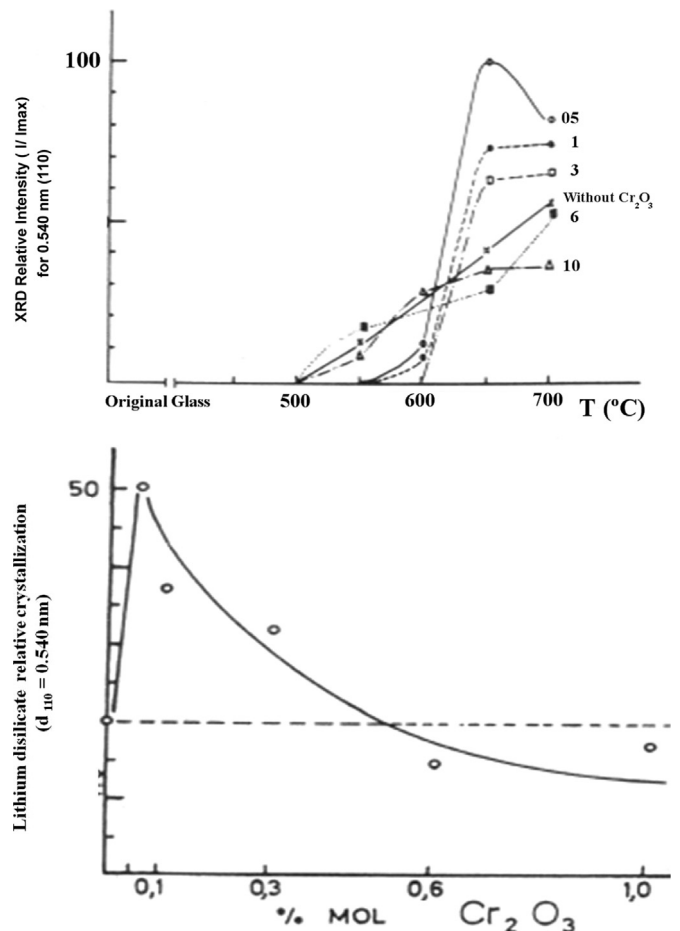
As can be seen in Fig. 3a, transmission electron microscopy

**Table 2**  
Crystalline phase growth from the 26Li<sub>2</sub>O·74SiO<sub>2</sub> (mol%) mother glass. D=Li<sub>2</sub>O·2SiO<sub>2</sub>, T=tridymite, C=cristobalite.

	05	1	3	6	10
original	-	-	-	Li <sub>2</sub> CrO <sub>4</sub> +T+C	Cr <sub>2</sub> O <sub>3</sub> +T
450	-	-	D≪	Li <sub>2</sub> CrO <sub>4</sub> +T+C	Cr <sub>2</sub> O <sub>3</sub> +T
550	-	-	D<	D	D
650	D≫	D>	D>	D	D



**Fig. 1.** Ternary phase diagram from Izquierdo and West (1980) [17].



**Fig. 2.** (a) Relative crystallization velocities for lithium disilicate and (b) maximum crystal growth (26Li<sub>2</sub>O·74SiO<sub>2</sub> glass with 0.05–1.00 mol% Cr<sub>2</sub>O<sub>3</sub>).

observations (TEM-carbon replicas) confirm the presence of liquid phase separation in all the glasses considered here before and after the heat thermal treatment, with higher volume fractions and sizes of droplets in compositions with the lower Cr<sub>2</sub>O<sub>3</sub> addition (Fig. 3b). The sizes of droplets increase with the thermal treatment temperature whilst this variation is lowered when the addition of

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