



**HAL**  
open science

# STUDY OF NUCLEATION PROCESS IN (SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Li<sub>2</sub>O) GLASSES, BY X-RAY ABSORPTION SPECTROSCOPY AND TRANSMISSION ELECTRON MICROSCOPY

A. Ramos, M. Gandais, J. Petiau

► **To cite this version:**

A. Ramos, M. Gandais, J. Petiau. STUDY OF NUCLEATION PROCESS IN (SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Li<sub>2</sub>O) GLASSES, BY X-RAY ABSORPTION SPECTROSCOPY AND TRANSMISSION ELECTRON MICROSCOPY. *Journal de Physique Colloques*, 1985, 46 (C8), pp.C8-491-C8-494. <10.1051/jphyscol:1985876>. <jpa-00225226>

**HAL Id: jpa-00225226**

**<https://hal.science/jpa-00225226v1>**

Submitted on 4 Feb 2008

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



HAL Authorization

STUDY OF NUCLEATION PROCESS IN (SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Li<sub>2</sub>O) GLASSES, BY X-RAY ABSORPTION SPECTROSCOPY AND TRANSMISSION ELECTRON MICROSCOPY

A. Ramos, M. Gandais and J. Petiau

*Laboratoire de Minéralogie-Cristallographie, Université Pierre et Marie Curie, 4 place Jussieu, 75230 Paris Cedex 05, France*

**RESUME** - Microscopie électronique (TEM) et spectrométrie d'absorption X (structure fine des seuils et EXAFS) sont utilisées de façon complémentaire pour étudier les toutes premières étapes de la nucléation cristalline dans des verres du système (SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-Li<sub>2</sub>O). La microscopie électronique fine a permis de caractériser les phases cristallines et la taille des cristaux (20-50 Å pour les premiers stades de nucléation, 200-500 Å pour la vitrocéramique finale). La spectrométrie d'absorption X a été réalisée aux seuils des deux éléments nucléants : le titane et le zirconium. Le titane évolue depuis le site de coordination 4 qu'il occupe dans le verre vers un site de coordination 6 dans la vitrocéramique. Cela est suivi en particulier par l'analyse du "prépic" au seuil d'absorption K du titane. L'environnement du zirconium reste très désordonné au stade final de la vitrocéramique.

**ABSTRACT** - TEM and X-ray absorption spectrometry (fine edge structure and EXAFS) are combined to study the earliest stages of crystalline nucleation in glasses of the system (SiO-Al<sub>2</sub>O<sub>3</sub>-Li<sub>2</sub>O). TEM has allowed the characterization of the crystalline phases and the crystal sizes (20-50Å in the first nucleation stages, 200-500Å in the final glass ceramic). X-ray absorption spectrometry has been performed at the K-edge of the two nucleating agents titanium and zirconium. The titanium site changes from a 4-fold coordinated situation in the "green" glass to a 6-fold one in the glass ceramic; that is directly given by the K-edge prepeak analysis. The zirconium environment remains highly disordered even at the final crystallized stage.

## I- INTRODUCTION

In spite of the recent development of studies in glass ceramics, some fundamental problems concerning nucleation in glasses are still unsolved for lack of experimental methods adapted to the characteristic dimensions of the phenomena. One of the main questions is to understand the role of the nucleating agents and the evolution of their environment during the earliest stages of nucleation. This investigation needs experimental methods working at the scale of middle range order (5-15 Å). Two methods are combined to approach the critical scale of structural order : X-ray absorption spectroscopy and transmission electron microscopy (TEM). On one hand TEM allows us to study the structural organization at the scale of several angstroms as soon as the crystallites reach a dimension of a few tens of angstroms. On the other hand X-ray absorption spectroscopy gives selective information about the first coordination shells around selected elements.

## II- SAMPLES

We have studied glasses of spodumene-like composition, close to (70% SiO<sub>2</sub>, 20% Al<sub>2</sub>O<sub>3</sub>, 3% Li<sub>2</sub>O, 2% MgO) containing ZrO<sub>2</sub> (2-5%) and TiO<sub>2</sub> (2-5%) as nucleating elements. Such a composition is used in industry to obtain very fine-grained glass ceramics (1). Samples corresponding to different ratios of molar concentrations of TiO<sub>2</sub> and ZrO<sub>2</sub> have been studied in order to elucidate their specific and joint roles as nucleant. Heat treatments have been performed in the range of temperature corresponding to the nucleation process (740°C to 800°C) and to the beginning of the

crystallization (850°C to 910°C). The samples were then quenched to room temperature and all measurements made at this temperature.

### III- ELECTRON MICROSCOPY

Up to now electron microscopy and diffraction have been performed for the glass before heat treatment (GG : "green" glass), the glass-ceramic (GC : 25mm at 780°C+25mm at 910°C) and two intermediate stages (N78 : 25mm at 780°C and N82:25mm at 820°C).

- The green glass is completely amorphous and does not show phase demixion (figure 1) contrary to glasses of cordierite-like composition also containing Zr as nucleating element (2-3).

- The two intermediate stages are similar. They show small crystals (20-50 Å) embedded in an amorphous phase (figure 2). The crystalline phase has not yet been identified.

- The glass ceramic is nearly completely crystallized and contains two crystalline phases. " $\beta$ -quartz" solid solution occupies the main part of the sample. It is formed of 200-500 Å crystals (figure 3a) and gives all the rings of the diffraction pattern except one (figure 3b). The second phase is likely " $\beta$ -spodumene" ss, the additional ring which is broadened being the most intense powder diffraction ring of  $\beta$ -spodumene. The width of the ring indicates crystal size in the range 20-50 Å. The comparison of the intensities of the rings gives roughly 95%  $\beta$ -quartz and 5%  $\beta$ -spodumene. The intermediate phase has disappeared.

### IV- X-RAY ABSORPTION SPECTROSCOPY

X-ray absorption spectroscopy has been used to investigate the changes in the environment of each of the two nucleating elements, zirconium and titanium, with their concentration and with heat treatments. EXAFS has been analyzed at the K-edge of zirconium (18000 eV) while structural information has been extracted from both EXAFS and the fine edge structure at the K-edge of titanium (4965eV). The extended structure (EXAFS) gives a partial radial distribution limited to the nearest and next nearest neighbours around the absorbing atom. The low energy features (below the main absorption jump) correspond to electronic transitions to localized empty states and inform about the electronic state of the absorbing atom and, via crystal field effects, about the coordination and geometry of its site.

The spectra were recorded by direct transmission measurement using the synchrotron radiation of LURE-DCI (Orsay). The monochromator was a 311 silicon double crystal. The obtention of a good energy resolution is important for the fine edge structure studies; it was about 1.5eV at the K-edge of titanium when the core level width is 0.8eV for the K shell of this element.

Zirconium EXAFS - The spectra remain nearly identical at all stages of the heat treatments (Fig.4). The only contribution is given by the oxygen coordination shell which is formed by six atoms at 2.10Å. This result is surprising since zirconium is expected to participate to crystalline phases after the crystallization process; in glasses of "cordierite" composition the participation of zirconium to crystalline phases had clearly been put in evidence by EXAFS (2). Therefore zirconium seems to keep a highly disordered environment apart from the coordination oxygen shell in the "spodumene" glasses; it is however impossible to decide from the only EXAFS information if this arrangement corresponds to an amorphous phase or to a crystalline one with a broad distribution of radial distances in the second neighbours shell.

Titanium edge structure - At the K-edges of 3d transition elements well separated features are observed at energies lower than the main absorption jump. They are due to "dipole-forbidden" transitions  $1s \rightarrow 3d$  which are partly allowed by  $d-p$  mixing and they result in high resonance peaks for final states corresponding to empty  $d$  levels and non-centrosymmetric sites (4-5). It is the case for titanium in the valence state 4 when it is 4-fold coordinated; for the same valence state but a 6-fold coordination, the "pre-edge" feature has a lower amplitude and is split in several components that the high resolution measurements allow to resolve. As the contributions of 4-fold and 6-fold titanium atoms to the pre-edge structure are purely additive, their quantitative analysis, after normalization of the whole spectrum, informs directly about the percentage of atoms in each coordination.

Figure 5 shows the preedges obtained after successive heat treatments. In the glass

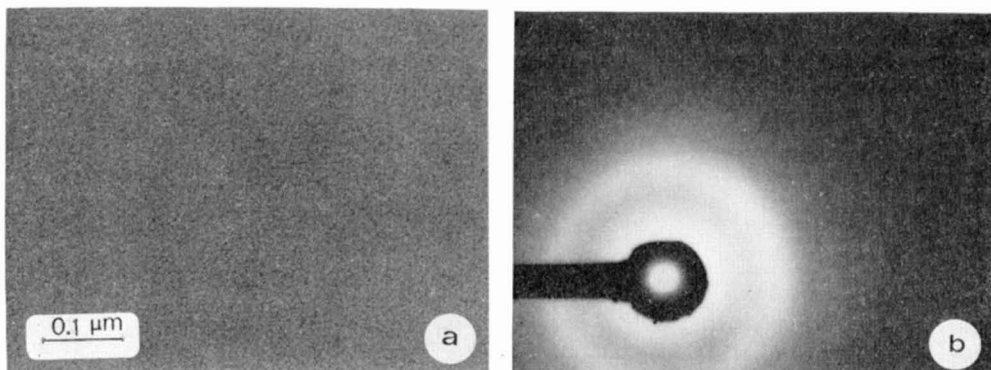


Fig. 1- Green Glass GG (without heat treatment). Micrography (1a) and electron diffraction (1b).

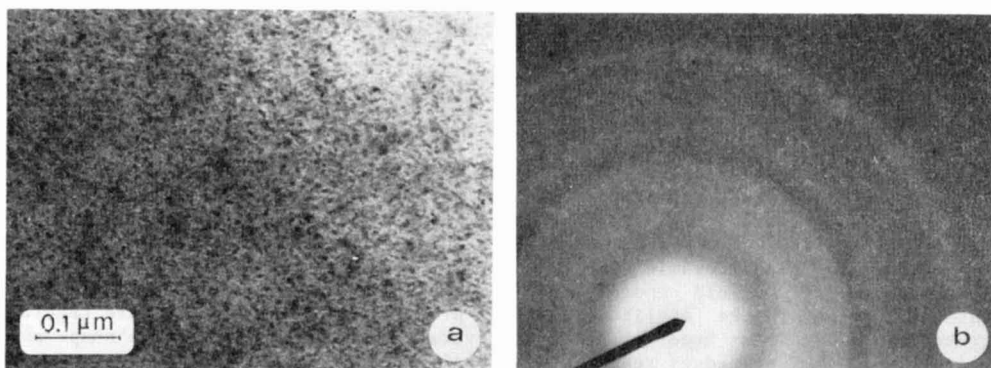


Fig. 2- Intermediate states N78 (25mn at 780°C). Micrography (2a) and electron diffraction (2b).

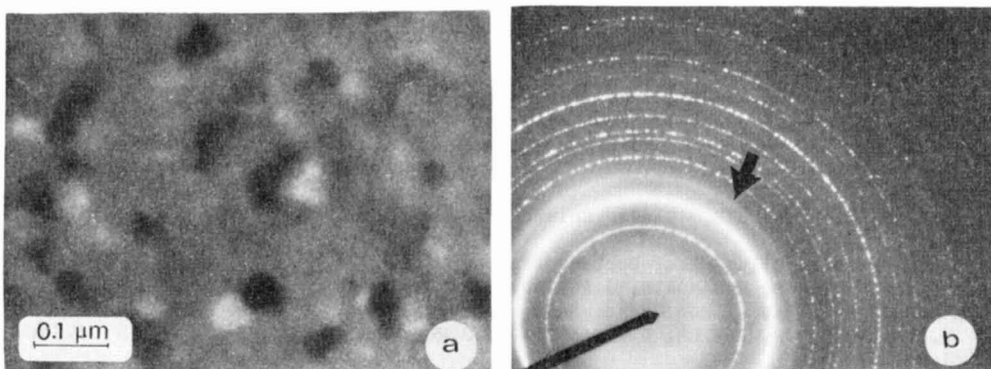


Fig. 3- Glass Ceramic GC (25mn at 780°C +25mn at 910°C). Micrography (3a) and electron diffraction (3b). The broadened ring is indicated by the arrow.

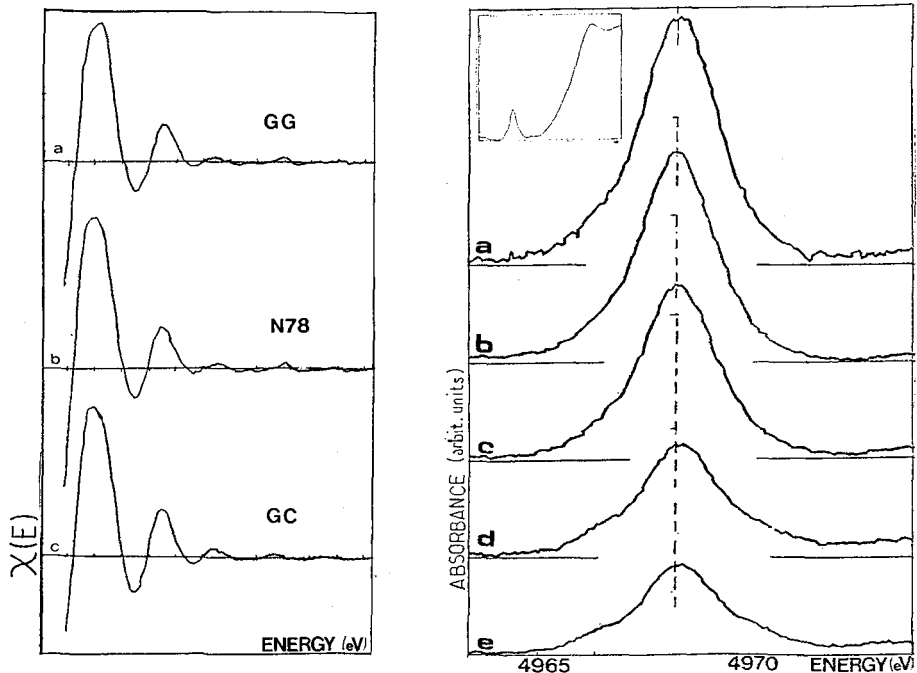


Fig. 4 (left) : EXAFS at Zirconium K-Edge. a - green glass GG, b - intermediate state (25mm at 780°C) N78, c - glass ceramic.

Fig. 5 (right) : Fine structure at Ti K-edge. a - green glass GG, b - 25mm at 760°C, c - 25mm at 780°C (N78), d - 25mm at 780°C+25mm at 890°C; e - glass ceramic (GC).

no evidence of 6-fold coordinated titanium is observed before nucleation treatments; however the amplitude of the pre-edge is lower than in pure regular tetrahedra as it has been observed in several crystalline phases. The shape and amplitude of the pre-edges reveal a progressive change of the coordination number from 4 to 6 as crystalline nucleation progresses. If the percentage of 4-fold coordinated titanium atoms is supposed to be 100% in the "green" glass, it has become less than 30% in the ceramic heat-treated at 910°C. This change of the coordination number accompanies the entering of titanium in a crystalline phase as EXAFS spectra have directly shown; the complete analysis of EXAFS has not yet been possible because of the presence of the baryum LIII-edge 200eV after the Ti K-edge.

We thank the staff of LURE for operating the synchrotron radiation facility and for having made possible X-ray absorption experimentation. The research of one of us (AR) has been partly supported by the CORNING European Research Center.

#### REFERENCES

- (1) G.H.BEALL, D.A.DUKE, *Glass Science and Technology*, 1 Acad. Press. (1983) 403-445
- (2) T.DUMAS, Thèse d'Ingénieur-Docteur (Paris 1984).
- (3) T DUMAS, A.RAMOS, M.GANDAIS, J.PETIAU. *J.Mat.Sci.Lett.* 4, (1985),129-132.
- (4) T.DUMAS, J.PETIAU *J. Non Cryst. Sol.* (accepted).
- (5) R.B.GREER, F.W.LYTTLE, D.R.SANDSTROM, J.WONG and P.SCHULTZ. *J.Non Cryst.Sol.* 55 (1983) 27-43.