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1 *Microstructural Insights on Lithium Aluminum Silicate (LAS) Glass Ceramics*

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9 **Abstract**

10 LAS glass-ceramics stimulate considerable attention in academic and industrial fields due to exceptional
11 properties, such as low thermal expansion coefficient, transparency or superior mechanical strength. We report
12 here an experimental investigation of LAS structure and microstructure using conventional techniques as XRD
13 or S/TEM, but also an innovative technique based on electron diffraction mapping. The later gives a topography
14 of the sample and a clear picture of the distribution between the glass and the spodumene particles. All the data
15 converge towards a model of hard spheres where 75% of the volume is composed of spheroid particles and
16 25% of the remaining volume is composed of glass, which is present in the inter-particle interstices. These
17 findings provide a new knowledge about the LAS system and may offer useful guidance for other researchers
18 in ceramic community.

19 **Keywords**

20 glass-ceramics; LAS; electron microscopy; crystal orientation mapping; hard sphere model

21 **Introduction**

22 Glass-ceramics (GC) are composite materials that combine in once a crystalline and a glassy phase [1,2]. The
23 great advantage of such materials compared to glasses or ceramics taken separately is their ability to combine
24 the desirable properties of both components. Hence, the amorphous part of GC allows for the ease of fabrication
25 and processing, while the synergy between the glass and crystalline components may confer to the composite

26 high mechanical strength (high fracture strength and toughness), thermal stability, and chemical durability in
27 comparison to glass. Glass-ceramics can also exhibit transparency or translucency, as well as opacity.

28 During the last five decades, GC materials have been the subject of intense researches due to their unique
29 properties and applications in various domains [3–5]. In optics (e.g., telescope mirror substrate blanks [6]),
30 cooking (e.g., cook top panel, cookware [7]), electronic packaging [8], dentistry [9] and transparent heat
31 protection (e.g., oven window [10]), $\text{Li}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2$ glass-ceramics (hereafter labelled LAS) specifically
32 received much attention [11].

33 Namely, the LAS GC system is considered so far as one of the most important GC materials due to several
34 outstanding properties, such as very low thermal expansion coefficient (near 10^{-7} K^{-1} in the 0-300°C range),
35 high transparency when desired, excellent chemical resistance, high mechanical strength, versatility in
36 composition to access specific characteristics, and the ability to be polished [2,5,6,11–18]. The main reported
37 crystalline phases observed in LAS GC vs. synthesis conditions are $\gamma\text{-LiAlSi}_2\text{O}_6$ and $\beta\text{-LiAlSi}_2\text{O}_6$ spodumene,
38 $\beta\text{-LiAlSiO}_4$ eucryptite, SiO_2 keatite (an isomorphous form of β -spodumene), and a series of species belonging
39 to the so called β -quartz solid solution (also named stuffed high-quartz solid solution) that correspond to Al-
40 substituted $\beta\text{-SiO}_2$ compounds isomorphous with $\beta\text{-LiAlSiO}_4$ (let us notice that the labeling may be different
41 for identical phases in the literature) [11].

42 As the demand for tailored materials with precise microstructural control continues to rise, it becomes
43 increasingly imperative to delve deeper the LAS GC (micro)structure using Scanning / Transmission Electron
44 Microscopy (S/TEM) that combines imaging, diffraction and spectroscopies at high spatial resolution. Hence,
45 LAS glass-ceramics were examined for different thermal treatments or chemical compositions rate of major
46 (Si, Al, Li) or minor (Zn, Na, Ca) common or exotic (B, La, Er, Y, La) constituents with ZrO_2 , TiO_2 or ZrTiO_4
47 as nucleating agents [19–34].

48 In most of the work carried out on LAS, the structure is dominated by the presence of nanosized, more or less
49 spherical, particles of spodumene [11,26,33]. Depending on the heat treatment used or the Li concentration,
50 these particles are well separated from each other or in contact. To date, only S/TEM images have been
51 proposed to picture the structure of crystalline phases of LAS GC. Nevertheless, it is very difficult to observe
52 directly the distribution of glass and crystals only with imaging. This article looks at LAS glass-ceramic

53 structures using a state-of-the-art microscopy technique rarely employed so far in the GC community, i.e. the
54 electron diffraction phase mapping of the crystals in the GC with a resolution down to 2 nm.

55

56 ***Material and method***

57 Glass raw materials were prepared with a $66\text{SiO}_2\text{-}22\text{Al}_2\text{O}_3\text{-}4\text{Li}_2\text{O-}1\text{ZrO}_2\text{-}3\text{TiO}_2\text{-}1.5\text{BaO-}1.4\text{ZnO}$
58 nominal composition (major elements expressed as weight percent oxides) from the respective binary
59 oxides (except for Li) and lithium carbonate. Precursors were mixed and heated at 1500°C for 48 hours in
60 air. The so-formed glass was then annealed at 550°C for 4 hours to relax internal stresses. To form GC,
61 LAS parent glasses were heated up to 900°C for 15 min with a $3^\circ\text{C}/\text{min}$ rate and quenched in air.

62 The thermal analysis curves of the glass-ceramics were measured at a constant heating rate of $10^\circ\text{C}/\text{min}$
63 between 500 and 1000°C (ATG/DSC 3+, Mettler Toledo). Crystalline phases (structure and microstructure)
64 and purity of the prepared samples were determined by X-ray powder diffraction (XRD). Patterns were
65 collected at room temperature on a Bruker D8 Advance instrument (monochromatic Cu K-L₃ ($\lambda = 1.540598$
66 Å) X-ray radiation and LynxEye detector) in the $15^\circ\text{-}85^\circ$ 2θ range with a 0.0078° step and $0.97\text{s}/\text{step}$. The
67 quantification of amorphous part was carried out using MgO as standard [35,36].

68 Scanning / Transmission Electron Microscopy (S/TEM) characterization was performed on a Cs-probe
69 corrected Themis Z G3 (Thermo Fisher Scientific). To limit sample degradation under electron irradiation
70 (see S.I.1), first images were acquired at 80 kV and low temperature ($\sim 178^\circ\text{C}$) with a low probe current
71 (~ 15 pA) and a small convergence angle (4.1 mrad). Second, in order to get image contrasts relative either
72 to atomic number (i.e. proportional to Z^2) or to diffraction patterns (i.e. linked to the orientation of crystals),
73 S/TEM Annular Dark Field (ADF) images of the same area were collected at two different camera lengths
74 (CL) to have different collection angles (5-32 mrad at 1.15 m CL, and 41-200 mrad at 0.145 m CL,
75 respectively). The sample was crushed in ethanol in an agate mortar to obtain *ca.* 100 nm thick grains. A
76 drop of this solution was then deposited on a gold grid covered with a thin amorphous lacey carbon film.
77 Phase mapping was performed using the ASTAR tool (*Automated Crystal Orientation Mapping technique*,
78 *ACOM-TEM* Nanomegas), at low temperature (103K) with a 2 nm step size.

79 ***Results***

80 Figure 1 displays the differential scanning calorimetry (DSC) curve for a LAS glass in the 500-1000°C
81 domain and STEM-ADF images of the LAS GC. The glass transition temperature (T_g) collected on a
82 monolithic sample occurs at 676°C (Fig 1a). Two exothermic peaks appear at ca. 814°C and 855°C. They
83 are associated respectively with the nucleation and crystallization of a Li aluminosilicate [37], that turns to
84 be spodumene (*vide infra*). After a monitored heat treatment up to 900°C, the resulting glass-ceramic is
85 brown-yellowish and transparent (see inset in Fig. 1a). Let us notice here that prior to this
86 germination/crystallization step, on the basis of *in situ* TEM micrographs collected between 25°C and
87 600°C (i.e., before T_g in ambient atmosphere and before degradation of the sample under the electron beam
88 in high vacuum conditions), the LAS glassy phase seems to be formed of two distinguishable amorphous
89 components (no diffraction spot), a bright and a dark one, the contrast and the reticulation between the two
90 interpenetrated subnetworks being strengthened with temperature (see S.I.2).

91 STEM micrographs of LAS-GC (Fig. 1.b-d) show two different structural features. First, 30-50 nm diameter
92 crystallised particles with a roughly round shape are detected (crystals appear in grey or white depending
93 on their orientation relative to the electron beam, Fig. 1.c.). They are assigned to a γ -spodumene phase (*vide*
94 *infra*). Second, 2-5 nm large dots homogeneously distributed are observed (Fig.1.d.). These particles are
95 allocated by EDX-STEM and EELS mapping to a "ZrTiO₄" phase with a Ti:Zr ratio not defined with
96 accuracy (see S.I.3, S.I.4). No amorphous phase was highlighted at this stage between the grains. Although
97 conventional microscopy techniques provide a wealth of information, further analyses are needed to find
98 out more about the structure of the GC. In that context, a Rietveld refinement on the collected X-ray pattern
99 of LAS GC was carried out (Fig. 2a).

100 The diffraction pattern indicates undoubtedly the presence of γ -spodumene phase, i.e. γ -LiAlSi₂O₆, as the
101 major phase. This is the thermodynamically metastable polymorph of the mineral. The observed refined
102 cell parameters are lower than those expected in the literature (i.e., $a = 5.184(1) \text{ \AA}$ and $c = 5.440(2) \text{ \AA}$ vs.
103 $a = 5.217(1) \text{ \AA}$ and $c = 5.451(2) \text{ \AA}$ [38]). This observation was already reported in the literature [39] and the
104 aforementioned discrepancy was explained either by a $\text{Li}^+/\text{M}^{2+}$ (e.g. $\text{M} = \text{Mg}$ or Zn) substitution process
105 taking place along with the presence of Li vacancies or by a $\text{Si}^{4+}/\text{Al}^{3+}$ substitution balanced by Li
106 interstitials. Based on a Rietveld refinement with a fundamental parameter approach, the calculated mean
107 size of the spodumene crystallites is estimated around $38 \pm 2 \text{ nm}$ (in full agreement with STEM analyses).

108 No size anisotropy was detected. The low intensity very broad peak at 30.5° in 2θ is only present when
109 both TiO_2 and ZrO_2 nucleating agents are used [28]. This unique peak is commonly associated to the (111)
110 Bragg reflection of ZrTiO_4 [40,41]. Unfortunately, due to the sole presence of one low intense peak, no
111 additional information could be obtained. Quantification of crystalline phases (γ -spodumene and " ZrTiO_4 ")
112 and glass lead to 72.7 and 27.3 ± 3 wt%, respectively, i.e. ca. 75.2 and 24.8 vol% after conversion taken
113 into account the densities of crystalline phases. Although these values are tainted by errors due the
114 inaccuracy of the exact " ZrTiO_4 " chemical composition (*vide supra*), they strongly remind us the hard-
115 sphere close-packing model (see Fig. 2b) in hexagonal compact structures with the ideal 74/26 vol% of
116 sphere/void ratio.

117 As well known, XRD gives an averaged representation of the real structural morphology of GC. However,
118 it is difficult at this stage to gain more information on the amorphous part of the glass ceramic. Indeed, in
119 contrast, ACOM-TEM phase mapping can locally probe the glass-crystallized distribution in GC. Formally,
120 electron diffraction is the technique of choice for the study of glass-ceramics, as its beam size of around 10
121 pm (vs. ~ 150 pm for X-rays) enables to probe the material very precisely and locally. This is particularly
122 useful for investigating heterogeneities or interfaces within glass-ceramic samples. What's more, by
123 coupling this technique with common microscopy techniques, the overall structure of GC, i.e. crystallized
124 and amorphous parts, can be imaged at the local scale. A correlation coefficient map can be deduced of this
125 set of diffraction patterns (DP). The intensities of the DP of each pixels are compared to the neighbour
126 diffraction patterns. This technique highlights the grain boundaries, permitting to visualize the crystallites
127 and thus the amorphous zone of the sample [42,43]. The TEM and the associated correlation coefficient
128 map are presented in Fig. 3.

129 The correlation coefficient map shows numerous spodumene crystallites of the order of 40 nm. Clearly,
130 this technique makes possible to distinguish crystallites from particles, i.e. agglomerates of single crystals.
131 Moreover, based on the examination of Fig. 3, γ - $\text{LiAlSi}_2\text{O}_6$ crystals turn to be in contact with each other
132 with a spheroid shape. Thanks to these results, it is possible to describe the distribution of different objects
133 in space with a high degree of accuracy combining the convergent results of XRD and ACOM-STEM
134 techniques. There are many "voids" between crystallites that show no diffraction signal. This result clearly

135 indicates the presence of non-diffracting phase, i.e. an amorphous phase, in interstices defined by crystalline
136 spheres.

137

138 **Conclusion**

139 The present investigation reports on the microstructure of the $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ glass-ceramic nucleated
140 with " ZrTiO_4 ". Analyses carried out using XRD and STEM, and more specifically, phase mapping based
141 on an automated crystal orientation technique, clearly validate a hard sphere close-packing model for the
142 LAS GC. Indeed, this latter is made up of ca. 75% vol crystals composed mainly of nanosized γ -spodumene
143 with " ZrTiO_4 " as trace, and ca. 25% of glass located in the interstices of the crystalline spheres

144 In this way, we have been able to highlight a new characterization technique that is still rarely used, if at
145 all, in the field of glass ceramics. Thanks to electron diffraction, "topographic" map of glass-ceramic
146 samples could be achieved. Thus, from these results, crystalline parts can be identified and information
147 obtained on their size and arrangement.

148

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157

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278 **Figure captions**

279 Fig. 1. Differential scanning calorimetry curve for a LAS glass heated at 10°C/min (a) and STEM-ADF of
280 the LAS GC (b) with a zoom-in of the red square zone at two different camera lengths ($L = 1.150$ (c) and
281 0.145 m (d)). For low L , the contrast observed is proportional to Z^2 , i.e. the square of the atomic number.
282 Conversely, for larger L , the contrast is linked to diffraction conditions.

283

284 Fig. 2. a) Rietveld refinement of a LAS-GC X-ray pattern (Cu K-L3 - $\lambda = 1.540598$ Å). b) Sketch-up of the
285 LAS-GC with ca. 74 vol% of γ -LiAlSi₂O₆, ca. 25 vol% of glass and ca. 1 vol% of ZrTiO₄.

286

287 Fig. 3. a) TEM micrograph of GC sample at 1 μm scale. Correlation coefficient map of the highlighted area
288 at 500 nm (b)), and 50 nm (c)) scale.

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