# In-situ Raman spectroscopy unveils metastable crystallization in lead metasilicate glass

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ABSTRACT

The formation of metastable phases is a relevant, challenging and yet underexplored subject in glass crystallization. In this work, we examined the isothermal crystallization of $PbO.SiO_2$ lead metasilicate glass by using in-situ Raman spectroscopy. We provide evidence for the evolution process from the glass to alamosite, the stable crystalline phase, which is intermediated by two distinct metastable phases at different temperatures. At 550 °C the crystallization pathway proceeded from the low $PbSiO_3$ to alamosite, whereas at 600 °C the crystalline phase evolved from the hexagonal $PbSiO_3$ to alamosite. We found no interconversion between these two metastable phases, indicating that both can precipitate prior to alamosite stabilization. These findings demystify the alleged complexity of the crystallization process of lead metasilicate glass, raised in the literature, whose data are critically analyzed and discussed herein.

## 1. Introduction

Over a century ago, while studying precipitation in highly supersaturated solutions, Ostwald [1] formulated his famous rule of stages. In terms of crystallization of glasses and supercooled liquids (SCL), this rule predicts that an initial crystalline phase nucleated from an unstable (glass) or metastable (SCL) state would often be one or more intermediate metastable phases, rather than the thermodynamically stable phase [2]. However, while in general this subject has been intensively explored in materials science, it has been scarcely studied by the glass community.

Lead metasilicate, $PbO.SiO_2$ (PS), glass is a very interesting model system. It has been pursued as a good research subject because, despite the low content of the glass former silica (only 50 mol%), it shows a very good glass-forming ability. Also, it serves as a simple model for studies aiming at understanding the role of Pb in silicate glass structure.

The crystalline phases that precipitate in heat-treated lead metasilicate glass are well-known, consisting of the stable alamosite ($PbSiO_3$), and two metastable modifications: hexagonal $PbSiO_3$ (H-PS) and "low temperature" $PbSiO_3$ (L-PS). Briefly, Geller et al. [3] reported that the optical properties of crystallized lead metasilicate are very similar to the mineral alamosite, which was confirmed by the X-ray diffraction study of McMurdie et al. [4]. Regarding metastable phases, Billhardt

et al. [5] were the first to describe the hexagonal phase, under the designation T-$PbSiO_3$, and Smart et al. [6] were the first to report the L-PS phase.

To the best of our knowledge, Lippmaa et al. [7] have performed the only spectroscopic work addressing the overall crystallization and phase transitions in lead metasilicate glass at different temperatures. These authors observed by $^{29}Si$ MAS-NMR gradual structural changes in lead metasilicate glass heat-treated at 550 °C, leading to the formation of alamosite. They discovered some differences by contrasting these spectral results to those found for samples heat-treated ex-situ for 24 h at 475°C, and for 24 h at 710°C. The authors concluded that the crystallization evolution in lead metasilicate glass, from which alamosite emerges, is a very complex process.

In this work, we examine in detail the isothermal crystallization kinetics of PS glass by in-situ Raman spectroscopy at 550 °C and 600 °C, aiming at shedding light and possibly demystifying some of the complexity in the system by providing additional evidence for Ostwald's rule of stages. This vibrational method is quite suitable for studying the crystallization kinetics of glasses [8], once it is sensitive to small quantities of well-ordered clusters that appear locally at relatively early crystallization stages as sharp peaks, against the broad glass bands that compose the spectral background [9].

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## 2. Experimental methods

The detailed preparation methods of the glass samples studied are found elsewhere [10, 11]; the specimens are from the same batch as in those works. The chemical compositions were evaluated by electron probe microanalysis (EPMA) on a JEOL JXA8230 5-WDS using a 15 nA current and 15 kV voltage on a 1 µm spot size in ten different points. The sample had a homogeneous composition, averaging 49.7 mol.% $SiO_2$ and 50.3 mol.% PbO with an estimated error of 0.5 mol.%.

Raman measurements were taken using a Horiba-Jobin-Yvon HR800 Evolution micro-Raman spectrometer. The laser wavelength of 633 nm was used as an excitation source and the scattered light was collected by a 50x long working-distance objective. The position of the silicon peak (520.7 $cm^{-1}$) was used to calibrate the equipment. Two very small polished samples ($\sim$ 1 $mm^3$), used to minimize temperature gradient effects, were mounted on a Linkam TS1500 micro-furnace. The sample was heated from room temperature until the target temperature (550 °C or 600 °C) at a heating rate of 20 °C/min step. It is assumed that the heating process has only a small influence on the crystallization effects. The spectra were collected at a fixed position in independent runs at 550 °C and 600 °C, for each of the small polished samples, using the 600 slits/mm grating between 10 and 1230 $cm^{-1}$, with a laser power of l mW on the sample. Each spectrum is an average of six measurements of 15 s each, taken every 2 minutes (until 30 min), five minutes (until 60 min) and finally every ten minutes thereafter. Each spectrum was normalized by the highest absolute intensity, usually occurring in the boson peak region of the spectrum.

## 3. Results and discussion

Smart et al. [6] have described the synthesis conditions to obtain ex-situ single-phase samples of the three lead metasilicate crystals. According to them, there are four different ways to obtain alamosite, consisting of (i) a series of sintering and grinding of lead oxide and quartz precursors; (ii) crystallization of PS glass above 540 °C; which the authors claimed to be ready; (iii) PS melt undercooling down to temperatures greater than 660°C, where it is left to crystallize for several hours; (iv) glass hydrothermal crystallization at 500°C and 300 bars for 48 h. These authors reported that the H-PS phase can be obtained solely by undercooling a PS melt to 650°C, and that the pure L-PS can be formed at 480 °C by glass crystallization for 14 days.

MAS-NMR [12-14] and Raman spectroscopy [11, 15] are frequently applied to investigate silicate glass structures in terms of the $Q^n$ population, which are related to the $(SiO_4)$ tetrahedra connectivity within the glass network, where n ranges from 0 to 4 bridging oxygens/tetrahedron. The description of PS overall crystallization accompanied by in-situ Raman spectroscopy is advantageous, taking into account that the Raman spectra of the known crystalline phases (namely alamosite, H-PS and L-PS) at room temperature have already been reported in the literature by Furukawa et al.[16, 17].

To interpret the in-situ experiments, the three crystalline phases were produced and stabilized ex-situ for a series of different temperature and time treatments. The ex-situ Raman spectra of H-PS, L-PS and alamosite phases were obtained respectively after isothermal crystallization: (i) from the undercooled melt at 650°C for 15 min, following the Smart et al. [6] synthesis conditions; (ii) from the glass at 540°C for 40 min; and (iii) from the glass at 540°C after 6 days. Regarding the crystal morphologies, we found the H-PS to be related to a hexagonal-like crystal shape, the L-PS phase associated to an ellipsoidal crystal habit, and the alamosite to a pyramidal-like geometry, as presents the Fig. 1. Their Raman spectra were labeled based on the work of Furukawa et al. [16, 17], and are shown in Fig. 2 along with the glass spectrum, which served as guides to follow the crystallization kinetics at high temperatures.

To this date, the analysis of the Raman spectra of the three lead metasilicate crystalline phases in the literature focus on the high-

frequency region (Fig. 2b), and its correlation with the crystal structure is described in terms of silicate tetrahedra connectivity by the $Q^n$ units [16, 17]. As enhanced by Siidra et al. [18], lead silicate crystals have elaborate structures, due to the topological and geometrical adaptation of silicate anions to the arrangements of the $Pb^{2+}$ cations. The alamosite crystalline structure is monoclinic, consisting of 12 silica tetrahedral chains interconnected by pyramidal spiral chains of lead [19-21]. This complex arrangement corresponding to three distinct $Q^2$ sites and four Si-O-Si bond angles, and is responsible for the high-frequency multicomponent bands [16, 17]. Detailed structural descriptions regarding the intermediate metastable phases are still unknown, even though X-ray diffraction pattern from H-PS, the so-called hexagonal phase can be indexed as a hexagonal unit cell, isomorphic to the hexagonal $PbGeO_3$ [22]. The high-frequency Raman spectrum for the H-PS phase exhibits a three-summit profile in a spread frequency range, proposed to comprise from $Q^0$ to $Q^3$ silicate groups [16, 17]. On the other hand, the L-PS phase shows an intense band at 960 $cm^{-1}$, which is primarily associated to a $Q^2$ structure [16, 17].

The Raman spectra of the lead silicate glasses were historically analyzed by gradually varying the lead concentration and observing the resulting spectral changes in relation to the vitreous silica [15, 23, 24]. The PS glass spectrum (Fig. 2) exhibits, at the low-frequency region, an intense peak often referred as the Boson peak (40 $cm^{-1}$), which is observed in all amorphous silicate materials, and whose nature is still a matter of discussion; and two peaks (centered on 93 $cm^{-1}$ and 137 $cm^{-1}$), both assigned to Pb-O vibration [15, 23-26]. The plateau observed between 460 and 550 $cm^{-1}$ is attributed to delocalized vibrations with mixed O-Si-O bond stretching and characteristic bond bending [14]. In its turn, the asymmetrical high-frequency envelope (800-1200 $cm^{-1}$) is due to the symmetric stretching vibrations of the $Q^n$ units [11, 15]. From the model proposed by Sampaio et al. [27], corroborated by molecular dynamics simulations, this band can be fitted by six Gaussians curves, which at room temperature are centered at 848 $cm^{-1}$, 898 $cm^{-1}$, 955 $cm^{-1}$, 1000 $cm^{-1}$, 1039 $cm^{-1}$, and 1098 $cm^{-1}$, and are assigned to the vibrations of $Q^0$, $Q^1$, $Q^2$, $Q^3$, $Q^{3'}$ and $Q^4$ species, respectively. The above chart in Fig. 2b illustrates the glass $Q^n$ decomposition then contrasted to the aforementioned crystalline spectra at high frequencies, enhancing that the $Q^n$ literature proposition is in the same regions.

Fig. 3 shows, for a fixed point, the time evolution of the Raman spectra obtained for the lead metasilicate glass while undergoing isothermal crystallization at 550 °C (Fig. 3a and b) and 600 °C (Fig. 3c and d). For each temperature, the spectral evolution at low-frequency (10-175 $cm^{-1}$) and high-frequency regions (700-1230 $cm^{-1}$) are illustrated separately. In both temperatures, the crystallization onset can be perceived by the new peaks that appear in the low-frequency region (at $\sim$ 50 and 95 $cm^{-1}$). Additionally, the spectra change gradually: (i) the Boson peak intensity decreases (Fig. 3a and c), indicating progressive conversion from the vitreous to the crystalline state [27]; (ii) while the $Q^n$ high-frequency envelope (Fig. 3b and d) evidences the continuous evolution from the glass to alamosite, the stable crystalline phase, intermediated by different metastable phases in each case.

Comparisons between the Raman spectra obtained in-situ at high temperatures, during crystallization (Fig. 3) and the three PS crystalline phase spectra at room temperature (Fig. 2) may guide the description of crystallization pathway. However, for comparing such temperatures it is necessary to take into account that the anharmonic effects might induce some peak shift and broaden, and more importantly, except for the spectra in the early and final stages, the processes display mixed phases. From the beginning of crystallization, these phases comprise the glassy phase; first along with the metastable phase, then with a mixture of the metastable phase and alamosite prior to a complete transformation to alamosite, within the region illuminated by the laser. At 550 °C the crystallization pathway proceeds from the L-PS to the alamosite phase, as indicated by the $\sim$960 $cm^{-1}$ peak arising in the $Q^n$ region (Fig. 3b), whereas at 600 °C, the crystalline phases evolve from the H-PS
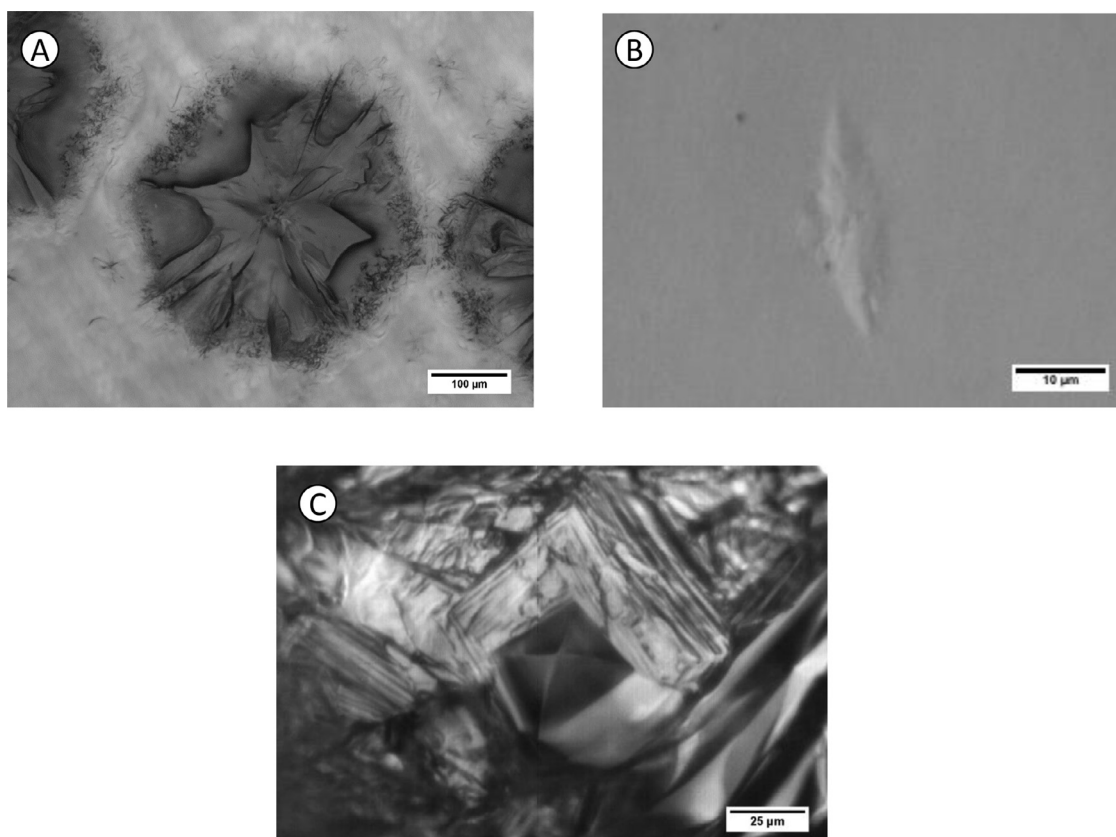
**Fig. 1.** Micrographs of heat-treated PS glass samples obtained using optical microscopy with reflected light evidencing the (a) H-PS (b) L-PS and (c) alamosite crystal morphologies. These single-crystals were obtained by isothermal treatment respectively at 650°C for 35 minutes; at 512°C for 1 hour and at 700°C for 10 minutes.

to the alamosite, as perceptible by the occurrence of a three-summit profile (Fig. 3d).

These results can explain the different MAS-NMR $^{29}$Si spectra obtained by Lippmaa et al. [7]. The spectrum for the sample heat-treated for 24 h at 710 °C is from alamosite, as identified by the authors themselves; however, they do not provide any information regarding the metastable crystalline phases. For the sample heated for 24 h at 475 °C they obtained an NMR spectrum assigned to $Q^2$ structures, which we suggest corresponds to the spectrum of L-PS, not necessarily pure but possibly mixed with alamosite. On the other hand, the spectra set from the heat-treated samples at higher temperatures, labeled by them as

550 °C, give rise to a metastable crystalline phase that exhibits an NMR signal corresponding to multi $Q^n$ structures reaching up to $Q^3$, which could be related to the H-PS phase that gradually evolves to alamosite.

No evidence of conversion between the metastable phases was found in our isothermal experiments. Therefore, we reaffirm the conclusion of Smart et al. [6], and suggest that either the L-PS or H-PS phase are the only intermediate crystalline phases prior to the alamosite stabilization at each of these temperatures. We plan to further investigate this system with in-situ X-ray diffraction and additional methods, to infer the physical causes of these pathways.
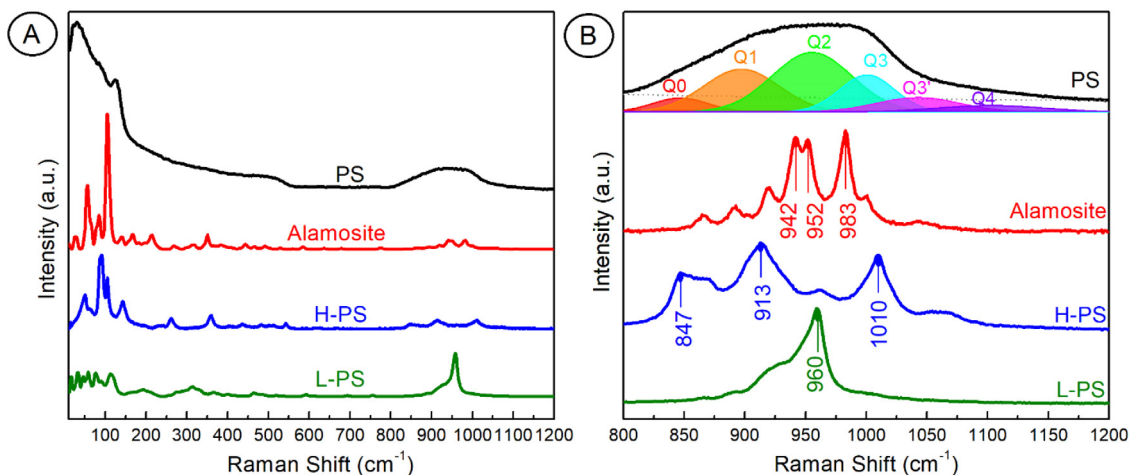


**Fig. 2.** (A) Full (10-1200 cm$^{-1}$) and (B) detailed high-frequency (800-1200 cm$^{-1}$) Raman spectra of lead metasilicate glass (PS) and its three crystalline phases alamosite, H-PS and L-PS taken at room temperature.
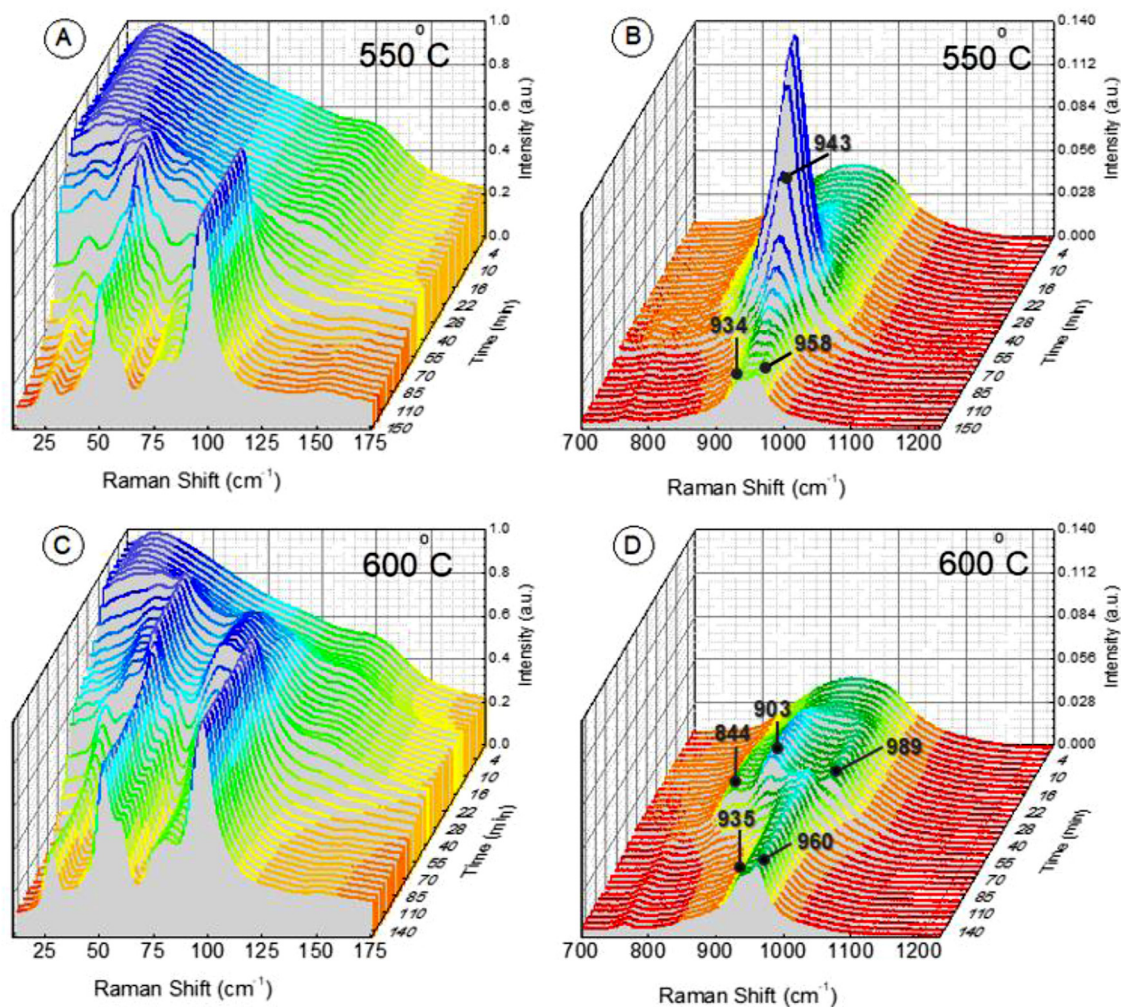
**Fig. 3.** Time evolution of the Raman spectra obtained for the lead metasilicate glass while in isothermal crystallization at a fixed position show, respectively, (A) the low-frequency (10 - 175 cm$^{-1}$) and (B) the high-frequency regions (700-1230 cm$^{-1}$) at 550 °C, and (C) the low-frequency (10 - 175 cm$^{-1}$) and (D) the high-frequency regions (700 -1230 cm$^{-1}$) at 600 °C.

## 4. Conclusions

Three phases crystallize in lead metasilicate glass, depending on the time and temperature, the stable alamosite, and the metastable H-PS and L-PS. This study of lead metasilicate glass by in-situ Raman spectroscopy provided a detailed description of the crystallization pathways, clarifying some of its alleged complexity. The crystal-crystal phase evolution occurs via distinct metastable phases at different temperatures. Raman spectra taken as a function of time at 550 °C revealed that the crystalline phases evolved directly from the L-PS to alamosite, whereas at 600 °C, the crystallization pathway proceeded directly from the hexagonal allotrope to alamosite.

These results shed light on an underexplored subject regarding glass crystallization, metastable phase formation. They rectify the assertion that alamosite can be readily obtained above 540 °C, and provide additional evidence for Ostwald's rule of stages, which predicts that crystal nucleation is often intermediated by metastable phases.

## Credit author statement

I declare that the subject of the present manuscript/research there is no financial interest.

## Declaration of Competing Interest

None.

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