A threshold heating rate for single-stage heat treatments in glass-ceramics containing seed formers

Alessio Zandona1,2 | Christoph B. M. Groß3 | Bernd Rüdinger3 | Joachim Deubener1

1Institute of Non-Metallic Materials, Clausthal University of Technology, Clausthal-Zellerfeld, Germany
2Condition Extrêmes et Matériaux: Haute Température et Irradiation, CNRS UPR 3079, Orléans, France
3Central Research & Development and Analytics, Schott AG, Mainz, Germany

Correspondence
Alessio Zandona, Institute of Non-Metallic Materials, Clausthal University of Technology, Clausthal-Zellerfeld, Germany.
Emails: alessio.zandona@tu-clausthal.de;
alessio.zandona@cnrs-orleans.fr

Funding information
Walter-Benjamin Scholarship, Grant/Award Number: ZA 1188/1-1

Abstract
The development of glass-ceramic materials is often achieved using an elementary microstructural strategy that splits the tasks of seed formation and functionality between two types of crystals. This strategy requires customized time-temperature ceramization protocols, which have been so far implemented using empirical parameters. Here, a more fundamental approach is proposed: the extent of overlap $O_e$ between seed formation and volume crystallization is evaluated by calorimetric and dilatometric measurements, targeting the computation of a threshold heating rate $q_t$ for effective single-stage heat treatments. The applicability of this novel parameter is tested in TiO$_2$-doped lithium magnesium aluminosilicate glass-ceramics, whose seed formation stage is thoroughly characterized by Raman spectroscopy and STEM. High-temperature X-ray diffraction demonstrates that insufficient seeding results in potentially weaker performances of the final products, due to large sizes and silica deficiency of the functional quartz solid solution crystals.

KEYWORDS
crystals/crystallization, glass, glass-ceramics, nucleation, quartz, quartz solid solution, seed formers, threshold heating rate, TiO$_2$

1 | INTRODUCTION

Glass-ceramics are functional materials of high technological and economical relevance, with applications spanning from medicine to nuclear waste immobilization and energy storage. They contain functional crystals in a residual amorphous matrix and are mostly obtained by a three-step process, involving: (1) the production of a homogeneous glass melt, (2) the forming of a glass article in the desired shape, and (3) a controlled glass crystallization protocol, achieved by thermally annealing the material above its glass-transition temperature.

The addition of nucleating agents (also seed formers) has been exploited since the early stages of glass-ceramics development to enhance and modulate glass crystallization. TiO$_2$ represents one of the best-established nucleating agents in aluminosilicate compositions and its efficacy essentially relies on the strong temperature dependence of its melt solubility: sufficiently fast melt quenching can indeed yield a glass that is metastably supersaturated in TiO$_2$ and therefore possesses a strong driving force for nucleation. TiO$_2$-bearing nanosized seeds, including TiO$_2$(B), anatase, and Mg-Al-titanate, can subsequently homogeneously precipitate in the material upon reheating and catalyze the further heterogeneous nucleation of a functional phase, such as quartz solid solution (Qss) in lithium and magnesium aluminosilicate glass-ceramics. The solubility of TiO$_2$ in silicate melts varies additionally as a function of composition.
efficiency as a nucleating agent, that is, the rate by which it can induce the formation of seed crystals and their final number density, can be substantially and systematically affected by changes in the glass stoichiometry, as recently inferred in the lithium magnesium aluminosilicate system (LMAS). One should note that TiO\textsubscript{2} seed formation has been shown to pervasively modify the nanostructure of the residual melt and to heavily affect its viscosity, complicating the classic schematic views on the role of nucleating agents.

This study has been therefore designed in order to gain a deeper, overarching understanding of the mechanism of TiO\textsubscript{2} seed formation in the LMAS system, taken as a prototypical representative of commercially available glass-ceramic materials relying on this additive. The focus was specifically placed on a detailed characterization of the stage of seed formation and its influence on the further heterogeneous nucleation and growth of Qss. Our results shed new light on the complex interplay between these processes, which are otherwise generally considered as decoupled events on a time-temperature kinetic scale. Moreover, it was possible to establish a novel fundamental approach to assess the capability of a glass containing nucleating agents to undergo successful single-stage ceramization, based on the computation of a threshold heating rate $q_t$ (see Section 2.4).

## EXPERIMENTAL PROCEDURE

### 2.1 Sample preparation

The glass samples were prepared by the melt-quench route at the laboratories of the company Schott AG as described elsewhere. Their composition (Table 1) was determined by X-ray fluorescence (XRF, PANalytical MagiX PRO) and flame atomic absorption spectroscopy (FAAS, Varian/Agilent Spectra AA 280FS); minor CaO, Na\textsubscript{2}O, P\textsubscript{2}O\textsubscript{5}, and K\textsubscript{2}O impurities originated from the employed raw materials. The three target stoichiometries belonged to the LMAS compositional system and contained 4 mol\% TiO\textsubscript{2} as a nucleating agent: the Al/Si ratio of the samples decreased from LMA\textsubscript{T} to LMSi\textsubscript{T}, whereas Li/Mg and (Li+Mg)/Al ratios were kept constant. Three additional TiO\textsubscript{2}-free reference samples were produced, namely LMAI, LMI\textsubscript{NT}, and LMSi.

To induce the formation of TiO\textsubscript{2}-bearing nuclei, LMA\textsubscript{T}-Tu, LMI\textsubscript{NT}-Tu, and LMSi-Tu (labeled with an additional –u to refer to the untreated starting materials) were subjected to preliminary heat treatments according to the following T-t-protocol: 5 K min$^{-1}$ to the target temperature (respectively, 705°C, 730°C, and 750°C), 120 min annealing time, furnace cooling to room temperature. The chosen temperatures were slightly higher than the glass transitions of the respective samples (Figure 3) and were selected after several attempts aiming at reproducibly obtaining seeded glasses without triggering the formation of Qss. Raman spectroscopy allowed to monitor the seed formation, as demonstrated in this work and elsewhere, whereas X-ray diffraction was used to check for the presence of aluminosilicate crystals. The resulting samples were labeled with an additional -s suffix, to recall the presence of TiO\textsubscript{2}-bearing crystalline seeds (LMAI-Ts, LMI\textsubscript{NT}-Ts, and LMSi-Ts).

| Oxide (mol\%) | LMAI-T | LMI\textsubscript{NT}-T | LMSi-T | LMAI | LMI\textsubscript{NT} | LMSi |
|---------------|--------|------------------------|--------|------|------------------------|------|
| Li\textsubscript{2}O | 9.3(2) | 7.4(2) | 6.2(2) | 9.5(2) | 7.6(2) | 6.3(2) |
| MgO | 8.5(7) | 7.0(6) | 5.8(5) | 9.3(5) | 7.7(4) | 6.3(3) |
| Al\textsubscript{2}O\textsubscript{3} | 18.3(6) | 14.9(4) | 12.4(4) | 18.8(6) | 15.3(4) | 12.7(4) |
| SiO\textsubscript{2} | 60.2 | 66(2) | 71(2) | 62(1) | 69(1) | 74.7(1) |
| TiO\textsubscript{2} | 4.2(3) | 4.1(3) | 4.1(3) | 4.1(3) | 4.1(3) | 4.1(3) |
| CaO | 0.08(2) | 0.06(1) | 0.07(1) | 0.06(1) | 0.05(1) | 0.05(1) |
| Na\textsubscript{2}O | 0.05(2) | 0.06(2) | 0.05(2) | 0.05(2) | 0.05(2) | 0.05(2) |
| P\textsubscript{2}O\textsubscript{5} | 0.010(3) | 0.010(3) | 0.010(3) | 0.010(3) | 0.010(3) | 0.010(3) |
| K\textsubscript{2}O | 0.010(3) | 0.010(3) | 0.010(3) | 0.010(3) | 0.010(3) | 0.010(3) |
| Oxide ratios | | | | | | |
| Li\textsubscript{2}O/MgO | 1.09 | 1.06 | 1.07 | 1.02 | 1.00 | 1.00 |
| (Li\textsubscript{2}O+MgO)/Al\textsubscript{2}O\textsubscript{3} | 0.97 | 0.97 | 0.97 | 1.00 | 0.99 | 0.99 |
| Al\textsubscript{2}O\textsubscript{3}/SiO\textsubscript{2} | 0.31 | 0.23 | 0.17 | 0.30 | 0.22 | 0.17 |

### 2.2 Raman spectroscopy

The starting materials and the samples subjected to preliminary heat treatments were characterized using a WITec Alpha300 confocal microscope, equipped with a frequency-doubled Nd/
YAG laser (532 nm) and a CCD detector. Spectra were collected at 0.5 W laser power, with 1 s integration time and 60 accumulations. To facilitate their comparison during data evaluation, a simple polynomial baseline was subtracted from the spectra, which were then normalized to the main vibrational band of the amorphous silicate network, at approximately 500 cm⁻¹.

2.3 Transmittance electron microscopy (TEM)

Samples LMAI-Ts and LMSi-Ts were thinned down to electron beam transparency by mechanical polishing and Ar⁺-ion broad-beam milling (Precision Ion Polishing System PIPS, Gatan). The TEM investigation was performed in a C₃ aberration-corrected FEI TITAN³ 80-300 electron microscope with 300 kV acceleration voltage. Employed analytical methods included scanning transmission electron microscopy (STEM) using a ring-shaped high-angle annular dark-field detector (Model 3000, Fischione) and energy-dispersive X-ray spectroscopy (EDXS) with a Super-X detector system (Bruker).

2.4 Differential scanning calorimetry (DSC)

Starting and seeded materials were processed into cylinders with a thickness of 1.2 mm and a diameter of 4 mm. They were measured at 1, 2, 5, 10, or 20 K min⁻¹ (600°C – 1000°C) using a Netzsch DSC 404 F1 Pegasus calorimeter, in lidded Pt-Rh crucibles under argon gas flow (50 ml min⁻¹). These upscans at different heating rates were used to determine the “extent of overlap” between seed formation and crystallization of the silicate glass matrix, defined as

\[ O_e(q) = T_p - T_c \]  

(1)

where \( q \) stands for the employed heating rate, \( T_p \) for the temperature of the exothermic maximum associated with the crystallization of Qss and \( T_c \) for the position, on the temperature axis, of the centroid for the same complex crystallization event (see Figure 4A). The heating rate dependence of \( O_e \) was approximated by linear regression of the data according to the equation

\[ O_e = A - Bq \]  

(2)

in which A and B are two sample-characteristic constants. The threshold heating rate \( q_t \) for effective single-stage ceramizations at which \( O_e = 0 \) could be then easily obtained as:

\[ q_t = \frac{A}{B} \]  

(3)

2.5 Optical dilatometer

Glassy and pre-treated samples were cut into small parallelepipeds (10 × 5 × 3 mm). Their elongation was measured using a DIL 806 (TA Instruments) while they were heated in air with a constant rate of 2 K min⁻¹ up to 1000°C.

2.6 High-temperature X-ray diffraction (HT-XRD)

Starting materials and seeded samples were processed into polished discs with a thickness of 1.5 mm and a diameter of 15 mm. They were measured using a PANalytical X Pert Pro MPD diffractometer in Bragg–Brentano geometry, equipped with a high-temperature chamber (Anton Paar HTK 1200 N) calibrated as described elsewhere. CuKα₁ radiation from an Empyrean Cu LFF HR X-ray tube was employed, operated at 40 mA/45 kV; the diffracted beam was collected by a Pixcel1D detector (3.347° active length, 255 active channels). In-situ measurements (5–80° 2θ, step size 0.026°, time per step 25.5 s, 5 min total measurement duration) were continuously collected for up to 55 h while the samples were subjected to isothermal annealing at temperatures between 720°C and 840°C, after a fast heating ramp of 20 K min⁻¹. Data evaluation was performed by Rietveld refinement using the software HighScore Plus (PANalytical). A LaB₆ standard (NIST 660a) was used for the determination of average crystallite sizes. Amorphous contents were estimated using a fully crystalline weighed-in CaF₂ standard and accordingly defined external glass-ceramic standards. Weight fractions were then converted into volume fractions after measuring the density of the glass-ceramic samples.

3 RESULTS

The TiO₂-containing glasses LMAI-Tu, LMInt-Tu, and LMSi-Tu were subjected to preliminary heat treatments respectively at 705°C, 730°C, and 750°C for 2 h to obtain seeded materials (LMAI-Ts, LMInt-Ts, and LMSi-Ts). These temperatures were selected slightly above the glass transition of the respective sample (Figure 3) and represented a compromise after several attempts between forming abundant TiO₂-bearing seeds and preventing the crystallization of the silicate matrix into Qss. Reaching sufficient seed formation in absence of Qss proved particularly challenging for sample LMAI-T, due to its lower glass stability (see Figure 3 and related discussion in the text). The overall crystallization sequence of the three analyzed compositions has been characterized elsewhere. The effects of the heat treatments were evaluated by Raman spectroscopy, also in comparison with the spectra of
TiO$_2$-free glasses LMAI, LMInt, and LMSi (Figure 1). All three TiO$_2$-containing samples exhibited similar changes after annealing for 2 h: the intensity of the band located at approximately 900 cm$^{-1}$, absent in the TiO$_2$-free references and generally attributed to low-coordinated Ti species in the glass structure, decreased markedly and suggested a change in coordination. Concurrently, new sharper bands appeared at lower wavenumbers (approximately 150, 200, 260, 400, and 640 cm$^{-1}$) and were assigned, according to previous reference measurements, to crystalline anatase and Mg-Al-titanate, in which Ti is octahedrally coordinated. The magnitude of these changes was higher in the Si richer samples, LMSi-T and LMInt-T, hinting at a stronger tendency towards TiO$_2$ segregation and crystallization in these samples.

The crystalline nuclei were characterized by STEM and EDX in the samples LMAI-Ts and LMSi-Ts (Figure 2). In adherence with the results of XRD and Raman spectroscopy, no aluminosilicate crystals could be observed in the glass-ceramics. In turn, Ti-bearing crystalline seeds were clearly visible in the STEM micrographs, with a diameter of approximately 5 nm in LMSi-Ts and up to 20 nm in LMAI-Ts. They appeared to be surrounded by Al- and Mg-enriched shells, affecting the general homogeneity of the remaining SiO$_2$-enriched amorphous matrix, as detailed in a previous work. Other authors have reported similar structures after annealing TiO$_2$-doped LAS glass-ceramics.

To investigate how the applied preliminary heat treatments may affect the overall crystallization process, the samples were measured by DSC, at first with a simple upscan at 5 K min$^{-1}$. The following observations could be extracted from the curves (Figure 3A–C):

- The glass transition ($T_g$) was generally shifted to higher temperatures after the preliminary heat treatments, as expected from previous works. The effect was more pronounced in the Si-rich samples; it can be interpreted in terms of a viscosity increase due to the segregation of TiO$_2$-bearing nanocrystals and the subsequent change in glass chemistry.
- A broad exothermic feature ($T_N$), clearly visible only in LMInt-Tu and LMSi-Tu and analogous to other authors’ observations in glass-ceramics containing nucleating agents, disappeared after the preliminary heat treatments. It was accordingly interpreted as the
calorimetric signature for the formation of anatase and Mg-Al-titanate nuclei in the samples.\textsuperscript{14,20,28,29}

- The main exothermic peak ($T_p$), previously assigned to the crystallization of the glass into Qss,\textsuperscript{14} displayed an earlier onset and was generally broadened after the preliminary heat treatments, possibly because of the inferred increase in viscosity after seed formation.\textsuperscript{19} The effect was particularly pronounced in sample LMAl- Ts.

- Specifically comparing the untreated glasses, $T_g$ and $T_p$ displayed the highest temperature difference in LMSi- Tu (196 K), an intermediate value in LMInt- Tu (159 K) and the lowest one in LMAl- Tu (118 K). This difference was used as an empirical estimation of glass stability upon thermal annealing.\textsuperscript{30}

- Similar inferences could be derived from dilatometric measurements of the same samples, after differentiating the obtained relative length changes with respect to temperature (Figure 3D–F).

Subsequently, the “extent of overlap” $O_e$ between seed formation and Qss crystallization could be determined for the untreated samples by performing DSC measurements at various heating rates using Equation 1. Over the chosen heating rate range, $T_p$ and $T_s$ progressively shifted to higher temperature and overlapped, until the latter one was practically undiscernible (Figure 4A). The values obtained for $O_e$ (Figure 4B) clearly decreased with increasing heating rates and were generally higher in the Si-richer samples. The threshold heating rate $q_t$ was then defined as the value above which no seed formation could possibly take place before the onset of Qss crystallization, leading to a simultaneous and uncontrolled ceramization process. It was extrapolated using Eq. 3 to approximately 25 K min$^{-1}$ for LMInt-Tu, whereas samples LMAl-Tu and LMSi-Tu exhibited threshold rates respectively lower and higher.

The crystallization of Qss was evaluated in the glass-ceramics by HT-XRD (Figure 5), to highlight differences between the homogeneous starting materials and their seeded counterparts. The samples were quickly heated up (20 K min$^{-1}$) above the previously selected seed formation temperatures, to induce immediate formation of Qss crystals. After performing Rietveld refinements, the results of the quantitative analysis were plotted in logarithmic form (Figure 6) to allow data evaluation within the assumptions.
of the Johnson–Mehl–Avrami–Kolmogorov (JMAK) model, as similarly described by other authors in LAS glass-ceramics. The curves obtained for LMAl-Tu and LMAl-Ts differed markedly, although they finally all converged to a similar amount of Qss (≈70 vol% in all samples): the seeded sample underwent crystallization after a lower induction time, but the reaction proceeded more slowly than in the respective parent glass, as expected from the above-mentioned broadening of the DSC signals. On the other hand, discrepancies between untreated and seeded materials were more subtle at LMInt-T and LMSi-T compositions. In these samples, moreover, two crystallization regimes appeared to be active, as previously noticed in LAS glass-ceramics: initially, the crystalline content increased fast but soon entered a second stage of slower growth, absent in LMAl-Tu and LMAl-Ts.

The JMAK kinetic analysis, focused on the first, faster crystallization stage, provided a direct means of comparison among the samples. The $n$ exponents determined at various temperatures from LMSi-Tu, LMInt-Tu, LMSi-Ts, and LMInt-Ts samples plotted in the range 0.5-1.7 (Figure 7A); they displayed a slight temperature dependence but virtually no difference between untreated and seeded materials. In turn, the $n$ values computed for LMAl-Tu and LMAl-Ts exhibited substantial discrepancies, with the untreated material plotting as high as 3.3(3) at 720°C. In these samples, the temperature dependence of the JMAK exponent was more evident and consistent with other glass-ceramic systems.
In addition, the experimental data were used to calculate the overall JMAK activation energy for crystallization in the various samples (Figure 7B). All starting materials displayed similar values; preliminary seed formation appeared to have no perceivable effect on LMAl-Ts, whereas LMInt-Ts and LMSi-Ts yielded noticeably lower activation energies than their untreated counterparts.

To support a meaningful interpretation of these results, average crystallite sizes and unit cell volumes of Qss were plotted for all in-situ high-temperature measurements as a function of the Qss amount in the samples (Figure 8A). A monotonic increase in average size was only visible at LMSi-T compositions, with virtually no differences between untreated and seeded materials; final crystallite sizes converged towards 42 nm in this sample. On the other hand, LMInt-T and especially LMAI-T exhibited an initial steep increment, followed by a stage of stagnation and then an apparent decrease. This complex behavior was more evident in the untreated starting materials, LMAI-Tu and LMInt-Tu, also achieving much higher crystallite sizes than their seeded counterparts. The final values were generally bigger in the Al-richer samples.

As for the unit cell volumes of Qss (Figure 8B), they displayed a linear correlation with the amount of Qss formed in the samples (as analogously observed in LAS glass-ceramics34). The curves pertaining to LMSi-T plotted lower than those of LMInt-T, whereas LMAI-T reached the highest values. These observations were in line with the known expansion of the Qss unit cell volume with a higher degree of structural stuffing,14,17,36-38 dependent on the availability of Al, Mg, and Li in the glass. At a comparable ceramization stage, the Qss unit cell volumes were interestingly higher in LMInt-Tu and LMAI-Tu than in their seeded counterparts; at LMSi-T composition, again, no clear differences were visible.

4 | DISCUSSION

The three analyzed base compositions (LMAI-T, LMInt-T, LMSi-T) revealed striking dissimilarities in the dynamics of TiO2-related seed formation and Qss crystallization, despite an equal degree of TiO2 doping. These observations appear to confirm the inverse correlation between TiO2 solubility in silicate melts and their overall SiO2 content estimated by other authors12,13: although all the glasses studied within this work could easily incorporate 4 mol% TiO2 above their liquidus temperature, the driving force towards seed formation (and therefore their supersaturation at high undercooling) appeared to intensify going from sample LMAI-T to LMInt-T and LMSi-T. This phenomenon, coupled with the similarly inferred increase in overall glass stability, particularly complicated the obtainment of a well-seeded material at LMAI-T compositions before the heterogeneous nucleation of Qss.

To corroborate these considerations, a threshold heating rate \( q_t \) for effective single-stage ceramization protocols was estimated (as defined in Section 2.4), evaluating the extent of overlap \( O_e \) between the calorimetric signatures of TiO2 seed formation and Qss crystallization as a function of different heating rates (Figure 4). This procedure followed the
assumption that, at least in this class of glass-ceramics, the seed formation induced by TiO₂ must ideally be completed before the crystallization of the glass matrix, to provide sufficient sites for the heterogeneous nucleation of the desired functional phase (Qss). This condition can only be satisfied at heating rates that are lower than $q_t$, whereas both processes take place simultaneously and in an uncontrolled fashion above this value. This approach yielded indeed a very good agreement with all experimental observations, despite the dissimilarities in formation mechanism, nucleation rate, and growth rate of both seeds and Qss possibly arising at different heating rates. The $q_t$ computed for LMInt-Tu (~25 K min⁻¹) plotted between those qualitatively assessable for LMAl-Tu (~15 K min⁻¹) and LMSi-Tu (>30 K min⁻¹), providing a straightforward method to estimate the maximum applicable heating rate that still allows sufficient seed formation before the appearance of Qss.

The reliability of this threshold heating rate $q_t$ for effective single-stage heat treatments was then tested by isothermal HT-XRD measurements, performed after approaching the target temperatures with 20 K min⁻¹. LMSi-Tu and LMSi-Ts displayed virtually no differences in terms of Qss crystallization kinetics, crystallite size, and structural parameters, suggesting that the Qss must have had a comparable number of available sites for heterogeneous nucleation in both materials at the beginning of the isothermal holds. In other words, LMSi-Tu was invariably able to produce sufficient TiO₂-bearing seeds at the comparatively fast heating rate of 20 K min⁻¹, even without a preliminary heat treatment. On the contrary, LMInt-T and especially LMAl-T compositions exhibited strong differences between untreated and seeded state: the crystallization kinetics of Qss differed markedly, whereas the average crystallite sizes in the untreated materials (~s) displayed a fast initial increase, followed by a gradual reduction. This observation was interpreted in terms of an initial absence of TiO₂-bearing nuclei, followed by a stage of overlap of seed formation and Qss crystallization, which would explain the gradual transition from relatively few big

**FIGURE 5** Excerpts of the first 10 diffractograms collected in-situ during the isothermal holds applied to: (A) sample LMAl-Tu at 735°C, (B) sample LMSi-Tu at 825°C, (C) sample LMAl-Ts at 735°C, (D) sample LMSi-Ts at 825°C. All visible reflections were assigned to and refined with the structure of Qss [Color figure can be viewed at wileyonlinelibrary.com]
crystals to the final statistical prevalence of smaller ones. In seeded LMAI-Ts and LMInt-Ts, this phenomenon was less evident due to the immediate availability of seeds; the Qss crystals resulted generally smaller.

Finally, LMAI-Ts and LMInt-Ts developed Qss crystals with noticeably lower unit cell volumes than their untreated
counters. These differences, interpreted in terms of a different degree of structural stuffing of the crystals, may be again explained through the modification of the glass matrix induced by the TiO₂-related seed formation. In fact, STEM characterization (Figure 2) revealed non-negligible incorporation of Mg and Al into the TiO₂-bearing nuclei after the preliminary heat treatments. It is therefore possible to hypothesize that, in case of an incomplete seed formation due to a too fast heating rate (as for LMAI-Tu and LMIINT-Tu during HT-XRD measurements), the glass matrix would be still richer in Mg and Al, available for the incipient Qss formation. As for the decrease in unit cell volume observed in all samples during the crystallization process, it might stem from the spatial growth of the Qss crystals through an increasingly Si-rich glass matrix, starting from their heterogeneous nucleation sites at the Mg- and Al-enriched shells around the seeds.

This hypothesis could also clarify the slower crystallization kinetics of seeded LMAI-Ts and the observed slight broadening of the DSC crystallization peaks of the seeded samples with respect to their starting materials: the pronounced chemical heterogeneity of the glass matrix around the nuclei might have acted as a sort of diffusion barrier, as already postulated by previous authors. In an alternative view, mediated through the Stokes–Einstein relation, one might correlate these phenomena with the increase in viscosity brought about by the chemical and nanostructural modification of the residual melts after seed formation.

5 | CONCLUSION

Model glass-ceramics in the LMAS system were analyzed to gain a deeper understanding of the mechanism of TiO₂ seed formation in glass melts. Evaluation of the extent of overlap between seed formation and crystallization of the silicate glassy matrix allowed to introduce a threshold heating rate for effective single-stage heat treatments. Based on these parameters, ceramization protocols can be optimized in order to avoid insufficient seeding and weaker performances of the final products, arising from large crystallite sizes or silica deficiency of the functional quartz solid solution crystals.

ACKNOWLEDGMENTS

The authors are grateful to Dr. Christian Patzig for performing the TEM investigation at the Fraunhofer IMWS in Halle (Saale), Germany. Alessio Zandonà acknowledges the Deutsche Forschungsgemeinschaft for providing funding through the Walter-Benjamin Scholarship, grant n. ZA 1188/1-1.

ORCID

Alessio Zandonà https://orcid.org/0000-0003-0091-9546

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How to cite this article: Zandona A, Groß CB, Rüdinger B, Deubener J. A threshold heating rate for single-stage heat treatments in glass-ceramics containing seed formers. J Am Ceram Soc. 2021;104:4433–4444. https://doi.org/10.1111/jace.17822.