**Diffusion-driven and size-dependent phase changes of gallium oxide nanocrystals in a glassy host**

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**Abstract**

Phase transformations at the nanoscale represent a challenging field of research, mainly in the case of nanocrystals (NCs) in a solid host, with size-effects and interactions with the matrix. Here we report the study of the structural evolution of $\gamma$-Ga$_2$O$_3$ NCs in alkali-germanosilicate glass – a technologically relevant system for its light emission and UV-to-visible conversion – showing an evolution drastically different from the expected transformation of $\gamma$-Ga$_2$O$_3$ into $\beta$-Ga$_2$O$_3$. Differential scanning calorimetry registers an irreversible endothermic process at $\sim$1300 K, well above the exothermic peak of $\gamma$-Ga$_2$O$_3$ nano-crystallization ($\sim$960 K) and below the melting temperature ($\sim$1620 K). Transmission electron microscopy and X-ray diffraction data clarify that glass-embedded $\gamma$-Ga$_2$O$_3$ NCs transform into LiGa$_5$O$_8$ via diffusion-driven kinetics of Li incorporation into NCs. At the endothermic peak, $\beta$-Ga$_2$O$_3$ forms from LiGa$_5$O$_8$ dissociation, following a nucleation-limited kinetics promoted by size-dependent order–disorder change between LiGa$_5$O$_8$ polymorphs. As a result of the changes, modifications of UV-excited NC light emission are registered, with potential interest for applications.
Introduction

Materials undergoing phase transformations at the nanoscale are emerging as a potential breakthrough in several technological areas. The achievement of reproducible cycles between high and low resistance phases at the submicrometer scale constitutes one of the most concrete results in the field of highly integrated rewritable data storage devices. An even more challenging target is the implementation of metal–insulator transitions in wide-band-gap nanosystems, as found in Ga-oxide upon amorphous-to-crystalline phase changes. Recent results regarding Ga containing oxide glasses suggest that optical properties – such as UV transmittance and UV excited light emission – can be conveniently modified by crystallization of Ga-oxide nanoparticles incorporated in the glass matrix. These results enable the use of nanocrystal (NC) growth– and NC phase changes inside a solid host – as a tool for functionalizing glass-based materials for information technology. The idea of achieving unprecedented data-storage capability and stability by inducing local modifications of structural and optical functions in glass – specifically by means of focused laser exposure – has recently been envisaged and preliminarily demonstrated in a prototypal system of silica glass. Promising results have also been obtained for silver-containing phosphate glass through the formation of fluorescent Ag clusters under laser exposure. As regards nanostructured glasses, the knowledge of the phase changes that NCs undergo in a solid matrix is important for evaluating possible strategies of nanocrystal-in-glass data-storage and their real potential.

The detailed mechanisms underlying structural phase changes at the nanoscale are not easily predictable in general, and particularly when the process involves NCs interacting with a solid host. This is the case of Ga oxide NCs in silicate glass, which is one of the prototypal systems of oxide-in-oxide nanostructured glasses together with SnO$_2$-doped silica. Stability and thermal evolution of Ga-oxide nanophases are expected to be largely different from the freestanding and pure compound. The role of a solid host in the incorporation of doping species inside Ga$_2$O$_3$ NCs has been recently investigated, but also the structural evolution of Ga$_2$O$_3$ is expected to be influenced. In fact, in glass, Ga-oxide can segregate in a crystal phase different from the thermodynamically stable β-Ga$_2$O$_3$ structure. Distinct Ga-oxide polymorphs are reported in the literature, indicated as α, β, γ, δ, ε, and κ, with quite different structures and stability properties. Among these phases, β-Ga$_2$O$_3$ is the thermodynamically stable one, with monoclinic structure. It was identified as a distinct polymorph with C-type rare earth sesquioxides, but new recent data suggest that δ-Ga$_2$O$_3$ is probably a nanocrystalline form of ε-Ga$_2$O$_3$ and not a distinct polymorph. This metastable phase in
fact transforms into orthorhombic \( \varepsilon \)-Ga\(_2\)O\(_3\) after heating above 770 K. Heating of \( \varepsilon \)-Ga\(_2\)O\(_3\) above 1140 K eventually leads to stable \( \beta \)-Ga\(_2\)O\(_3\).\(^{28}\)

In glass, phase separation and crystallization of Ga oxide nanophases in the amorphous matrix has been investigated in recent years by different groups with the aim of studying the possible crystalline nanosystems that are able to host optically active ions with particularly efficient IR light emission.\(^{29-34}\) In these studies different Ga oxide structures have been stabilized in glass. Interestingly, the reported results show that, besides \( \beta \)-Ga\(_2\)O\(_3\),\(^{29-33}\) \( \gamma \)-Ga\(_2\)O\(_3\) can also grow in the form of embedded NCs in oxide glasses,\(^{3-5,33}\) occasionally with additional mixed oxides such as LiGaO\(_2\), LiGaSi\(_2\)O\(_6\), when lithium is present in the matrix, or (Ga\(_2\)O\(_3\))\(_3\)(GeO\(_2\))\(_2\).\(^{35-38}\) The composition of the initial glass plays a clear role in determining the resulting Ga-oxide nanophase. In lithium germanosilicate glasses, we have recently found that the growth of \( \gamma \)-Ga\(_2\)O\(_3\) NCs proceeds from secondary phase separation and crystallization of native Ga-rich nano-heterogeneities generated by liquid–liquid phase-separation during glass quenching.\(^2\) This result prospects the possibility of tailoring the NC size by controlling the nucleation process. At the moment, however, no detailed information is available on the stability range and phase transformations of \( \gamma \)-Ga\(_2\)O\(_3\) NCs – as well as of the other related Ga-oxide nanophases – when embedded in a glass matrix, despite their importance in possible applications.

In this article we fill the gap of knowledge on thermal stability and phase changes of \( \gamma \)-Ga\(_2\)O\(_3\) after its emergence as NCs in an amorphous solid host. A specific Ga-containing alkali–germanosilicate glass has been chosen to assure phase separation of \( \gamma \)-Ga\(_2\)O\(_3\) NCs with a not too large mean NC size and concentration, so as to avoid detrimental light scattering in the view of optical applications. For this purpose, the selected glass comprises an amount of Ga\(_2\)O\(_3\) larger than 15 mol\% (a value we verified to be not enough to promote NC formation at relatively low temperature) and significantly lower than 30 mol\% (a concentration we observed to give rise to strong light scattering from phase separation even in as-quenched glass). The investigated glass also includes GeO\(_2\) – in equal amount of SiO\(_2\) – to lower melt viscosity and melting temperature with respect to the pure silicate (about 100 K lower than in GeO\(_2\)-free variant), and alkali ions to provide partial charge compensation for Ga substituting for Si and Ge in the glass.

Starting from the comparison between thermally induced changes in \( \gamma \)-Ga\(_2\)O\(_3\) nanopowder and \( \gamma \)-Ga\(_2\)O\(_3\) nanophase in glass, our investigation gives an insight into the role of the solid alkali-oxide host in the structural evolution of Ga-oxide guest nanophases. The investigation highlights a complex and still unrevealed evolution through reactions with alkali ions diffusing from the matrix, resulting in structural changes and decomposition. Our results show for the first time the formation of \( \beta \)-Ga\(_2\)O\(_3\) from embedded \( \gamma \)-Ga\(_2\)O\(_3\) via Li diffusion and formation of the LiGa\(_2\)O\(_3\) spinel phase. The data suggest a relationship between the endothermic process that gives rise to \( \beta \)-Ga\(_2\)O\(_3\) and the order–disorder change of LiGa\(_2\)O\(_8\), whose occurrence turns out to be influenced by size-effects and eventually promotes LiGa\(_2\)O\(_8\) dissociation into \( \beta \)-Ga\(_2\)O\(_3\). The analysis of the role of the Li/Na ratio and of NiO as a crystallizing agent is used to verify the model of reactions extracted from measurements at different temperatures and from isothermal analysis of the structural evolution of the nanostructured glass. As a result, the data give a tool for a clear design of stability and changes of the embedded crystal phase. Finally, taking into account some recent results on the light emission properties of \( \gamma \)-Ga\(_2\)O\(_3\) NCs in glass,\(^2\) we analyze the photoluminescence (PL) of the obtained nanophases, providing a basis for the evaluation of a phase-controlled strategy for tailoring optical functions of Ga-oxide containing glass-based systems.

**Experimental procedure**

**Preparation of nanostructured glasses**

Glasses with nominal composition 7.5Li\(_2\)O–2.5Na\(_2\)O–20Ga\(_2\)O\(_3\)–35GeO\(_2\)–35SiO\(_2\) (mol\%) were prepared through the conventional melt-quenching method. The raw materials were amorphous
SiO₂ (special purity grade), GeO₂ (special purity grade), Li₂CO₃ (chemically pure), Na₂CO₃ (chemically pure), and Ga₂O₃ (chemically pure). For comparison purpose, glasses with composition different from the abovementioned one were also synthesized. In the case of Ni-containing samples, the NiO reagent (analytical grade) was added. The amount of reagents in each batch was calculated in order to prepare 20–70 g of the final product. The starting materials were weighed using an analytical balance with an accuracy of 0.001 g. In each preparation, the raw powders were thoroughly mixed in a beaker for 15–20 min. The glasses were prepared in an uncovered platinum crucible (∼45 ml) in an electrically heated furnace at a temperature of 1753 K for 40 min. The melt was poured onto a stainless steel plate and quenched by pressing with another stainless steel plate to obtain samples of about 2 mm of thickness. The as-quenched glass was cut to the desired shape with a low-speed diamond saw or a grinding disc using water as a coolant. Samples were then polished for optical measurements or ground for powder diffraction or electron microscopy analysis.

For ex situ characterization of structural modifications, part of the as-quenched bulk samples was heat-treated in a muffle at various temperatures according to data obtained from differential scanning calorimetry (DSC) analysis. In such cases, heat treatments were performed, with an accuracy of the temperature control within ±2 K, either placing the samples into the furnace at room temperature or directly at the treatment temperature. The latter procedure was used for prolonged isothermal treatments as a function of the treatment duration. Instead, to identify the crystalline phases formed at the extrapolated onset and peak extremum temperatures in DSC curves, samples were treated at room temperature with the same heating rate as in DSC measurements. After treatment, the samples were quenched after removing them from the furnace either immediately, in the case of treatment at extrapolated peak onset temperature, or after staying for 10 min, in the case of treatment at the DSC peak extremum temperature.

LiGa₅O₈ and γ-Ga₂O₃ reference samples

LiGa₅O₈ was prepared by solid state reaction. Raw materials were ground together in an agate mortar and then sintered at 1273 K for 16 h in air. Nanopowder of γ-Ga₂O₃ was synthesized via a non-aqueous sol–gel route.³² 1 g of gallium(III) acetylacetonate was dissolved in 20 ml of anhydrous benzyl alcohol in a glovebox (O₂ < 0.1 ppm and H₂O < 0.1 ppm). The solution was then poured in a 45 ml PTFE liner and transferred to a steel autoclave (Parr Instrument Company) and hermetically sealed. The autoclave was removed from the glove box and stored in a heated furnace at 473 K for 2 days. The resulting milky suspension was centrifuged and the obtained precipitate was carefully washed with diethyl ether, and dried in air at 333 K for 12 hours. Eventually, to completely remove any organic residual, powders were heated in air at 693 K for 1 h.

Material characterization

DSC measurements from room temperature up to about 1470 K were performed on a Netzsch DSC 449F3 high-temperature thermoanalyzer in a platinum pan with cover, at a heating rate of 10 K min⁻¹ in Ar, using bulk samples of 10–15 mg. The reproducibility of endothermic and exothermic peak extremum temperature in the investigated samples is within 2 K.

X-ray diffraction patterns of powdered samples were recorded on a D2 Phaser diffractometer (Bruker) employing nickel-filtered CuKα radiation. High-temperature diffraction patterns were obtained from 300 to 1470 K using a diffractometer X’Pert PRO (PANalytical) equipped with a high-temperature X-ray diffraction chamber model HTK 1200 (Anton Paar). A heating rate of 10 K min⁻¹ was used during in situ XRD measurement, with a stasis of 10 min before scanning, each with a duration of about 20 min. Crystalline phases were identified by comparing the peak position and relative intensities in the X-ray diffraction pattern with the ICDD PDF-2 database. A Tecnai G2 F20 transmission electron microscope, equipped with a Schottky gun operated at 200 kV acceleration...
voltage, was used to acquire high angle annular dark field (HAADF)-scanning TEM (STEM) images of the samples.

Photoluminescence spectra were obtained upon excitation at 250 nm using a xenon lamp and a MS2004i SOL instruments Ltd (Belarus) monochromator with a bandwidth of 4 nm and collecting the emitted light through a second monochromator MS3504i SOL instruments Ltd with a spectral resolution of 2 nm and a photosensor module H7844 Hamamatsu.

**Results and discussion**

**Thermal evolution of glass and the nanophase**

The DSC curves in Fig. 1 give a first insight into the main features of the thermal evolution of the mixed oxide system, including the effects of nickel doping and the changes in the Li/Na ratio with respect to the composition $7.5\text{Li}_2\text{O}–2.5\text{Na}_2\text{O}–20\text{Ga}_2\text{O}_3–35\text{GeO}_2–35\text{SiO}_2$. Such variants give us a tool for checking the role of Li and Na ions in the structural changes, also comparing the induced effects with those caused by NiO addition as the crystallizing agent. In all the investigated compositions we register the occurrence of an exothermic peak in the temperature range $945–1010$ K, about $110–130$ K above the glass transition temperature, evidenced by a smooth step in the DSC curves. In addition, at higher temperatures (in the range $1280–1335$ K), almost all the samples undergo an endothermic process, except Li-free materials. Lithium removal indeed causes a relevant modification of the thermal evolution. The exothermic peak significantly shifts to higher temperature, a second exothermic peak is observed just above $1200$ K, whereas no endothermic process occurs. By contrast, sodium removal from the composition does not drastically change the first steps of the thermal evolution (glass transition and exothermic peak), but it moves the endothermic process towards higher temperatures. Interestingly, a similar shift of the endothermic peak is observed as a result of nickel addition, even though, in that case, it is accompanied by an opposite minor shift of the exothermic peak towards lower temperature.
Fig. 1 DSC curves of glasses with molar composition, (a) 7.5Li₂O–2.5Na₂O–20Ga₂O₃–35GeO₂–35SiO₂; (b) 7.5Li₂O–2.5Na₂O–20Ga₂O₃–35GeO₂–35SiO₂ doped with 0.1NiO; (c) 10Li₂O–20Ga₂O₃–35GeO₂–35SiO₂ doped with 0.1NiO; (d) 7.5Li₂O–2.5Na₂O–20Ga₂O₃–35GeO₂–35SiO₂ doped with 1NiO; and (e) 10Na₂O–20Ga₂O₃–35GeO₂–35SiO₂ doped with 0.1NiO. Circles indicate the treatment temperatures (at $T_{ep} - 40$ K) considered in isothermal treatments. Curves are vertically shifted for clarity.

In any case, apart from such differences (discussed in more details in a next section), such a preliminary analysis shows that the observed succession of exothermic and endothermic processes is an intrinsic feature of the investigated mixed Li–Ga–Ge–Si oxide system, quite independent of doping and partial alkali substitution, whereas fully Na-substituted Li-free composition does not undergo the endothermic process, even with NiO addition. The first exothermic peak at about 970 K has recently been associated with crystallization of $\gamma$-Ga$_2$O$_3$ in the amorphous alkali–germanosilicate matrix. By contrast, no study has been carried out so far on the endothermic process registered in Fig. 1. The analysis of the compositional variants gives some preliminary information. Li$_2$O, with respect to Na$_2$O, promotes phase separation in the investigated glass composition and plays a key factor in the mechanisms taking place in the endothermic process.

The XRD patterns and TEM images reported in Fig. 2 – collected at room temperature on samples heated at representative temperatures based on the DSC data – provide an overview of the structural and morphological changes occurring in the crystalline nanophase. For comparison, we report the XRD pattern of as-quenched glass (curve 1 in Fig. 2a), consisting of a broad amorphous halo only, and of material treated at the exothermic peak temperatures (curve 2 in Fig. 2a), in which we observe reflections ascribable to $\gamma$-Ga$_2$O$_3$, as previously reported. The treated sample is transparent (Fig. 2b), as the initial glass, in spite of the segregation of the crystalline $\gamma$-Ga$_2$O$_3$ phase evidenced in the XRD pattern. TEM analysis indeed displays a large concentration of embedded NCs of few nm (5 ± 2 nm from TEM images in Fig. 2c).

Fig. 2 (a) XRD patterns of 7.5Li$_2$O–2.5Na$_2$O–20Ga$_2$O$_3$–35SiO$_2$–35GeO$_2$, doped with 0.1NiO, (1) as-quenched from the melt, (2) after 5 hours at 960 K, (3) 1 hour at 1210 K, and (4) heated at 10 K min$^{-1}$ from 300 to 1300 K with a final stay of 10 min before quenching. XRD patterns are vertically shifted for clarity. Reflections of $\gamma$-Ga$_2$O$_3$, LiGa$_5$O$_8$, and $\beta$-Ga$_2$O$_3$ phases are indicated by sticks, according to PDF files ICDD PDF2 #00-020-0426, ICDD PDF2 #01-076-0199, and ICDD PDF2 #00-041-1103, respectively. (b) Photo and (c) HAADF-STEM images of the material after treatment at the exothermic peak temperature for 15 min. (d) Photo and (e) HAADF-STEM images after treatment at 1210 K.
After heating at a temperature close to the extrapolated endothermic peak onset temperature, we register (curve 3 in Fig. 2a) additional lines (specifically at 15.3°, 24.2°, 26.6°) consistent with the occurrence of the LiGa₅O₈ spinel phase. The sample is not transparent (Fig. 2d). TEM analysis shows the occurrence of bigger crystals, several tens of nanometers in size, with a well defined cubic crystal habit (TEM image in Fig. 2e).

LiGa₅O₈ is strictly related to γ-Ga₂O₃ through a partial substitution of Li ions for Ga ions in octahedral crystallographic sites. Interestingly, XRD analysis of samples treated for 10 min at 1300 K (curve 4 in Fig. 2a) indicates that the final result of the process registered by the DSC endothermic peak is not the phase change from γ-Ga₂O₃ to LiGa₅O₈, but instead the formation of β-Ga₂O₃.

### Embedded nanocrystals vs. nanopowders

The link between the endothermic process and the formation of β-Ga₂O₃, just pointed out from the data in Fig. 1 and 2, cannot be immediately ascribed to the expected evolution of the involved crystalline phase and gives a somewhat counterintuitive result. In fact, on the one hand, monoclinic β-Ga₂O₃ is by far more stable than spinel γ-Ga₂O₃, and the spinel-to-monoclinic transformation is thus expected to reduce the energy of the system with a resulting exothermic process which cannot justify the endothermic peak observed in DSC. On the other hand, at about 1410 K, LiGa₅O₈ is known from early studies to undergo an endothermic process of transformation to a high temperature polymorph, analogous to other spinel compounds. Low- and high-T polymorphs are strictly related to each other, the low-T one being an ordered superstructure of the high-T phase.

To verify what kind of thermal evolution the involved phases would undergo separately (not embedded in a matrix) with respect to the glass embedded nanophase, we carried out a direct comparison between the changes observed in in situ XRD measurements at different temperatures up to 1475 K in the reference samples of γ-Ga₂O₃ nanopowder from solution-based synthesis and LiGa₃O₈ powder from solid state reaction (Fig. 3a and b, respectively) and in nanostructured γ-Ga₂O₃-containing glass (Fig. 4). The transformation of γ-Ga₂O₃ nanopowder into β-Ga₂O₃ occurs at about 1100 K, whereas LiGa₃O₈ undergoes a polymorphic transformation at about 1430 K (Fig. 3c and d, respectively). The transformation occurring in LiGa₃O₈ is reversible and appears as an endothermic DSC peak by heating and an exothermic peak by cooling. The responsible structural transformation involves a change from a low temperature ordered phase to a less ordered one whose XRD pattern shows the lack of several reflections of the low temperature phase originating from ordering-related superstructures. The data of nanostructured glass in Fig. 4 show that LiGa₃O₈ co-exists with γ-Ga₂O₃ (see data collected at 1175 K), before the formation of β-Ga₂O₃ that starts to be detected at 1275 K, accompanied by the endothermic DSC peak. Importantly, this process is not reversible and, in fact, no exothermic peak is observed by cooling (the DSC curve during cooling is not shown). Therefore, the endothermic peak in the range 1280–1335 K cannot be ascribed to a reversible polymorphism of the formed LiGa₃O₈. Finally, heating at 1750 K, re-melting gives rise to the initial glass with the same thermal evolution through γ-Ga₂O₃, LiGa₃O₈ and β-Ga₂O₃.
Fig. 3 XRD patterns at increasing temperature of (a) $\gamma$-Ga$_2$O$_3$ and (b) LiGa$_5$O$_8$ reference powder samples. Patterns are vertically shifted for clarity. DSC curves of the same samples are displayed in (c) and (d), respectively.
The results in Fig. 3 and 4 point out the crucial role of the interactions between the nanophase and the matrix in the thermal evolution of the embedded NCs. In fact, the registered changes do not correspond to any feature encountered in the transformation paths of \( \gamma\)-Ga\(_2\)O\(_3\) and LiGa\(_3\)O\(_8\) phases separately. Specifically, there is no exothermic process of \( \gamma\)-Ga\(_2\)O\(_3\) transformation into \( \beta\)-Ga\(_2\)O\(_3\). Furthermore, the LiGa\(_3\)O\(_8\) phase disappears in concomitance with \( \beta\)-Ga\(_2\)O\(_3\) growth during an endothermic process not ascribable to LiGa\(_3\)O\(_8\) polymorphism alone.

**Isothermal heating and reaction kinetics**

Data from isothermal heating experiments at about 1210 K provide us a deeper insight into the relationships among the crystalline phases identified along the thermal evolution of the glass-embedded NCs. In Fig. 5 we show XRD patterns collected at 300 K on nanostructured glasses heated at 1210 K with duration times increasing from 0.5 to 160 hours.
Fig. 5 XRD results on 7.5Li₂O–2.5Na₂O–20Ga₂O₃–35GeO₂–35SiO₂ doped with 0.1 of NiO after isothermal heating at 1210 K for the indicated duration time. XRD patterns are vertically shifted for clarity. Reflections ascribable to a minor amount of LiGaGeO₄, according to PDF files ICDD PDF2 #01-079-0213, are indicated by asterisks.

The data, obtained after prolonged heating at a temperature lower than the endothermic peak, give us the possibility to follow the relevant processes on a time scale easy to be controlled experimentally. From Fig. 5, we see main effects on the progressive transformation of the γ-Ga₂O₃ XRD pattern into that of LiGa₅O₈, and the appearance of the β-Ga₂O₃ reflections which reveals early growth. Additional reflections of minor intensity, ascribable to LiGaGeO₄, become detectable after very long treatments (>72 h) in the final steps of the isothermal heating experiment (see stars in Fig. 5). Therefore, we can argue that Li₂O does not permanently re-dissolve in the glass after β-Ga₂O₃ formation but instead shows some very slow back reactivity with the Ga-oxide component.

However, no evidence of such reflections is registered in any other measurement, neither in ex situ nor in in situ experiments even on samples treated at temperatures higher than 1210 K. The formation of LiGaGeO₄ can thus be assigned to very slow processes which do not take part in the main thermal evolution of the nanophase, and it will not be discussed further. As regards the main transformation of γ-Ga₂O₃ into LiGa₅O₈, the experimental intensity ratio $R_{\text{exp}}$ between the main reflections at 64.2° and 36.3° – occurring in both γ-Ga₂O₃ and LiGa₅O₈ patterns but with different intensity ratios ($R_γ$ and $R_{\text{Li}}$, respectively) – turns out to be a quite sensitive parameter for a semi-quantitative estimation of the change of the relative amount of these phases.

In the approximation of simple additive relationship $I_{64°,36°}|_{\text{exp}} = a_γ I_{64°,36°}|_γ + b_{\text{Li}} I_{64°,36°}|_\text{Li}$ between the intensity $I_{64°,36°}$ of reflections at 64.2° and 36.3° (where $a_γ$ and $b_{\text{Li}}$ practically coincide with the relative amounts of γ-Ga₂O₃ and LiGa₅O₈ respectively, considering that the diffraction densities of the two phases differs by less than 4%), we obtain $b_{\text{Li}} = R_{\text{Li}}[1 - R_γ/R_{\text{exp}}]/[R_γ - R_γ]$, with $a_γ + b_{\text{Li}} = 1$. In Fig. 6, we report the amount of [LiGa₅O₈] normalized to the total amount of the two Ga-oxide
phases (i.e. \( b_{Li} \)) for different isothermal treatment durations. The formation of \( \text{LiGa}_5\text{O}_8 \) follows a kinetics that is consistent with a 3-dimensional diffusion-driven mechanism, as expected in a process mostly induced by Li diffusion from the glass matrix. The data of \( \text{LiGa}_5\text{O}_8 \) formation can in fact be reproduced by Jander's equation of 3D diffusion reaction for spherical particles,

\[
[1 - (1 - b_{Li}(t))^{1/3}]^2 = kt \quad (1)
\]

with \( k = 8 \times 10^{-7} \text{ s}^{-1} \). In the inset of Fig. 6, we also report the cubic root of the relative amount of decreasing \( \gamma\text{-Ga}_2\text{O}_3 \) phase, \( [1 - b_{Li}(t)] \), linearly fitted as a function of \( t^{1/2} \). Instead, the growth of the \( \beta\text{-Ga}_2\text{O}_3 \) phase – monitored by the XRD intensity at 35.2° vs. heating time at 1210 K as reported in Fig. 6 – follows a sigmoid along the isothermal experiment.

**Fig. 6** Variations of the crystalline phases after isothermal treatments at 1210 K vs. time in 7.5Li_2O–2.5Na_2O–20Ga_2O_3–35GeO_2–35SiO_2 from XRD data of Fig. 5. \( \text{LiGa}_5\text{O}_8 \) (circles), \( \beta\text{-Ga}_2\text{O}_3 \) (triangles), and \( \gamma\text{-Ga}_2\text{O}_3 \) (squares) are reported, respectively, normalized to the total amount of Ga-oxide phases, in arbitrary units, and normalized to the maximum value. Curves are the results of the fit with the indicated functions from the kinetic expression in eqn (1) and (2).

Such a behaviour is encountered in solid-state processes with nucleation mechanisms undergoing restrictions on the growth of the number of nuclei. These restrictions – typical of solid-state decomposition and mainly related to coalescence between nucleation sites during the process – eventually cause a change of sign in the rate \( dN/dt \) of the nuclei number, corresponding to the inflection point of the sigmoid in the kinetics of transformation. As a matter of fact, the data can be fitted by an Avrami–Erofeev equation for a 3-dimensional single-step nucleation process,

\[
[-\ln(1 - \beta(t))]^{1/4} = k't \quad (2)
\]

where \( \beta \) is proportional to the amount of \( \beta\text{-Ga}_2\text{O}_3 \) phase, and \( k' = 4 \times 10^{-6} \text{ s}^{-1} \). It is worth noting that the diffusion-driven \( \gamma\text{-Ga}_2\text{O}_3 \)-to-\( \text{LiGa}_5\text{O}_8 \) kinetics and the kinetics of the \( \beta\text{-Ga}_2\text{O}_3 \) growth are not directly related to each other. In fact, the decrease of \( \gamma\text{-Ga}_2\text{O}_3 \) with the formation of \( \text{LiGa}_5\text{O}_8 \) – through Li-diffusion from the matrix – comes to completion when only a minor fraction of the total Ga oxide component in the material is transformed into \( \beta\text{-Ga}_2\text{O}_3 \) (see XRD data in Fig. 5). The modification of \( \gamma\text{-Ga}_2\text{O}_3 \) into \( \text{LiGa}_5\text{O}_8 \) indeed starts to occur (in situ XRD data in Fig. 4) well below the temperature of the endothermic peak registered in DSC measurements that is related to the formation of \( \beta\text{-Ga}_2\text{O}_3 \). In Fig. 7 we report the changes in the XRD amplitude and FWHM of the reflection at 36.3° (occurring both in \( \gamma\text{-Ga}_2\text{O}_3 \) and \( \text{LiGa}_5\text{O}_8 \)) along the isothermal experiment. The
data suggest that the sum of the two phases does not change relevantly, so confirming that their changes are strictly correlated with each other without intervention of any transformation into β-Ga₂O₃. In other words, β-Ga₂O₃ is not directly involved in the disappearance of γ-Ga₂O₃. Rather, the isothermal heating experiment points out that the formation of β-Ga₂O₃ is the result of some kind of subsequent evolution of LiGa₅O₈ during the endothermic process.

**Fig. 7** Full width at half maximum (FWHM, open circles) and amplitude (Amp, filled circles) of reflection at 36.3° (common to γ-Ga₂O₃ and LiGa₅O₈) in XRD patterns in Fig. 5 of samples undergoing an isothermal heating experiment. The product of their values is also reported (triangles).

**The endothermic process**

As a result of the isothermal heating experiment, the origin of the endothermic process in the range 1280–1335 K appears strictly connected with the LiGa₅O₈ phase. However, as we have directly verified in the reference LiGa₅O₈ sample (Fig. 3), the only known transformation LiGa₅O₈ undergoes is a reversible change into a high temperature polymorph, occurring at about 1410 K in bulk material.⁴⁰ Remarkably, no certain information is instead available, to the best of our knowledge, about the melting temperature of LiGa₅O₈, which anyways should be above 1720 K.⁴⁰,⁴⁴,⁴⁵ Actually, from 1410 K up to the melting point, the high temperature polymorph is not completely stable, and indications of decomposition with loss of lithium were reported after prolonged treatment above 1420 K.⁴⁴ In that temperature region, decomposition was observed to be accompanied by detection of weak β-Ga₂O₃ XRD reflections. Incidentally, such a propensity to decompose is consistent with the indication of incongruent melting of LiGa₅O₈ reported in an early study on the phase diagram of the Li₂O–Ga₂O₃–B₂O₃ system.⁴⁵ Ultimately, all these observations suggest that the structural instability of LiGa₅O₈ at high temperature and its tendency to decompose with lithium release (according to the reaction 2LiGa₅O₈ → 5β-Ga₂O₃ + Li₂O) can play a role in the endothermic process at about 1300 K, despite its very high melting temperature. In other words, the endothermic peak – anticipated and prepared at a slightly lower temperature by diffusion-driven formation of LiGa₅O₈ from γ-Ga₂O₃ NCs – gives rise to β-Ga₂O₃ NCs through a process that likely involves LiGa₅O₈ decomposition. Such an analysis, however, poses the problem of the quite low temperature of the endothermic peak, which does not fall in, and it is definitely lower than the reported temperature range of LiGa₅O₈ decomposition. It is indeed lower than the order–disorder transition from the low temperature polymorph to the high temperature one. Nevertheless, the reduced NC size and the
constraints imposed by the matrix can play a role in reducing the temperature of the process responsible for the nanophase destabilization.

We can evaluate the role of the NC size in the endothermic peak comparing samples modified by the presence of crystallizing agent such as Ni or additional Li, as in the set of samples in Fig. 1, so as to give rise to LiGa$_5$O$_8$ NCs with different size at the onset of the endothermic process (Fig. 8).

Fig. 8 XRD patterns of glass with molar composition, (a) 7.5Li$_2$O–2.5Na$_2$O–20Ga$_2$O$_3$–35GeO$_2$–35SiO$_2$; (b) 7.5Li$_2$O–2.5Na$_2$O–20Ga$_2$O$_3$–35GeO$_2$–35SiO$_2$ doped with 0.1NiO; (c) 10Li$_2$O–20Ga$_2$O$_3$–35GeO$_2$–35SiO$_2$ doped with 0.1NiO; and (d) 7.5Li$_2$O–2.5Na$_2$O–20Ga$_2$O$_3$–35GeO$_2$–35SiO$_2$ doped with 1NiO. The patterns are shifted for clarity. Samples were treated with the same heating rate as in DSC measurements from room temperature up to the temperatures indicated by open circles in the DSC curves in Fig. 1. The values indicated in the figure denote the size of LiGa$_5$O$_8$ NCs estimated from the XRD peak at about 64.2° by using the Scherrer's equation. The registered endothermic peak extremum temperature $T_{ep}$ shows a clear correlation with the NC size $r$ as determined by the Scherrer analysis of the XRD patterns in Fig. 8. Interestingly, the analysis suggest a linear dependence of $T_{ep}$ on $1/r$ (Fig. 9), reproduced by an equation of the form,

$$T_{ep} = T_{ep}^{bulk} \left(1 - \frac{\phi}{r}\right)$$  \hspace{1cm} (3)

where the intercept $T_{ep}^{bulk}$ for $r \to \infty$ falls approximately in the same temperature range of the endothermic order–disorder transformation of bulk LiGa$_5$O$_8$. Such a dependence resembles the relationship describing the depression of melting temperature, with respect to bulk, observed in several nanosystems. In that case, the constant $\phi$ is proportional to the difference ($\gamma_{sol} - \gamma_{liq}$) between surface energy in the solid and liquid phase. Similarly to that situation, the difference ($\gamma_{ord} - \gamma_{dis}$) in surface energy between ordered and disordered LiGa$_5$O$_8$ polymorphs is expected to be positive – with a resulting lowering of $T_{ep}$ at decreasing $r$ – since a more ordered nanophase surface is likely associated with higher interface energy with the surrounding amorphous matrix.
**Fig. 9** NC size dependence of the endothermic peak extremum temperature $T_{ep}$ in the set of nanocrystallized samples of Fig. 8. The full line is the linear fit of the data according to eqn (3). The melting temperature region (from literature) and reversible order–disorder transition temperature of bulk LiGa$_5$O$_8$ are also indicated.

Even though the data in Fig. 9 suggest a role of LiGa$_5$O$_8$ polymorphic transformation in determining the temperature of the endothermic peak, the polymorphic transformation cannot justify the full chain of events underlying the endothermic process. In fact, according to data in Fig. 4, the final product after the endothermic peak is not the high temperature LiGa$_5$O$_8$ polymorph but, rather, the formation of $\beta$-Ga$_2$O$_3$. Furthermore, the endothermic peak is not related to a reversible process.

Therefore, the full consideration of the available experimental results points to ascribe the endothermic process to the decomposition of LiGa$_5$O$_8$ NCs into $\beta$-Ga$_2$O$_3$ and Li$_2$O, promoted by the destabilization of NCs by LiGa$_5$O$_8$ polymorphic transformation at temperatures influenced by size effects and matrix interaction.

**Photoluminescence of transformed nanocrystals**

In Fig. 10 we present the results of photoluminescence measurements (using an excitation wavelength of 250 nm) on the nanostructured glass – compared with as-quenched glass – along the main steps of the nanophase thermal evolution. The spectral position and bandwidth are consistent with the luminescence observed in previous studies on pure Ga$_2$O$_3$ phases and Ga-oxide nanosystems, either pure or embedded in solid.$^{3,4,7,51}$ The broad and efficient luminescence excitation at wavelengths shorter than 280 nm is strictly related to the direct allowed optical gap of the material, and constitutes the most important optical feature for applications.$^3$ The mechanism of light emission is connected to the radiative recombination of donor and acceptor pairs consisting of an oxygen vacancy, acting as a donor, and a complex of oxygen and gallium vacancies behaving as acceptors.$^{3,47}$ Additional distinct spectral contributions in the green and UV regions are sometimes observed and can be respectively ascribed to electron–hole recombination between oxygen and gallium vacancies and to exciton-like decay mediated by sub-band gap levels.$^{51-54}$
Looking at Fig. 10, we can notice two important features. First, we observe that the higher the treatment temperature, the higher is the luminescence intensity. Second, the spectral distribution of light emitted intensity shows a blue-shift at higher photon energy, except for the sample treated at the endothermic peak temperature (1285 K) where β-Ga2O3 is formed. In this sample the PL spectrum is red-shifted compared to the others. As regards the spectral shift, we have to remark that similar differences were observed among Ga-oxide phases, including alkali-containing compounds like LiGa5O8, but no definite explanation was ever proposed.

Actually, attention should be paid in comparing our PL spectra with previously reported ones if collected in different excitation conditions, because the spectral shift can often occur as a result of excitation wavelength dependence. Nevertheless, within the set of spectra in Fig. 10 at fixed excitation at 250 nm, the observed shift provides a reliable evidence of changes occurring in the emitting nanophase. On the one hand, the phase transformation into β-Ga2O3 – whose crystal structure is largely different from the starting γ-Ga2O3 and LiGa5O8 spinel phases – may have a direct role in the change in spectral distribution because the structural environment of oxygen and gallium vacancies, responsible for light emission, is significantly modified. On the other hand, the spectral shifts accompanying heat treatments below the endothermic peak are instead more likely related to a different effect. On the basis of the studies already quoted on the origin of Ga-oxide light emissions, the observed spectral changes are compatible with modified relative intensities of overlapping contributions from different light emitting sites, whose energy structure is probably quite independent of the small structural differences between γ-Ga2O3 and LiGa5O8 spinel phases. Such a modification is easily conceivable considering that the relative population of oxygen and gallium vacancies can significantly be modified during the thermal evolution of the system. The interaction with the surrounding matrix (with oxygen and lithium diffusion) and the NC coalescence (with change of surface-to-volume ratio) can indeed greatly modify the nanophase defectiveness. As a result, not only the spectral position of the PL band is affected by the treatment, but also the overall PL efficiency turns out to be influenced, even at a fixed amount of the separated phase. This is evident...
from the two samples with the most intense spectra, in which the crystal fraction estimated from XRD patterns turns out to be equal to the nominal amount of Ga$_2$O$_3$ component in both cases, whereas the PL intensity differs by more than a factor of 2.

**Conclusions**

The thermal evolution of $\gamma$-Ga$_2$O$_3$ in the alkali–germanosilicate amorphous host shows the occurrence of transformation mechanisms, definitely distinct from those expected along the known evolution of the pure and freestanding phase, either in bulk or at the nanoscale, evidenced by an endothermic transformation previously uncharacterized. The results of DSC analysis, XRD and TEM characterizations provide clear-cut evidence of interactions with the surrounding matrix. After the exothermic process of $\gamma$-Ga$_2$O$_3$ nano-crystallization, the evolution of the nanophase is influenced, in a first step, by Li ion diffusion from the glass, which determines LiGa$_5$O$_8$ formation. In a second step, by increasing the temperature, size effects and the influence of the surrounding amorphous matrix on the interface energy induce an order-to-disorder LiGa$_5$O$_8$ change. The latter step, caused by a non negligible propensity of the high-temperature LiGa$_5$O$_8$ polymorph to dissociate, finally entails into an irreversible endothermic process with the formation of $\beta$-Ga$_2$O$_3$.

Photoluminescence measurements show modifications of spectral distribution and integrated intensity of the nanophase light emission, whose features are reflections of the overlapping contributions from donor–acceptor pair recombination and decay processes at defect sites.

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**Notes and references**

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