

Controllable formation of the crystalline phases in Ge-Ga-S chalcogenide glass-ceramics

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Abstract:

We prepared chemically stoichiometric, S-poor and S-rich Ge-Ga-S glasses and annealed them at a temperature that was 20°C higher than its respective glass transition temperature. We aimed at tuning the formation of the different crystals in chalcogenide glass-ceramics. Through systematic characterisation of the structure using X-ray diffraction and Raman scattering spectra, we found that, GeS₂ and GeS crystals only can be created in S-rich and S-poor glass-ceramics, respectively, while all GeS, Ga₂S₃ and GeS₂ crystals exist in chemically stoichiometric glass-ceramics. Moreover, we demonstrated the homogeneous distribution of the crystals can be formed in the S-rich glass-ceramics from the surface to the interior via composition designing. The present approach blazes a new path to control the growth of the different crystals in chalcogenide glass-ceramics.

Introduction

Chalcogenide glasses are finding their increasing application in photonics, because of their high optical nonlinearity, wide transmission range up to 25 μm, and low phonon energy [1, 2]. Whilst these advantages are essential for the implementation of all-optical devices based on

chalcogenide glasses, one of the drawbacks is their weak mechanical strength and thus low laser damage threshold [3]. It has been reported that, nanocrystals can be created via thermal annealing of the glass above the glass transition temperature, forming so-called glass-ceramics, and the hardness of the chalcogenide glasses can be improved via such a thermal annealing process [4]. For example, while the glass-ceramics is created in chemically stoichiometric $(\text{GeS}_2)_x(\text{Ga}_2\text{S}_3)_{1-x}$ system, GeS_2 crystals usually are formed on the surface of the glass while Ga_2S_3 crystals are located in the interior of the glass [5-10]. Therefore, the reproducible and controllable formation of the nanocrystals is still a subject of the research.

Some methods, such as adding of the alkali halide or PbS quantum dots into chalcogenide glasses, have been developed to control the formation of the nanocrystals in various systems including $\text{GeS}_2\text{-Sb}_2\text{S}_3\text{-In}_2\text{S}_3$ [11], $\text{GeS}_2\text{-Ga}_2\text{S}_3$ [12], $\text{GeS}_2\text{-Sb}_2\text{S}_3\text{-CsCl}$ [13-15], $\text{GeS}_2\text{-In}_2\text{S}_3$ [16], and $\text{GeS}_2\text{-In}_2\text{S}_3\text{-CsI}$ [17,18]. However, the relatively high halide content in chalcogenide glasses causes the difficulty in controlling the size of the nanoparticles and leads to poor chemical durability, and sometimes the dopants in the chalcogenide glasses are liable to induce the precipitation of the different crystals simultaneously. Moreover, the different crystals could have different refractive index from the host glass, and this could induce a large optical loss in the glass-ceramics. Therefore, the development of the new method to control the growth of the nanocrystals is highly desired.

We noted that, in most of previous literature, the starting materials for the creation of glass-ceramics were selected from the tie-line of the glass-forming region, for example, $(\text{GeS}_2)_x(\text{Ga}_2\text{S}_3)_{1-x}$, since it was much easier to induce both GeS_2 and Ga_2S_3 crystals and their variances via thermal annealing [12, 19, 20]. An interesting question is thus raised: can we control the formation of the different crystals in the glass-ceramics via tuning the chemical compositions? In another word, are chemical compositions along the tie-line of the glass-forming region the best option for creating glass-ceramics?

In the present paper, we prepared two groups of Ge-Ga-S glasses containing 4 at.% and 8 at.% Ga, respectively. The glass composition changed from S-rich to chemically stoichiometric and S-poor with increasing Ge content. The glasses were annealed at a temperature which was 20°C higher than their individual glass transition temperature, and then the structure of the glasses and glass-ceramics was investigated as a function of annealing durations. We aimed at tuning the formation of different nanocrystals via composition design.

Experiments

Ge-Ga-S bulk glasses were prepared by the melt-quenching technique. The detailed description of the glass preparation can be found in Ref. [9]. The chemical compositions of the glasses were analysed by energy dispersive X-ray spectrometer (EDX) installed on a scanning electron microscope. For each glass, we scanned five different positions on the surface and the averaged results were used as the final composition of the glass. The results showed that the difference between the nominal and final composition was less than 0.5 at.%. The amorphous nature of the glass was confirmed by X-ray diffraction (XRD) using a conventional X-ray diffractometer in a 2θ scan mode. About 15 mg powder was sealed into an aluminium pan for T_g measurements using a differential scanning calorimeter (Mettler-Toledo, DSC 1). The refractive indices of the glasses were measured using a Metricon Model 2010 prism coupler with the errors less than 0.001.

X-ray diffraction analysis was performed on a Bruker X-ray diffractometer using Cu $K\alpha$ radiation from 10° to 70°. Raman spectra were recorded using a T64000 Jobin-Yvon-Horiba micro-Raman spectrometer equipped with a liquid-nitrogen-cooled CCD detector. The 830 nm laser line was used as an excitation source, and the laser power was kept as small as possible to avoid any photo-induced effects. The resolution of the spectrometer was about 1 cm^{-1} .

Results and Discussion

For $\text{Ge}_x\text{Ga}_8\text{S}_{92-x}$ glasses, chemically stoichiometric composition is $\text{Ge}_{26.67}\text{Ga}_8\text{S}_{65.33}$ and thus the glasses with Ge less than 26.67 at.% are called S-rich and those with Ge higher than 26.67 at.% are S-poor. The same definition is applied to $\text{Ge}_x\text{Ga}_4\text{S}_{96-x}$ where the chemically stoichiometric composition is $\text{Ge}_{30}\text{Ga}_4\text{S}_{66}$. Figure 1 shows T_g as a function of Ge content in the glasses. It was found that, T_g increases before it reaches a maximum, and then decreases with increasing Ge content in the glasses containing the same Ga content, and the maximum T_g appeared at the glass with a stoichiometric composition. Since T_g is usually considered as a measure of the glass network, the maximum T_g indicates that the stoichiometric glass has the best network connectivity [21].

We further annealed the glasses with different durations, and measured their structure using XRD and Raman spectra. We observed that, S-rich and S-poor glass-ceramics contain different crystals, e.g., only GeS_2 crystals appear in S-rich while only GeS crystals exist in S-poor glass-ceramics. On the other hand, all GeS_2 , GeS and Ga_2S_3 crystals can be found in the chemically stoichiometric glasses. Below are the typical XRD and Raman results of the chalcogenide glass-ceramics.

Figure 2 is the XRD patterns for $\text{Ge}_{22.5}\text{Ga}_4\text{S}_{73.5}$, $\text{Ge}_{30}\text{Ga}_4\text{S}_{66}$, $\text{Ge}_{36}\text{Ga}_8\text{S}_{56}$ glasses with different annealing time. Each panel includes the XRD patterns for the fresh and annealed glasses. It can be found that from Figure 2(a), the fresh $\text{Ge}_{22.5}\text{Ga}_4\text{S}_{73.5}$ glass exhibit broad feature and the same XRD patterns exist at the annealing time up to 100 h. Then the sharp peaks appear and overlay with these broad features. These peaks become stronger in the sample with a prolonged annealing time of 360 h. The strongest peak at $2\theta=15.6^\circ$ is a typical feature of GeS_2 crystals, and all the other sharp crystalline peaks also can be well indexed to GeS_2 crystal (JCPDS-40-0443). In contrast, S-poor $\text{Ge}_{36}\text{Ga}_8\text{S}_{56}$ glass exhibits different crystallization behaviour as shown in Figure 2(c). While the fresh glass shows broad amorphous features, some sharp diffraction peaks appear in the glass with 400 h annealing time. Clearly, these diffraction peaks

match with the standard XRD patterns of GeS single crystal (JCPDS-51-1168) very well. Especially, three strongest peaks at $2\theta=26.83^\circ$, 33.34° and 34.20° are exactly same as the standard diffraction red lines as shown in Figure 2(c). We did not observe any feature corresponding to the strongest GeS₂ diffraction peak at $2\theta=15.6^\circ$, indicating that no GeS₂ crystal exists in the Ge₃₆Ga₈S₅₆ glass-ceramics.

Figure 2(b) is the XRD patterns for the chemically stoichiometric Ge₃₀Ga₄S₆₆ glass and glass-ceramics. Here, the XRD peaks of GeS₂, Ga₂S₃, and GeS crystalline phases are marked by blue triangle, green square, and red circle, respectively. Except the strongest peak at $2\theta=15.6^\circ$, that can be assigned to GeS₂ crystal (as marked by blue dot line, JCPDS-40-0443), most diffraction peaks are overlaid each other, and thus hard to be distinguished. However, we found two weak diffraction peaks that are located at $2\theta=60.02^\circ$ and 62.05° , respectively. These two peaks are no longer overlaid with others, and thus they can be uniquely assigned to Ga₂S₃ crystal (as marked by green dotted line, JCPDS-50-0811) and GeS crystal (as marked by red dotted line, JCPDS-51-1168), respectively. The results indicate that, all GeS₂, GeS and Ga₂S₃ crystals exist simultaneously in the chemically stoichiometric glass-ceramics. Furthermore, Scherrer formula is used to determine the average crystalline sizes of GeS₂, Ga₂S₃, and GeS in Figure 2. It can be found that the average crystalline size is determined to be 22.9 nm and 28.5 nm in S-rich and S-poor glass-ceramics, respectively, while the average crystalline size reaches 66.3 nm in the chemically stoichiometric glass-ceramics. Here all the average crystalline sizes are calculated by the Full-Width Half-Maximum of the strongest peaks in Figure 2. The results indicate that the crystalline grains have a rapid growth in the chemically stoichiometric glass-ceramics, while the crystalline grains still grow slowly in S-rich and S-poor glass-ceramics although having a longer annealing duration.

It appears that, the formation of the different crystals can be tuned by glass compositions, e.g., GeS₂ and GeS crystals only can be created in S-rich and S-poor glass-ceramics, respectively,

while all the GeS_2 , GeS and Ga_2S_3 crystals are formed in the chemically stoichiometric compositions. Usually, X-ray beam covers a large area on the surface of the glass, and thus the experimental results reflect statistical information of the distribution of the different crystalline phases. While the content of the crystalline phases is lower or the size of the crystalline grains is small, the corresponding diffraction peaks are weak and thus hard to be distinguished from strong diffraction peaks of other crystalline phases. This is especially true for Ga_2S_3 crystalline phase since Ga content in the glass is lower. Moreover, the stress in the glass matrix could induce a slight shift of the crystalline diffraction peaks compared with those in the standard JCPDS card. To solve this problem, next we will employ Raman spectra to detect the different crystalline phases, since laser beam in Raman scattering experiments can be focused into a size at a scale of micrometre, and thus it can probe the structural information in a local area where the signals from the small number of the crystalline grains can be enhanced.

Figure 3 is the corresponding Raman spectra of the $\text{Ge}_{22.5}\text{Ga}_4\text{S}_{73.5}$, $\text{Ge}_{30}\text{Ga}_4\text{S}_{66}$, $\text{Ge}_{36}\text{Ga}_8\text{S}_{56}$ glasses with different annealing time. All the glasses show a main band around 342 cm^{-1} that can be ascribed to the edge-shared symmetrical stretching modes of GeS_4 or GaS_4 , and this band can be extended to 430 cm^{-1} . However, after thermal annealing, several sharp Raman peaks appear in the glass-ceramics with different composition. Based on the XRD results above, the possible crystalline phases are GeS_2 , GeS and Ga_2S_3 in Ge-Ga-S glass ceramics. Raman spectra of these crystalline phases have been investigated in the previous literature [22-30], and their assignments are listed in Table 1.

Table 1. The different structural units and their Raman crystalline peaks.

Structural units	Raman crystalline peaks (cm^{-1})
<i>GeS₂ crystal</i> [22-24]	105, 131, 139, 153, 165, 172, 181, 220, 242, 253, 344, 361, 374, 411, 434

<i>S₈ structure</i> [25]	152, 218, 472
<i>GeS crystal</i> [26-28]	111, 114, 124, 132, 208, 212, 215, 238, 242, 269
<i>Ga₂S₃ crystal</i> [29, 30]	148, 233, 234, 288, 330, 388, 389

Next, we assign Raman spectra in Figure 3 to the different structural units as followings:

- (1) S_8 structure only appears in S-rich glasses and its intensity should decrease with increasing Ge-content in the glasses we investigated. Moreover, since 218 cm^{-1} Raman peak for S_8 is close to 212 cm^{-1} peak for GeS crystals, and the stress between the glass matrix can induce few wavenumber shifts, therefore the existence of S_8 structure can be evident only when both 218 cm^{-1} and 472 cm^{-1} peaks appear in the glasses.
- (2) The existence of GeS_2 crystals mostly comes from the strong and sharp peaks at around 343 cm^{-1} , 361 cm^{-1} , 411 cm^{-1} and 434 cm^{-1} , accompanying with several weak Raman peaks at a small wavenumber of 105 cm^{-1} , 131 cm^{-1} , 139 cm^{-1} , 153 cm^{-1} , 165 cm^{-1} , 172 cm^{-1} , and 181 cm^{-1} etc.
- (3) Some of the Raman peaks for GeS crystal are overlaid with those for other crystals. For examples, 242 cm^{-1} peak is close to 242 cm^{-1} for GeS_2 and 234 cm^{-1} for Ga_2S_3 crystal. Therefore the existence of GeS crystals can be evident only when both 212 cm^{-1} and 242 cm^{-1} peaks appear in the glass-ceramics.
- (4) Ga_2S_3 crystals have weak Raman crystalline peaks at 147 cm^{-1} , 238 cm^{-1} , 286 cm^{-1} , 382 cm^{-1} , and 390 cm^{-1} due to the relatively lower Ga content in the glass.

It can be found from Figure 3(a) that, the amorphous phase is kept well in the $\text{Ge}_{22.5}\text{Ga}_4\text{S}_{73.5}$ glass with an annealing time less than 100 h, and then some sharp Raman peaks appear in the glass with a prolonged annealing time up to 360 h, indicating that a detectable amount of the crystals are created. The Raman peaks at 105 cm^{-1} , 131 cm^{-1} , 153 cm^{-1} , 343 cm^{-1} , 370 cm^{-1} , 411

cm^{-1} , and 431 cm^{-1} (as marked by the blue dotted lines) can be ascribed to the GeS_2 crystals. Moreover, since the glass composition is S-rich, it is reasonably expected that S_8 structure will appear in the glass-ceramics. Therefore, simultaneous appearance of Raman peaks at 218 cm^{-1} and 472 cm^{-1} (as marked by pink dotted lines) can be considered as a symbol of S_8 structure. The peak near 151 cm^{-1} could contain the contributions from both GeS_2 and S_8 since both of them have vibrations near 150 cm^{-1} [22, 25]. Noteworthy is that the S_8 units in the glass network are amorphous since we cannot observe any sharp XRD diffraction peaks related to the S_8 crystals in Figure 2(a). On the other hand, for the S-poor $\text{Ge}_{36}\text{Ga}_8\text{S}_{56}$ glass, long annealing time induces several Raman crystalline peaks at 114 cm^{-1} , 212 cm^{-1} , 242 cm^{-1} , 269 cm^{-1} , and 310 cm^{-1} as marked by the red dotted lines in Figure 3(c). Since the XRD results in Figure 2(c) clearly show that there are no GeS_2 or Ga_2S_3 crystals in the $\text{Ge}_{36}\text{Ga}_8\text{S}_{56}$ glass-ceramics, these Raman crystalline peaks are fully assigned to the vibrations of GeS crystals.

On the contrary, the chemically stoichiometric $\text{Ge}_{30}\text{Ga}_4\text{S}_{66}$ glass-ceramics exhibit many Raman crystalline peaks as shown in Figure 3(b). Since no features can be observed at 474 cm^{-1} , S_8 structure can be excluded from $\text{Ge}_{30}\text{Ga}_4\text{S}_{66}$ glass-ceramics. Other Raman crystalline peaks and their assignments are marked using different coloured dotted lines. Clearly the materials contained crystalline GeS_2 (as marked by blue dotted lines), GeS (as marked by red dotted lines), and Ga_2S_3 (as marked by green dotted lines). The results are in excellent agreement with the conclusions from XRD measurements.

It has been reported that the different crystals can be formed in the surface and interior of the chalcogenide glass-ceramics in the previous investigations [9, 11-12, 31-34]. In order to examine whether the distribution of these crystals is homogeneous, we polished the annealed $\text{Ge}_{27}\text{Ga}_4\text{S}_{69}$ chalcogenide glass-ceramics with different thickness and measured Raman spectra at several different positions as shown in Figure 4. It can be seen that, the whole Raman profiles contain several sharp Raman crystalline peaks at 105 cm^{-1} , 131 cm^{-1} , 220 cm^{-1} , 344 cm^{-1} , 376

cm^{-1} , 411 cm^{-1} , and 436 cm^{-1} (as marked by purple dotted lines) that come from GeS_2 crystal, overlapping with the broad band for $\text{Ge}_{27}\text{Ga}_4\text{S}_{69}$ glasses. All the spectra from the random positions in the same surface exhibit almost identical Raman profiles in terms of the positions of the Raman peaks although the intensities of these peaks are slight different. This clearly indicates that, the formations of the crystalline phases can be controlled not only on the surface but also in the interior of the materials via tuning chemical compositions of the glass-ceramics. The present results have substantial impact on the applications of the chalcogenide glass-ceramics. For example, Ge-Ga-S systems are considered the best to host rare earth doping in order to generate mid-infrared emission for the potential applications in mid infrared lasers, and it has been reported that the mid-infrared emission can be significantly enhanced in the glass-ceramics [9, 19]. However, all these results have been achieved in the chemically stoichiometric glasses. As evident in the present investigation, the formation of the different crystals can be tuned via glass composition designing. These crystals could have different refractive index from the glass hosts, and the mismatching of the refractive index between the precipitated crystals and the glass host is a major reason to induce large optical scattering in the glass-ceramics. For example, the refractive index of GeS_2 and Ga_2S_3 crystals is 2.01 [35] and 2.29 [36], respectively, and the refractive index of $\text{Ge}_x\text{S}_{1-x}$ increases with increasing ratio of Ge/S [37], while that of Ge-Ga-S glass varies from 2.0 to 2.5 depending on the actual compositions. Therefore, we can design glass composition with the less refractive index contrast between the glass host and the crystals in order to reduce the optical loss of the glass-ceramics.

Conclusions

In summary, we have demonstrated that the formation of the different crystals in Ge-Ga-S glass-ceramics is controllable via tuning the glass compositions. Through systematic structural characterisation using XRD and Raman spectra, it was demonstrated that, GeS_2 and GeS crystal

can be in the S-rich and S-poor glass, respectively, while all GeS₂, GeS and Ga₂S₃ crystals can be found in the chemically stoichiometric compositions. Moreover, it was found that, while the different crystals register on the surface and interior in the chemically stoichiometric glass-ceramics, the distribution of the crystals in the S-rich and S-poor glass-ceramics is homogenous. This opens up the way to design the glass compositions tailoring the physical properties of the glass and glass-ceramics for the applications in photonics.

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Figure Captions:

Figure 1. T_g as a function of Ge content in the $\text{Ge}_x\text{Ga}_8\text{S}_{92-x}$ and $\text{Ge}_x\text{Ga}_4\text{S}_{96-x}$ glasses.

Figure 2. XRD patterns of $\text{Ge}_{22.5}\text{Ga}_4\text{S}_{73.5}$, $\text{Ge}_{30}\text{Ga}_4\text{S}_{66}$, $\text{Ge}_{36}\text{Ga}_8\text{S}_{56}$ glasses with different annealing time. Here, the JCPDS cards of GeS_2 (No. 40-0443), Ga_2S_3 (No. 50-0811), and GeS (No. 51-1168) crystals are also shown as solid lines with blue, green and red colour, respectively.

Figure 3. Raman spectra of $\text{Ge}_{22.5}\text{Ga}_4\text{S}_{73.5}$, $\text{Ge}_{30}\text{Ga}_4\text{S}_{66}$, $\text{Ge}_{36}\text{Ga}_8\text{S}_{56}$ glasses with different annealing time.

Figure 4. Raman spectra of the polished $\text{Ge}_{27}\text{Ga}_4\text{S}_{69}$ glass-ceramics with different thickness.









