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IR $Li_2Ga_2GeS_6$ nanocrystallized GeS_2-Ga_2S_3-Li_2S electroconductive chalcogenide glass with good nonlinearity

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GeS_2-Ga_2S_3-Li_2S electroconductive glasses were prepared by the conventional melt-quenching method through carefully controlling the heating rate. Comparing with the reference of glass-forming region, our investigated GeS_2-Ga_2S_3-Li_2S system was extended to the cation ratio of 0–20% Li with around 40% Ga. GeS_2-Ga_2S_3-Li_2S glass-ceramics containing IR $Li_2Ga_2GeS_6$ nonlinear nanocrystals were obtained by the more carefully controlled heating rate. Its optical nonlinearity was investigated by the Maker fringe measurements, the maximum second harmonic intensity was observed to be 0.35 of the reference Z-cut quartz. IR $Li_2Ga_2GeS_6$ nonlinear crystals were directly obtained at the composition of $40GeS_2$-$30GaS_{1.5}$-$30LiS_{0.5}$.

Second harmonic generation (SHG) is not allowed in either isotropic or centro-symmetrical materials like glasses, but active crystals inside glass matrix can break its homogeneity and permanent SHG can be observed[1,2]. Recently, chalcogenide glass-ceramics containing well-known nonlinear crystals (β-GeS_2[3,4], $AgGeGaS_4$[5], $CdGa_2S_4$[6]), which represented a promising avenue for future nonlinear optical technologies in the mid-IR region. In this case, the isotropic structure of glass was broken by the precipitated nonlinear crystals induced by heat treatment, which induced SHG in glass-ceramics, also induced declination of transmittance[1,2]. One kind of new $Li_2Ga_2GeS_6$ sulfide compound was firstly synthesized by Kim *et al.*[7], which was an isomer of $AgGaGeS_4$. $Li_2Ga_2GeS_6$ was phase-matched with SHG efficiency of approximately 200 times of α-SiO_2, and also showed a high laser damage threshold (3.65 eV) which made it be served as one kind of potential nonlinear optical (NLO) materials in the IR frequency converters. However, the size of $Li_2Ga_2GeS_6$ crystal (around $0.20 \times 0.15 \times 0.15$ mm^3 from Kim's data) limited its practical applications, and as far as we know, no larger $Li_2Ga_2GaS_6$ crystal was synthesized up to now. On the other hand, the glass-forming ability of GeS_2-Ga_2S_3-Li_2S system has been studied in detail as amorphous fast ion conductor[8–10]. In this paper, to our knowledge, we firstly fabricated GeS_2-Ga_2S_3-Li_2S glass-ceramics containing IR nonlinear $Li_2Ga_2GaS_6$ crystals (see Table 1) by the conventional melt-quenching method[11] through carefully controlling the heating rate.

Results

It was seen from Table 1 that ΔT (ΔT=T_x-T_g, T_g is the glass transition temperature, T_x is the crystallization temperature and T_p is the crystallization peak temperature) of GGL6 and GGL19 glasses was about 90°C, indicating their good thermal stability, so their crystallized processes could be easily controlled. The glass-forming ability was primarily reported on the region of higher Li_2S content, from 40% to 60% of 1/2 Li_2S, because glasses with higher electroconductivity would be expected in the region with maximum Li_2S concentration[8–10]. However, our present studies indicated that the glass-forming region of this system could extend to the 0–20% range of Li content with around 40% 1/2 Ga_2S_3, which is shown in Fig. 1. Glass was not obtained with more than 28% Li-cation ratio, but nonuniform $Li_2Ga_2GeS_6$ crystal was directly obtained in the composition containing 30% of 1/2 Li_2S (GGL30).

When the glasses were annealed at lower temperature (<420°C) for long time, well-distributed crystals were obtained but no SHG appeared, so 420°C was chosen as T_{HT} of GGL19. Figure 2 illustrates the UV–vis–NIR transmittance spectra of GGL19 glass matrix and glass-ceramics. Its transmittance remarkably decreased under

Table 1 | The investigated compositions of GeS_2-Ga_2S_3-Li_2S chalcogenide glasses along with T_g, T_x and T_p of the glass-forming compositions

composition	$LiS_{0.5}$	$GaS_{1.5}$	GeS_2	T_g(°C)	T_x(°C)	T_p(°C)
GGL6	6	37.5	56.5	418	510	524
GGL19	19	41	40	422	508	527
GGL30(crystals)	30	30	40	—	—	—

the heat-treatment of T_{HT} =420°C. The glass became closed to opaque when it was annealed for 6 hours at T_{HT}= 420°C (labeled as sample 420-6 h). With further annealing time, the glass-ceramic samples became opaque because more crystals were precipitated in the glasses to make transmittance declined.

To check the crystalline phases, XRD patterns of some representative samples were done and shown in Fig. 3. After 6 hours of heat treatment at T_{HT}=420°C, more strong diffraction peaks appeared and intensities became stronger after longer durations of heat treatment, but only one crystalline phase appeared in the samples which was in good agreement with the experimental data of $Li_2Ga_2GeS_6$ crystal from Kim *et al*[7].

Figure 4 shows the Maker fringe patterns of annealed GGL19 glass-ceramics. They are lobe shapes even second harmonic (SH) intensity is as small as 0.05 of Z-cut quartz, which can be considered as a consequence of bulk crystallization[4–6]. Broad Maker fringe pattern from surface crystallized samples[4,6] did not appear as the precipitation of crystals in glasses. Relatively remarkable SHG signals emerged when the heat-treating durations was more than 6 hours. There exited a trend that SH intensity increased with longer annealing time or higher annealing temperature. The maximum value could reach as high as 0.35 of Z-cut quartz (reference sample) from samples 420-10 h and 430-3 h. But for longer duration (13 hours) at T_{HT}=420°C, the intensity declined to 0.3 of the reference (not shown here).

We succeeded in fabricating IR transmitting GeS_2-Ga_2S_3-Li_2S electroconductive glasses containing large amount of IR optical nonlinear $Li_2Ga_2GeS_6$ crystals and studying its second-order optical nonlinearity. With higher concentration of Li_2S and Ga_2S_3, GGL19 glass-ceramics showed good SH intensity. The maximum SH intensity of GGL19 is about 0.35 times of the Z-cut quartz under the optimized condition of crystallization process (T_{HT}=420°C for 10 h).

IR nonlinear $Li_2Ga_2GeS_6$ crystals with non-uniform yellowish transparent grains, were also directly obtained from 5 g batch of the raw materials in the composition GGL30 (see Table 1). The size of obtained $Li_2Ga_2GeS_6$ crystals was about 0.3 × 0.25 × 0.3 mm^3, which was bigger than that of Kim (0.2 × 0.15 × 0.15 mm^3)[7], it was verified to be so susceptive to H_2O, this character was further validated by XRD and Maker fringe measurements.

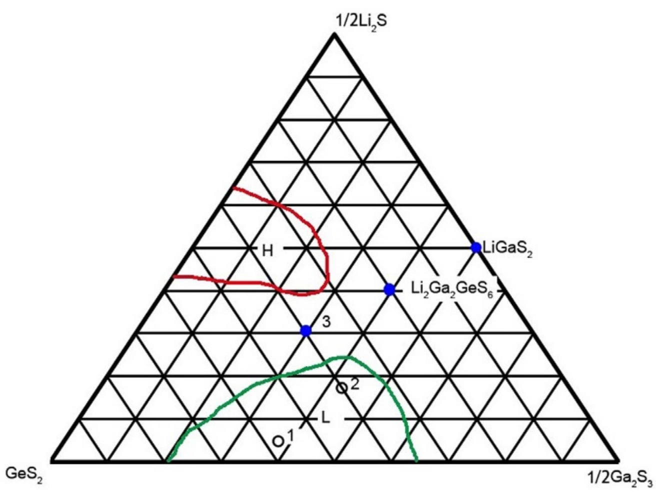

Figure 1 | The glass-forming region of GeS_2-Ga_2S_3-Li_2S system.

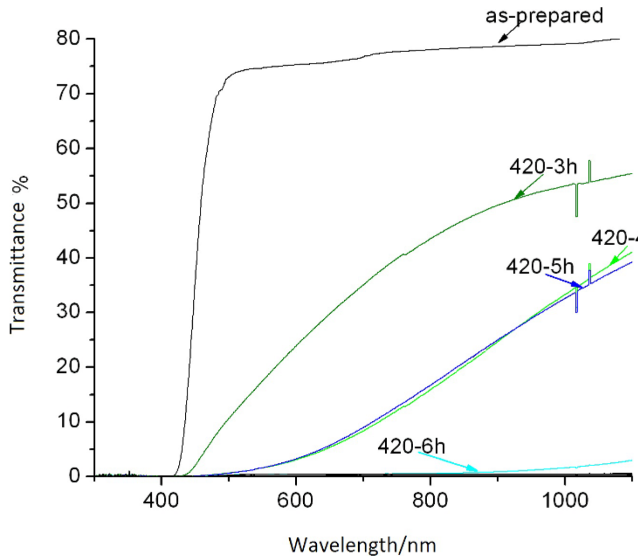

Figure 2 | Optical transmittance spectra of as-prepared GGL19 glass and glass-ceramics under different annealing time.

Discussion

We assume that the nonlinear optical behavior of the obtained glass-ceramics is analogous to that of polycrystalline powder with randomly oriented non-centro-symmetric particles dispersed in glasses. In this case, it was demonstrated that the crystallized volume fraction favored the enhancement of the second-order nonlinearity in glass-ceramics[3]. Bysides, as described by Kurtz and Perry[12], the SH intensity in polycrystalline powder could be analyzed according to r/l_c ratio where r is the particle size and l_c is the coherent length of the particle. Consequently, the small SH intensity for samples which was annealed less than 6 hours was probably due to the small amounts of precipitated $Li_2Ga_2GeS_6$ crystals and the size of the more precipitated $Li_2Ga_2GeS_6$ crystals was too small compared to l_c (about 5 μm). It is well known that the crystallization process becomes completed

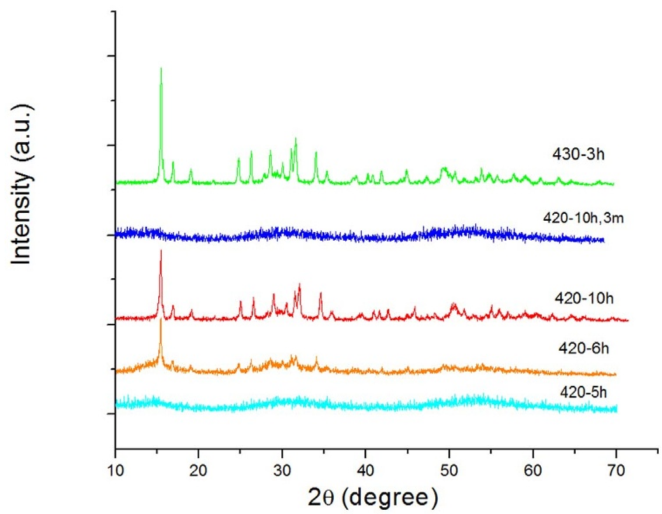

Figure 3 | XRD patterns of nanocrystallized GGL19 glass-ceramics at T_{HT}=420°C under different annealing time and the experimental data of $Li_2Ga_2GeS_6$ crystals (from Kim)[7].

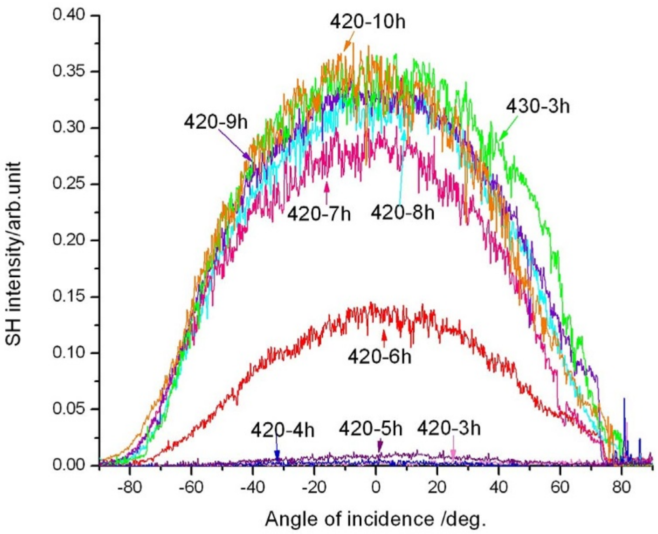

Figure 4 | Maker fringe patterns of nanocrystallized GGL19 glass-ceramics at T_{HT}=420°C under different annealing time.

well with the increase of the number and the particle size of precipitated $Li_2Ga_2GeS_6$ through longer annealing time or higher temperature, and also SH intensity increases, but which also causes an enhanced scattering loss and effectively diminishes the NLO effects. We speculated that the higher concentrations of Li_2S and Ga_2S_3 resulted in an increase in the number of precipitated $Li_2Ga_2GeS_6$ crystals which enhanced SH intensity of GGL19 samples. Similar trend was also observed in (100–x) $Li_2B_4O_7$-x $SrBi_2Ta_2O_9$ glass–ceramic composites, where SH intensity was also enhanced with higher concentrations of $SrBi_2Ta_2O_9$[2]. Finally, it is seen from Fig. 5 that an optimized condition of crystallization process (T_{HT}=420°C for 10 h) was obtained and the maximum SH intensity was about 0.35 times that of Z-cut quartz. However, the characterization of the crystal size and the crystallized volume fraction was difficult as a result of its deliquescence.

IR nonlinear $Li_2Ga_2GeS_6$ crystals was verified to be so susceptive to H_2O that it could be dissolved into water in a few minutes and left only floccus. This phenomenon was further confirmed by the XRD and Maker fringe tests of GGL19 glass-ceramics. After keeping sample 420-10 h in a silicagel desiccator for 3 months (labeled as Sample 420-10 h, 3 m), the XRD peaks approximately disappeared (Fig. 3) and the SH intensity declined to only 1.5% of Z-cut quartz. The details of this phenomenom are still unclear.

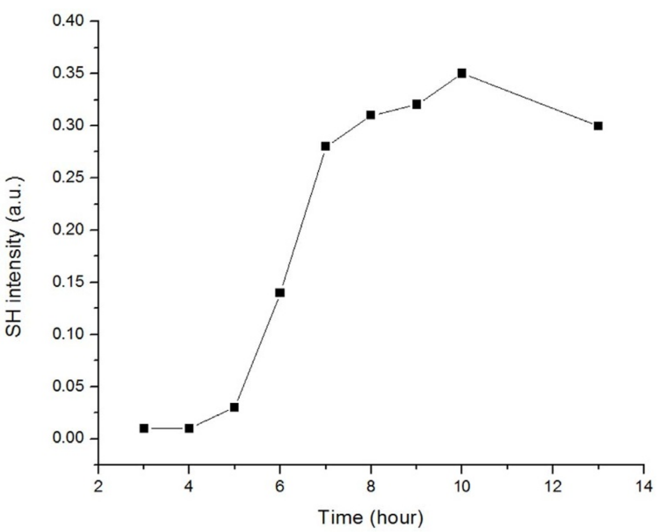

Figure 5 | Variation of SH intensity of nanocrystallized GGL19 glass-ceramics at T_{HT}=420°C under different annealing time.

Methods

We studied the second-order optical nonlinearity of the glass-ceramics under different heat-treatment conditions. GeS_2-Ga_2S_3-Li_2S bulk glasses were prepared by the conventional melt-quenching method in a vacuum sealed SiO_2 tube from commercial Li_2S, GeS_2 and Ga_2S_3[8,9]. According to Yamashita *et al.*[10], however, synthesized Li_2S was used for preparing glasses to eliminate oxygen presented in commercial reagent-grade Li_2S, which was synthesized from sulfur vapor and lithium metal in a Y-shaped silica tube ($2Li + S(g) \rightarrow Li_2S$), and then was mixed with GeS_2 and Ga_2S_3 to prepare GeS_2-Ga_2S_3-Li_2S glasses[10]. Lithium reacts with liquid sulfur (at 120°C when sulfur melts) is very complicated, which can be described as:

$$4Li+(n+1)S(l)\rightarrow Li_2S+Li_2S_n \ (2\leq n\leq 4)$$

The by-product of this reaction, Li_2S_n ($2 \leq n \leq 4$), is unstable and explosive. We experimentally succeed in preparing GeS_2-Ga_2S_3-Li_2S glasses with elements Li, Ge, Ga, and S as raw materials by the conventional melt-quenching method. Explosion from Lithium reacting with liquid sulfur was avoided by carefully controlling the heating rate. Firstly, we increased the temperature very slowly and started to rock the sample in our designed rocking stoven at 120°C, and kept this temperature for 1 hour. Continually, the temperature was increased at the rate of 1°C/min from 120°C to 750°C and at a rate of 0.5°C/min from 750°C to 950°C, and finally was kept 10 hours to make the raw materials react fully in the oven at 950°C.

Glass plates (Φ8 mm × 0.75 mm) were obtained from bulk and polished to optical quality, and then were sealed for annealing in a fused quartz tubes. The T_g, T_x and T_p of glasses were determined by the differential scanning calorimetry (DSC, NETZSCH STA 449C). The annealing temperature T_{HT} and period depended on T_g and the crystallizing process. The UV–vis–NIR transmissive spectra were recorded using a Shimadzu UV-1601 spectroscopy system between 200 and 1100 nm wavelength. SH intensity of glass-ceramics was measured by a fundamental wavelength of a *Q*-switched neodymium doped YAG laser (1064 nm) via the Maker fringe method[13]. Z-cut quartz with the thickness of 1.11 mm was used as a reference. The crystallization of heat-treated samples was studied by the X-ray diffraction (XRD, PANalytical X'Pert PRO) using Cu Ka radiation at room temperature. The particle size of $Li_2Ga_2GeS_6$ crystals was determined by Dark-field optical digit microscope (VHX-600 Japanese KEYENCE). The morphology of glass-ceramics was characterized by SEM (JSM-5610LV, JEOL Ltd., Japan).

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Author contributions

P.Z. fabricated samples. Q.L. and P.Z. wrote the main manuscript text and P.Z. prepared figures. All authors reviewed the manuscript.

Additional information

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