Preparation and properties of La_2O_3-Ga_2S_3 glass-ceramics for IR materials

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Key words: Sulfide glass, Glass-ceramics, Microstructure, Infrared transmission

1. Introduction

Durable mid IR window materials are desirable for uses in environments involving moisture, impact by solid and liquid particles, high temperatures, rapid heating and cooling rates [1]. IR transmission, thermal and mechanical properties have been studied for the candidates including single crystals, ceramics and glasses.

Chalcogenide glasses [2] are typical IR transmitting materials due to the low-phonon energies of glass networks. Among them, Ga_2S_3-based glasses [3] are of interest for practical applications because of high glass transition temperature (>500°C), good–chemical-durability and –mechanical-properties and non-toxicity. It is also known that gallium sulfide makes glass in various systems with sulfides, oxides and halides [3, 4].

Glass-ceramics with controlled microstructure [5] remain glass features of easy shape formation and surface smoothness [6] and, moreover, possess improved mechanical properties, compared to the precursor glasses. In our previous study, isothermally-treated La_2O_3-Ga_2S_3 glasses with a composition of 30 mol% La_2O_3-70 mol% Ga_2S_3 homogeneously precipitated small needlelike crystals with 1-2 μm in length and with large numbers [7]. In this study, heat treatment conditions, phase,

microstructure, Vickers hardness and IR transmittance are studied for La_2O_3-Ga_2S_3 glass-ceramics. The effect of Nd_2S_3 addition on crystallization behavior and the properties is also evaluated.

2. Experimental

Sample preparation was briefly described in a previous work [8]. Glass samples were prepared at the Optoelectronics Research Centre, University of Southampton. The batch compositions of samples are $30La_2O_3$-$70Ga_2S_3$ and $1Nd_2S_3$-$29La_2O_3$-$70Ga_2S_3$ in molar ratio. The names of these samples are expressed as LG and NLG hereinafter, respectively. Isothermal treatments for crystallization were performed at 615°C at which the viscosity of the super cooled liquids is in the range of 10^8~10^9 Pa·s [8].

X-ray diffraction (XRD) analysis was used to confirm the existence of residual glassy phase and to detect crystalline phases. Microstructure was evaluated by FE-SEM (JEOL, JSM-6340F) for the fracture surfaces etched by 20 mass% HNO_3 aqueous solution. Vickers hardness H_v was measured at 10-12 indentations on the polished surface of each sample with 0.98 N load and 15 s time. IR transmittance was measured in the range of 2 and 10 μm with a IR spectrophotometer (Shimazu, IR440) using polished plate samples with 1.3 mm in thickness.

3. Results

3.1 Phase

Fig. 1(a) shows the XRD patterns of LG samples isothermally-treated for 36, 48 and 96 h. All the samples indicate $(LaO)_4Ga_{1.33}S_4$ with a sheet structure consisting of (LaO), (GaS_3) and ($Ga_{0.33}S$) layers [9]. The phases only observed in the samples treated for 48 and 96 h are α-(LaO)GaS_2 with a sheet structure consisting of (LaO) and (GaS_2) layers [10] and γ-Ga_2S_3 with a zinc blend structure [11] in addition to $(LaO)_4Ga_{1.33}S_4$. The phases of α-(LaO)GaS_2 and γ-Ga_2S_3 appear in a temperature-composition phase diagram [3] for the 30 mol% La_2O_3-70 mol% Ga_2S_3 composition. The phase $Ga_6La_{3.33}S_{14-x}O_x$ with a melilite structure [12] confirmed in our previous work [8] for the same batch composition is not detected. The reason is not clear until now. A liquid-liquid phase separation may be related to the sequential crystallized phases.

Fig. 1(b) shows the XRD patterns of NLG samples isothermally-treated for 18, 48 and 96 h. The primary phase is $(LaO)_4Ga_{1.33}S_4$ in the sample treated for 18 h and then α-(LaO)GaS_2 and γ-Ga_2S_3 crystallize in long-term heat-treatments (48-96 h). Guittard et al. also reports similar phase changes in the solidification process of La_2O_2S-Ga_2S_3 melts at higher temperatures [13]. The result suggests that the following reaction occurs

during the isothermal treatment.

$$(LaO)_4Ga_{1.33}S_4 + \text{super cooled liquid} \rightarrow (LaO)GaS_2 + \gamma\text{-}Ga_2S_3 \quad (1)$$

3.2 Microstructure

Fig. 2(a)-(c) show the SEM micrographs of the isothermally-treated LG samples. Needle-shaped crystals with ~1 μm in length are sparsely observed for 36 h. The number of the crystals increased with increasing treatment time. The columnar crystals interlace with each other and spherical crystals appear in the surrounding of the columnar crystals after 96 h.

Fig. 2(d)-(f) show the SEM micrographs of isothermally-treated NLG samples. A large number of plate-like crystals ($(LaO)_4Ga_{1.33}S_4$) with ~0.5 μm in length is observed for 18 h as the primary crystalline product (Fig. 2(d)). The number of this crystal increased with time in the range of 6 and 18 h. The columnar crystals appear in the later stage (24-96 h) (Figs. 2(e) and (f)). Spherical crystals with 0.02-0.2 μm in diameter are also observed between the columnar crystals.

3.3 Vickers hardness

Fig. 3 shows the variations of Vickers hardness H_v with isothermal treatment time in

the LG and NLG samples. As-prepared LG and NLG glasses have a H_v value of ~4.5 GPa. H_v of LG samples increases gradually with treatment time and reaches ~5.0 GPa after 96 h. As for NLG samples, H_v increases with time from 4.5 GPa to 5.3 GPa after 24 h and then remains constant within experimental error in the period of 24-96 h.

3.4 IR transmission

Fig. 4(a) shows IR transmission spectra of the LG samples. All samples have a IR absorption edge of 8 μm due to a component of La_2O_3. This value is similar to that of polycrystalline Y_2O_3 [1]. The mid IR transmittance of LG samples decreases with increasing treatment time in the range of 3 and 5 μm. After 72-96 h, the mid IR transmittance reduces to < 50%.

In NLG samples shown in Fig. 4(b), there are two absorption bands due to the 4f-4f forced electric dipole transition of Nd^{3+}, i.e., $^4I_{9/2} \rightarrow {}^4I_{13/2}$ for the 2.4 μm band and $^4I_{9/2} \rightarrow {}^4I_{11/2}$ for the 5 μm band [14]. The mid IR transmittance of the NLG samples also decreases with treatment time up to 24 h. However, the NLG samples treated 48 and 96 h shows relatively-higher mid IR transmittance, compared to the 18 and 24 h samples, and still have the mid IR transparency over 60% even in the long-term isothermally-treatment (96 h).

4. Discussion

The relationship between phase and microstructure is discussed at first. In the early stage of crystallization, a nano-size, liquid-liquid phase separation may exist [15]. The detailed analysis of microstructure with transmission electron microscopy is a future topic. In LG samples with a batch composition of 30 mol% La_2O_3-70 mol% Ga_2S_3, α-(LaO)GaS_2 and γ-Ga_2S_3 were mainly crystallized. The size of columnar crystals increases with increasing heat treatment time in the range of 1 and 2 μm and the number also increases.

On the other hand, as for the NLG samples with 1 mol% Nd_2S_3 doping, $(LaO)_4Ga_{1.33}S_4$ nano-crystals with 0.5 μm in width are precipitated as a primary product. This phase has a large different composition in comparison to a La/Ga ratio 29/70 of the batch composition. Moreover, Nd_2S_3 doping promotes crystallization (to reduce the crystallization time) and a possible reaction expressed by Eq. (1) is related to the controlled microstructures with smaller crystals ~0.7 μm in size even for long-term isothermal treatments (48-96 h). From the spectral fine shape of the 4f-4f transition of Nd^{3+} (Fig. 4(b)) and XRD analysis (Fig. 1(b)), Nd^{3+} ions may be incorporated into α-(LaO)GaS_2 crystals in the later stage of heat-treatments (24-96 h).

The properties are also related to the microstructures of La_2O_3-Ga_2S_3 glass-ceramics.

The glass with 30 mol% La_2O_3-70 mol% Ga_2S_3 has a relatively high H_v of 4.5 GPa in chalcogenide glasses [16] and fluoride glasses [17] and it is a similar value of some phosphate glasses [18]. In the case of non-doping (LG samples), H_v gradually increased with heat-treatment time up to 5.0 GPa after 96 h. The increase of H_v corresponds well to the increase of columnar crystals in both size and volume fraction. However, the non-doped glass-ceramics (LG) with the high H_v value degrade the mid IR transparency less than 50%.

As for Nd_2S_3 doping, smaller crystals with ~0.5 μm in size were precipitated and increased in number in the first stage (0-21 h) and then the columnar crystals less than 1 μm may crystallize with the spherical crystals (Eq. (1)). The microstructure has no change at the second stage (48-96 h) (Figs. 2(e) and (f)). Vickers hardness H_v and the mid IR transmittance reflect the microstructure of Nd_2S_3-doped La_2O_3-Ga_2S_3 glass-ceramics. H_v increases with the volume fraction of $(LaO)_4Ga_{1.33}S_4$ crystals at the first stage (<24 h) and remains almost constant at the second stage (24-96 h). The glass-ceramics containing $(LaO)_4Ga_{1.33}S_4$, α-(LaO)GaS_2 and γ-Ga_2S_3 crystals with < 1μm in size have still transparency over 60% in the mid IR region. The minimum mid IR transparency of the 18 and 24 h samples (Fig. 4(b)) may be related to the difference in refractive index between the crystal and the residual glass (Fig. 1(b)) [19, 20].

Although the 4f-4f forced electric dipole transitions of Nd^{3+} degrade the mid IR transparency, other rare-earth sulfides without the electric dipole transitions at the IR region such as Y, Ho, Er, Tm and Yb may also have similar effects to control microstructure in La_2O_3-Ga_2S_3 glass-ceramic systems.

5. Conclusion

La_2O_3-Ga_2S_3 glass-ceramics for mid IR transmitting materials were prepared by isothermal treatments at 615°C. Glass-ceramic samples with the batch composition of 1 mol% Nd_2S_3-29 mol% La_2O_3-70 mol% Ga_2S_3 and with 1.3 mm in thickness shows a high H_v value of 5.3 GPa with a mid IR transparency of >60%. The properties are related to the microstructure consisting of a large numbers of $(LaO)_4Ga_{1.33}S_4$, α-(LaO)GaS_2 and γ-Ga_2S_3 crystals with < 1 μm in size.

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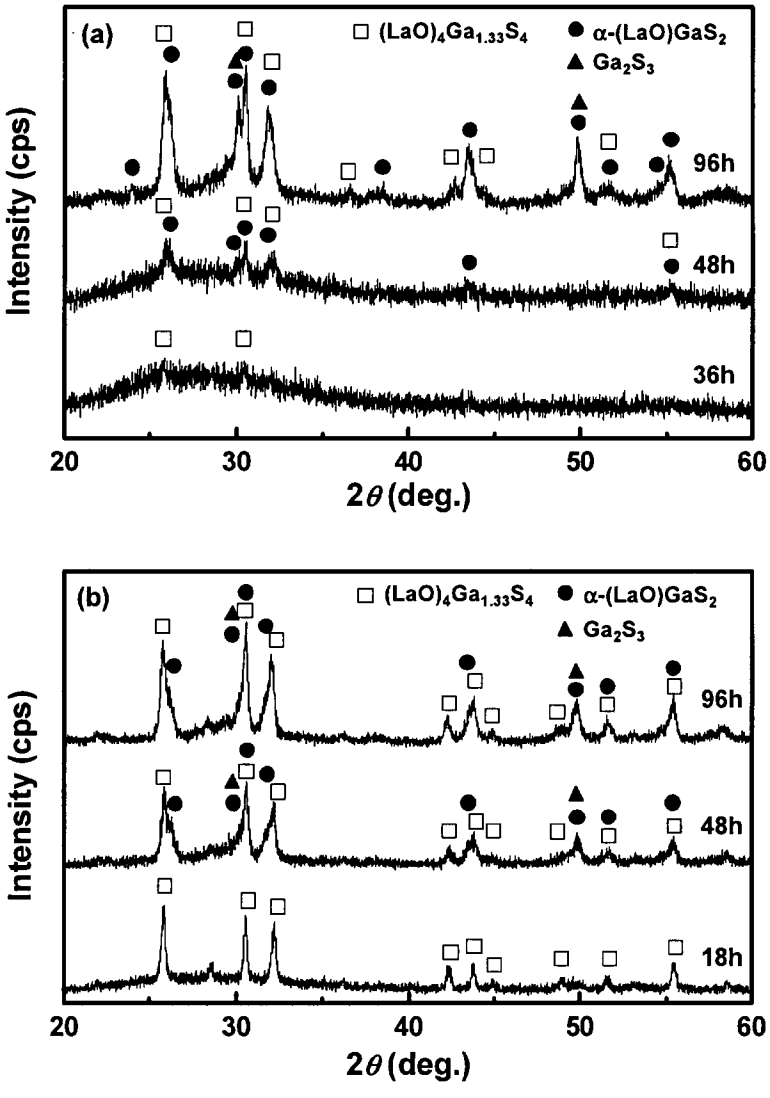
Figure caption

Fig.1 X-ray diffraction patterns of La_2O_3-Ga_2S_3 glasses isothermally-treated at 615°C. (a) LG and (b) NLG samples.

Fig.2 SEM micrographs of La_2O_3-Ga_2S_3 glasses isothermally-treated at 615°C. (a) LG, 36 h, (b) LG, 48 h, (c) LG, 96 h, (d) NLG, 18 h, (e) NLG, 48 h, (f) NLG, 96 h.

Fig.3 Variations of Vickers hardness H_v with heat treatment time for LG and NLG samples.

Fig.4 IR transmission spectra of (a) LG and (b) NLG samples isothermally-treated at 615°C.



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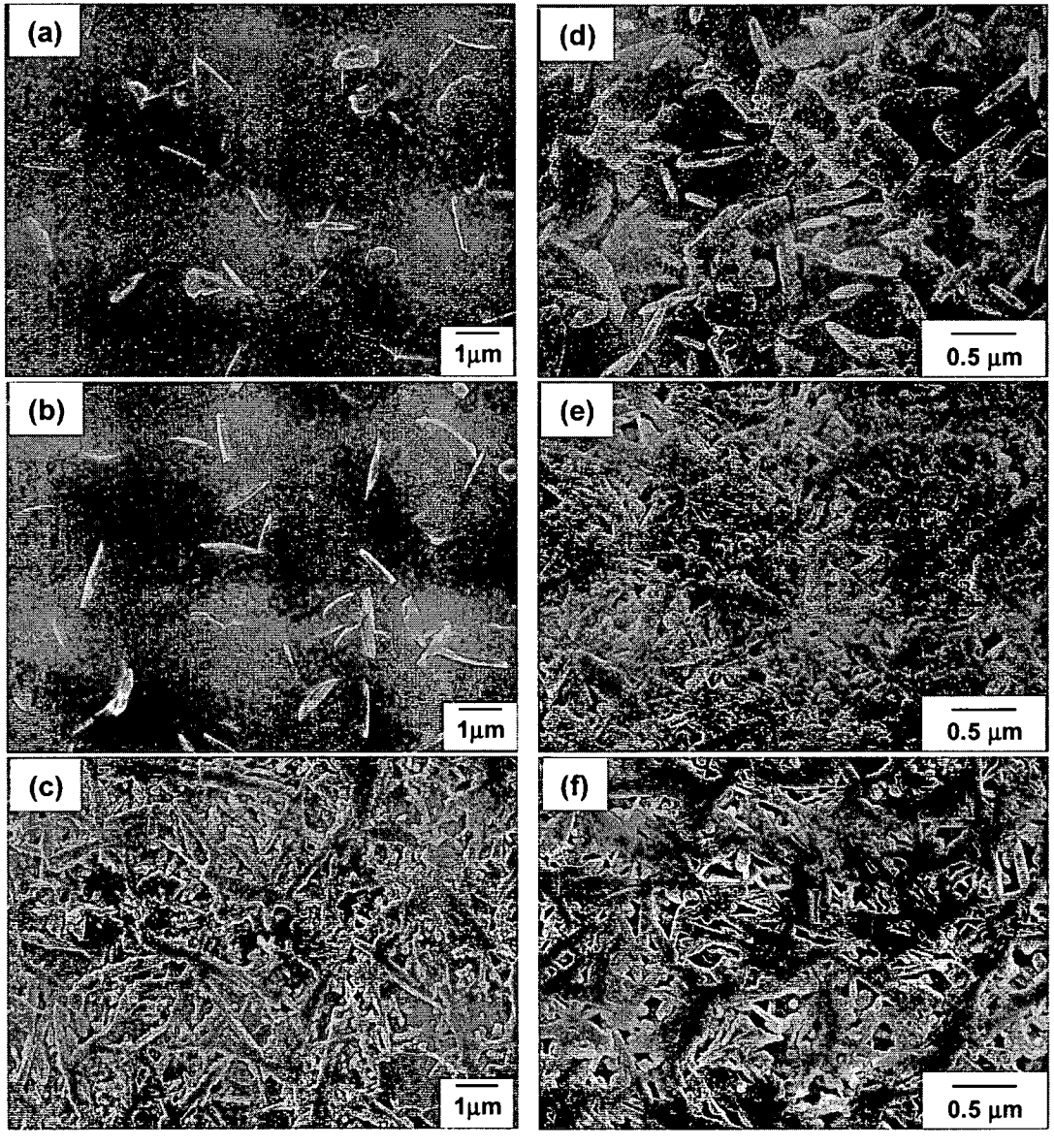

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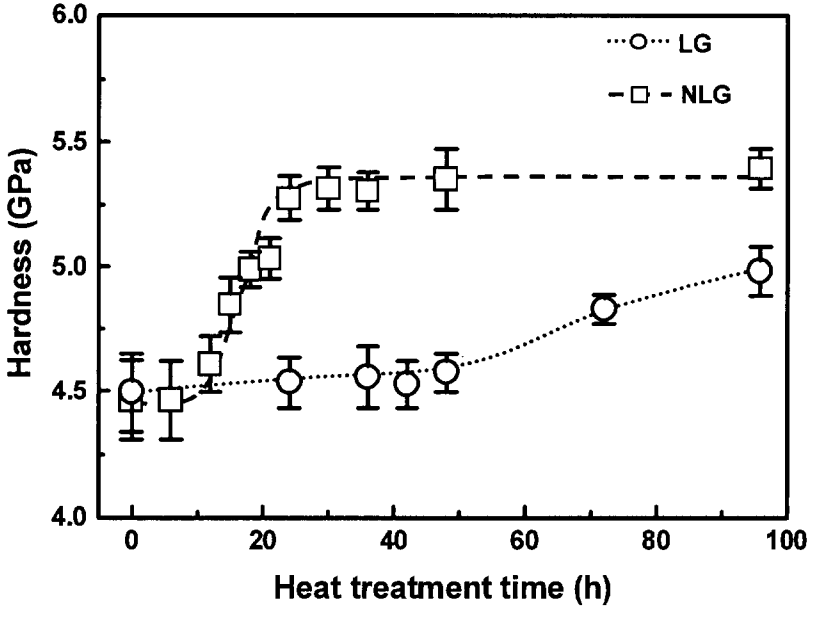

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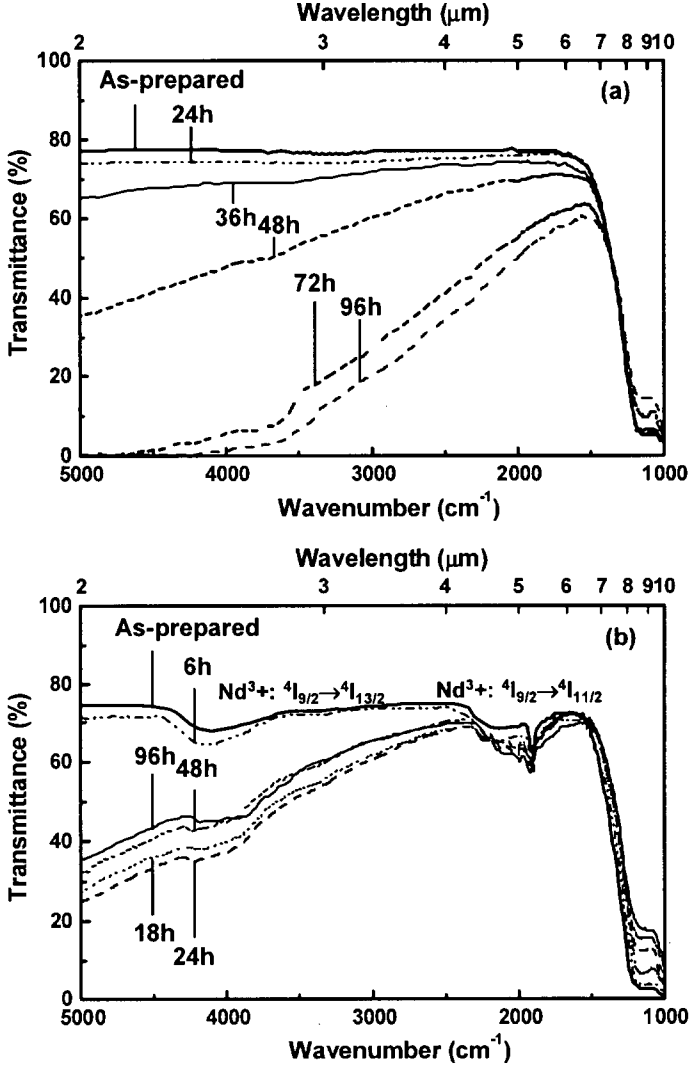

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