Thermal Properties of Ga_2S_3-Based Glass and their Consideration during Fibre Drawing

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Abstract

Thermal properties of gallium lanthanum sulphide and oxysulphide glasses relevant to fibre are evaluated. Time-temperature-transformation diagrams of gallium lanthanum sulphide and oxysulphide glasses are presented based on the results of X-ray diffraction analysis and microstructural observations. Thermal stability of these glasses for fibre drawing is discussed along with the viscosity data of super cooled liquid samples. Favorable fabrication conditions for gallium lanthanum sulphide glass fibres are proposed to minimize microcrystal formation during heating.

Gallium sulphide (Ga_2S_3)-based glasses are a new important family of infrared optical fibre materials [1]. Ga_2S_3-based glasses have some favorable properties for practical applications including non toxicity, chemical stability, high glass transition temperature and high rare-earth solubility. We have successfully fabricated gallium lanthanum sulphide (GLS) glass fibres by the rod-in-tube method [2]. However, it is difficult to fabricate GLS glass fibres without crystallization because of its relatively-poor thermal stability [3]. Here we focus on the evaluation of the thermal stability of Ga_2S_3-based glasses with the goal of fabricating their optical fibres without any microcrystals.

The difference between glass transition and onset crystallization temperatures, ΔT, is commonly used as a criteria of glass stability [4]; glasses with high ΔT values, e.g., > 100°C, are usually drawn into fibres. ΔT is measured with thermal analytic techniques under a constant heating rate. However, even when glass samples show large ΔT values over 100°C, one sometimes fails to fabricate their fibres without crystallization. In this letter an alternate approach to understanding the thermal stabilities of Ga_2S_3-based glasses is described based on time-temperature-transformation (TTT) diagram and microstructural observations. TTT diagram can express the crystallization starting conditions by the combination of temperature and time of isothermal treatments [5]. The TTT diagrams of Ga_2S_3-La_2S_3 and Ga_2S_3-La_2O_3 glasses are combined with their viscosity data to grasp heating conditions for fibre drawing.

Bulk glass samples with molar compositions of $70Ga_2S_3 \cdot 30La_2S_3$ (GLS) and $70Ga_2S_3 \cdot 30La_2O_3$ (GLSO) were prepared by melting the mixed powders in a vitreous carbon crucible in an inert atmosphere and subsequent quenching. The weight loss after melting is less than 2% for both GLS and GLSO glass samples. The typical temperatures of glass transition, T_g, and onset crystallization, T_x, of GLS glass were 556°C and 681°C, respectively; those of GLSO glass were 556°C and 738°C, respectively [3]. GLSO glass have a larger ΔT (= T_x -T_g) value of 182°C than GLS glass (ΔT = 125°C); GLSO glass is likely to be fabricated into fibre form easily, compared to GLS glass, judging from these ΔT values. Glass sample plates having two ground and/or polished

surfaces with a typical dimension of 10 x 10 x 1.5 mm were isothermally-treated in a tube furnace with a prescribed temperature for various times in a N_2 flowing atmosphere and quenched. Sample surfaces were cleaned by alcohol before thermal treatments. Since a few minutes is required for the sample temperature reaching the prescribed furnace temperature at ~ 600°C, the minimum of holding time is set as 10 min. Crystalline phases were determined by X-ray diffraction (XRD) analysis with Cu Kα using both bulk and powdered samples. Microstructures were observed by transmission optical microscopy. Viscosities of glass samples were measured in the range of 10^5 and 10^8 Pa•s by parallel plate rheometry using a thermo-mechanical analyser [6].

Fig.1 (a) and (b) show typical XRD patterns of isothermally-treated GLS samples. All samples isothermally-treated exhibit the monoclinic $Ga_4La_2S_9$ ($66.7Ga_2S_3$•$33.3La_2S_3$) phase (Fig. 1 (a) and (b)) in agreement with a previous study [7]. Since the GLS glass sample has a batch composition of $70Ga_2S_3$•$30La_2S_3$, excess amount of Ga_2S_3 may form α-Ga_2S_3 nano-size crystals between lamellae of $Ga_4La_2S_9$, as Morgan et al. pointed out [7]. Tetragonal $Ga_6La_{10/3}S_{14}$ ($64Ga_2S_3$•$36La_2S_3$) phase [8] is only detected in the initial stage of crystallization, at temperatures lower than 630°C when XRD analysis was performed on the surface of bulk GLS glass samples, as shown in Fig. 1 (b). This result contradicts one of previous studies [9]. Author [9] argues the main crystalline phase of GLS glass samples, with a batch composition of $70Ga_2S_3$•$30La_2S_3$, is $Ga_6La_{10/3}S_{14}$. This contradiction may, however, be resolved as follows. The measured density of our GLS glass was 4.03 g/cm^3 and density increased linearly with increasing La_2O_3 concentration in the line of $70Ga_2S_3$•$(30-x)La_2S_3$•xLa_2O_3 [10] and reached up to 4.26 g/cm^3 for $70Ga_2S_3$•$30La_2O_3$ [11]. Ding et al. [9] reported the measured density of GLS glass was 4.06 g/cm^3 suggesting relatively-higher oxygen concentration, compared with our GLS glass. A certain amount of La_2O_3 may promote the formation of melilite phase $Ga_6La_{10/3}S_{14-x}O_x$ as detected in GLSO glass (Fig. 2).

Fig. 2 shows a typical XRD pattern of isothermally-treated GLSO samples. This pattern is identical to that of tetragonal $Ga_6La_{10/3}S_{14}$ ($64Ga_2S_3$•$36La_2S_3$) [8]. Since GLSO glass have a batch composition of $70Ga_2S_3$•$30La_2O_3$ and the weight loss during

melting is small less than 2%, the melilite phase in the GLSO glass probably contains oxygen and its chemical formula may be as $Ga_6La_{10/3}S_{14-x}O_x$. The melilte is the only crystalline phase identified in the range of 615° and 700°C for GLSO glasses.

The TTT diagrams of GLS and GLSO glasses during isothermal treatments are drawn by using XRD results to identify crystalline phases and microstructural observations to determine the initial crystal formation. At the initial stage of crystallization, microcrystals with < 10 μm size were observed sparsely in the heat-treated samples whose XRD pattern showed an amorphous state halo. Fig. 3 (a) and (b) indicate the TTT diagrams of GLS and GLSO glasses with the viscosity data of their super cooled liquid states. The solid lines in Fig. 3 (a) and (b) express the boundary conditions between glassy (super cooled liquid) state and microcrystal formation. The dotted line in Fig. 3 (a) shows the boundary temperature of $Ga_6La_{10/3}S_{14}$ ($64Ga_2S_3 \cdot 36La_2S_3$) phase formation in GLS samples.

Fibre drawing by the rod-in-tube method is typically performed above the temperature at which the viscosity is 10^5 Pa•s [3]. The temperature of GLS glass with a viscosity of 10^5 Pa•s is 650°C approximately; microcrystals are observed solely at the surface of GLS samples isothermally-treated at 650°C for 10 min, as shown in Fig. 4 (a). Note the trace of grinding promotes the crystallization (Fig. 4 (b)). Such a heterogeneous crystallization is related to the following conditions the surface temperature of glass samples first reaches to the nucleation temperature of crystals and the surface roughness reduces the barrier of nucleation [12]. One of findings of this study is that the surface of GLS glass samples should be polished perfectly to reduce the amount of microcrystals and to lengthen the time interval before onset crystallization at the expected fibre drawing temperature. To use perfectly-polished samples and to apply an extrusion method to make fibre preforms with core/clad structure at relatively lower temperatures, for instance, 580° - 600°C for the GLS glass, with viscosities of 10^7 - 10^8 Pa•s [13] is one of useful methods for avoiding crystal formation at the interface between core and clad during preform fabrication process. This method may minimize crystal formation during sequential fibre fabrication process.

The expected fibre drawing temperature of GLSO glass with a viscosity of 10^5 Pa•s is above 700°C, the TTT diagram reveals there is a 30 min interval before crystallization at 700°C. At 700°C sample shape transforms plate into droplet by reducing its viscosity; dendritic-microcrystals form at surface shown in Fig.5. The results suggest GLSO glass fibre without crystallization can be fabricated easily in agreement with our experience.

In conclusion, time-temperature-transformation diagrams of gallium lanthanum sulphide (GLS) and oxysulphide (GLSO) glasses are presented based on the results of X-ray diffraction analysis and microstructural observations. Thermal stability of GLS and GLSO glasses at the expected fibre drawing temperatures with a viscosity of 10^5 Pa•s can be compared each other using the TTT diagrams with the viscosity data of super cooled liquid samples. The crystal morphology in the GLS glass suggests the perfect-polishing of sample surfaces minimizes crystal formation during fibre fabrication. GLSO glass is more thermally-stable than GLS glass and would be fabricated its fibre easily.

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Figure captions

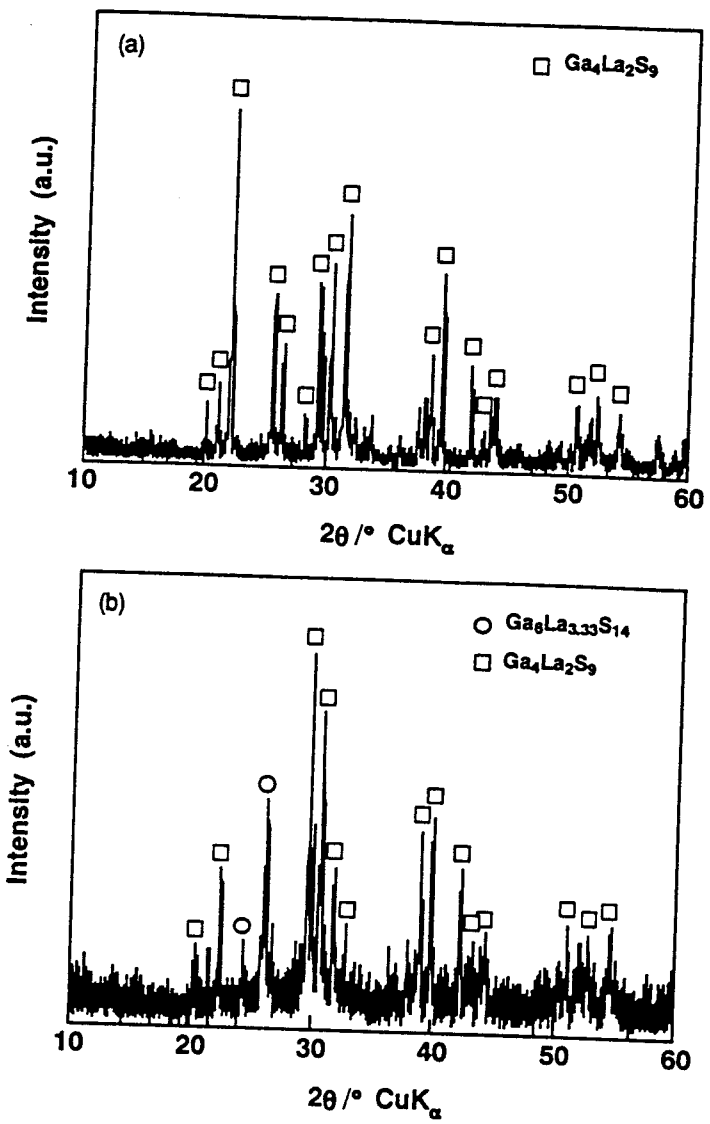
Fig.1 X-ray diffraction patterns of gallium lanthanum sulphide (GLS) glass samples isothermally-treated (a) at 630°C for 2hrs and (b) at 600°C for 6hrs. The batch composition of GLS samples is 70 mol%Ga_2S_3•30 mol%La_2S_3.

Fig. 2 X-ray diffraction pattern of gallium lanthanum oxysulphide (GLSO) glass samples isothermally-treated at 630°C for 72 hrs. The batch composition of GLSO samples is 70 mol%Ga_2S_3•30 mol%La_2O_3.

Fig.3 TTT diagrams of (a) GLS and (b) GLSO glasses during isothermal treatments. Viscosity data of super cooled liquid states is also shown in these figures.

Fig. 4 Transmission optical micrographs of the GLS glasses treated at 650°C for 10 min. Sample surfaces before heating were (a) polished and (b) ground by silicon carbide #3,000 papers.

Fig. 5 Transmission optical micrograph of the GLSO glass treated at 700°C for 1hr.



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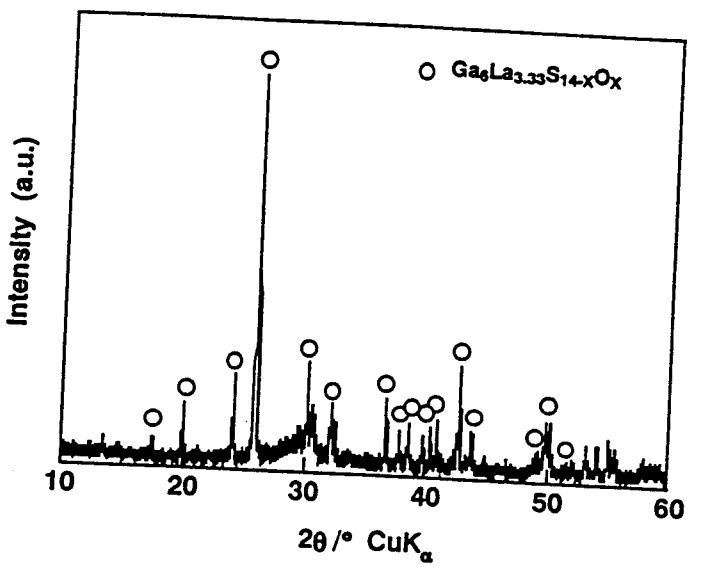

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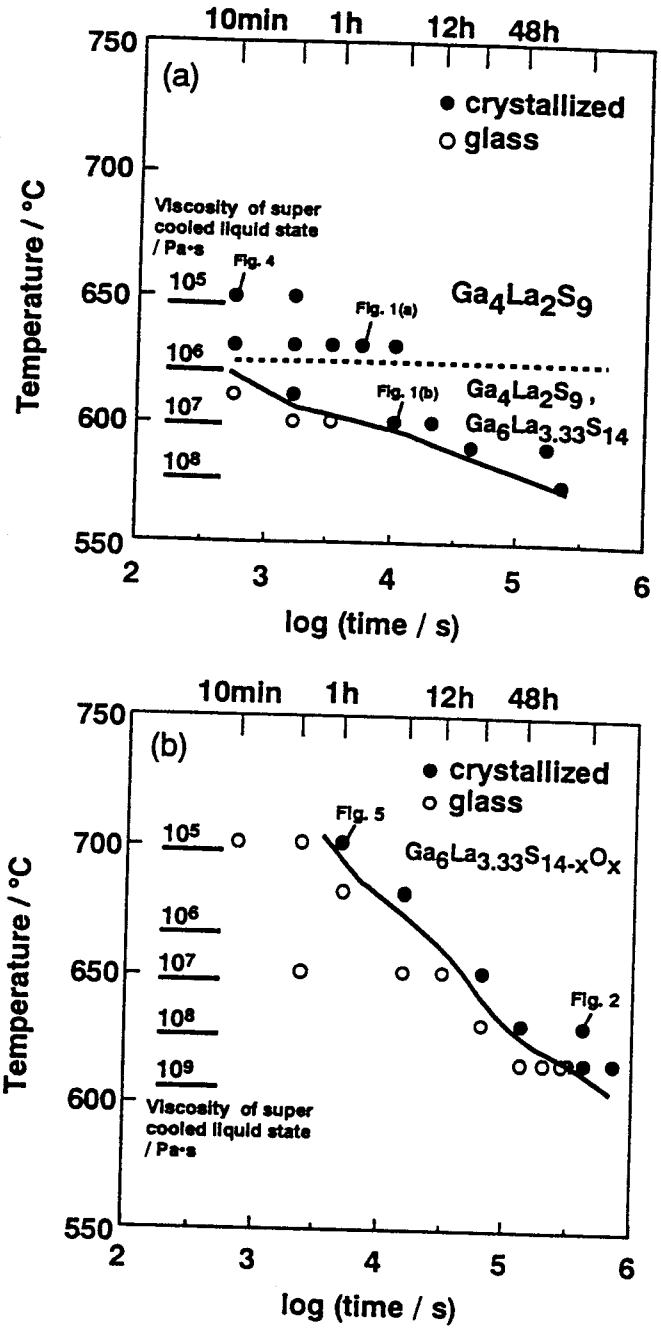

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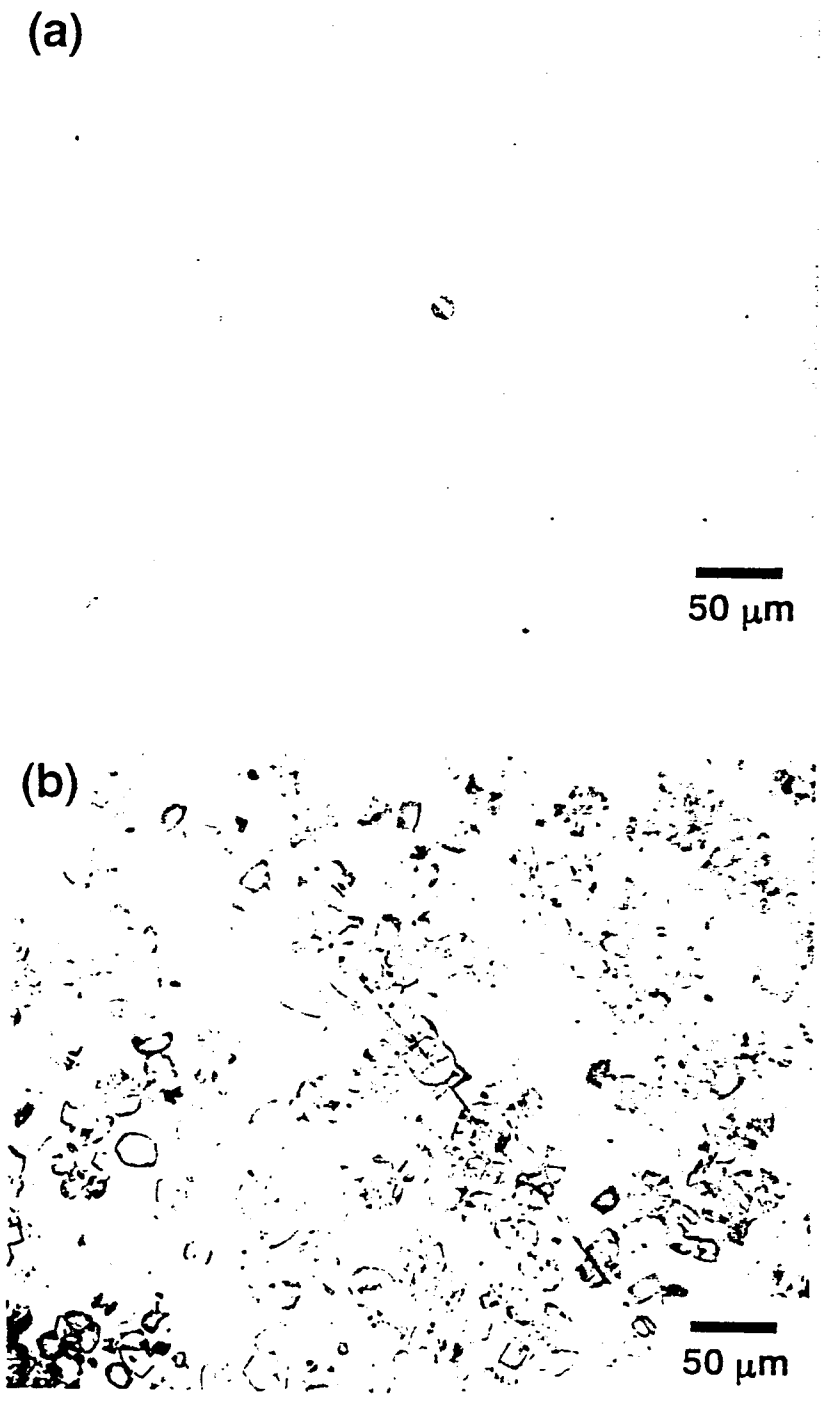

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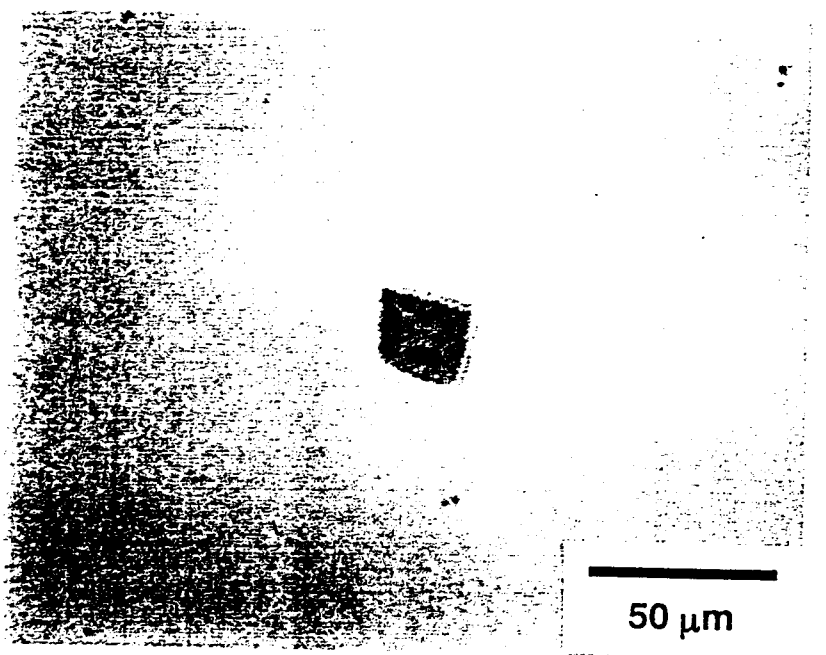

Fig. 5 Transmission optical micrograph of the GLSO glass treated at 700°C for 1hr.