



Study on crystallization behavior of novel silver chloride based chalcogenide glasses



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ABSTRACT

In the present work, samples in composition of $(100-x)/2As_2S_3-(100-x)/2Ag_2S-xAgCl$ ($x = 40, 45, 50, 55mol\%$) were prepared. X-ray diffraction and differential scanning calorimetry under non-isothermal conditions were recorded from which crystalline phases, characteristic thermal temperature, criteria for thermal stability against crystallization and crystallization kinetic parameters are obtained for evaluation of their glass formation and crystallization behaviors. Raman spectroscopy was used in following the structural changes with variation of AgCl content. Thermal treatments were made on amorphous samples under different conditions, and the nonlinear dependence of crystallization behaviors on AgCl content is discussed. Results of the present work obtain the optimal silver chloride based chalcogenide glass composition as the stable membrane material for application in ion-selective electrodes for dual Ag^+/Cl^- ions determination.

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1. Introduction

Chalcogenide (ChG) glasses represent one class of functional materials with several distinctive features such as wide range of transmission in the infrared spectrum, high indicator of refraction with non-linear dispersion, unique photosensitivity, good electrochemical performance, etc. Among wide applications of ChG glasses in different fields, their usage as membranes in ion-selective electrodes (ISE) for heavy metal ions determination have attracted extensive concerns and interests in the past decades [1–3]. Although these membranes could be produced from polycrystalline sulfides or selenides, in many cases ChG glasses possess advantages of the higher selectivity and the better reproducibility of analytical characteristics due to their high potential stability in acids and oxidising solutions [3]. In particular, ChG glasses have shown long time of life in relation to the dissolution in electrolytes and resistance to aggressive environments, such as acids, strong oxidising agents and corrosive media. These latter features of the electrode response were useful for the application of waste, industrial and sea water analyses, ultrapure metal production, multisensor “electronic tongue” systems, etc. Moreover, the introduction of halogen atoms in ChG glasses tends to increase the defectiveness and

flexibility of the structural network, thus facilitating mobility and exchange of ions between the membrane surface layer and the investigated solution. In this context, halide based ChG glasses are often used as membranes in the place of their polycrystalline counterparts for ISE registering heavy metal ions.

In this paper, we report our recent work on novel $As_2S_3-Ag_2S-AgCl$ glasses. In comparison with detection for heavy metal ions, some investigation showed that vitreous ChG sensors displayed no anion ion response whereas it occurred for glassy-crystalline alloys [1]. For possible application of these AgCl-based ChG glasses as the silicon-based thin-film sensors for dual Ag^+/Cl^- ions detection, the present paper focuses on studying their thermal stability and crystallization process. X-ray diffraction (XRD) and differential scanning calorimetry (DSC) under non-isothermal (NI) conditions are recorded from which crystalline phases, characteristic thermal temperature and crystallization kinetic parameters are obtained for evaluation of their glass formation and crystallization behaviors.

2. Experimental procedure

Glass compositions for the present work are $(100-x)/2As_2S_3-(100-x)/2Ag_2S-xAgCl$ ($x = 40, 45, 50, 55mol\%$, noted as G40, G45, G50 and G55, respectively). Different ratio of $AgCl/(As_2S_3+Ag_2S)$ was considered in order to investigate the effect of halide on glass formation and thermal stability against crystallization. Bulk glass samples were prepared by the melt-quenching method using high

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purity arsenic, sulfur, silver chloride and silver sulfide as raw materials. The purified raw materials were weighed with the precision of 0.01% followed by vacuum-sealing in quartz ampoules. The diameter and wall thickness of quartz ampoules are 10 mm and 2 mm, respectively. The glass batches were heated at heating rate of 3 k/min to 920 °C in a rocking furnace and heat preservation for 10 h, then cooled down to 700 °C. The melts were quenched in the water from 700 °C to room temperature. The obtained glass samples were then annealed at 100 °C for 4 h. The bulk samples were grounded to fine powder for DSC and XRD measurements. The DSC (TA D2000, New Castle, DE) measurement is carried out on samples to understand crystallization kinetics under non-isothermal (NI) conditions. DSC measurements are conducted in a flowing nitrogen atmosphere using an aluminum container at different heating rates (5, 10, 15, 20 and 25 K/min). The instrument was calibrated for all the heating rates using aluminum standard. XRD (MAX R1, precision $\pm 0.02^\circ$; Rigaku, Tokyo, Japan) was performed on powder samples at 40 kV and 30 mA using CuK radiation to identify the type of crystallites.

3. Results and discussion

3.1. Glass formation and thermal stability against crystallization

XRD and DSC experiments are performed to investigate the formation and the crystallization of As_2S_3 - Ag_2S - $AgCl$ glasses. Fig. 1 presents XRD patterns (a) and DSC traces (b) of all as-prepared samples. It is observed from XRD patterns that samples G40, G45 and G50 show characteristic broad glassy diffraction patterns, while the sample G55 displays several intense crystalline XRD peaks. According to the location of these XRD peaks by comparison with the JCPDS standard card, they can be assigned to $AgCl$ crystal phase. Thus we conclude that on the basis of an equal As_2S_3 and Ag_2S content, glass formation is available within $AgCl < 55$ mol% in the present glass system.

From DSC curves measured at the heating rate of 10 K/min, the glass transition temperature (T_g), the onset temperature of crystallization (T_x), the temperature corresponding to the maximum crystallization rate (T_p) and the melting temperature (T_m) were obtained and all data are summarized in Table 1. As shown in Fig. 1(b), the T_g , T_x and T_m [4] have been defined as the temperatures which correspond to the intersection of two linear portions adjoining the transition elbow of the DSC traces in the endothermic and exothermic directions.

DSC curves (Fig. 1 b) of all samples also shows two visible crystallization peaks (noted as T_{P1} for at the lower temperature and

T_{P2} for at the higher one), where T_{P1} and T_{P2} of the sample G55 become much broader due to the crystallization effect. Moreover, the DSC traces of all studied compositions show a single T_g , confirming no phase separation in all as-prepared samples [5]. As shown in Table 1, T_g decreases with the increasing $AgCl$ content. This is obviously associated with the structural role of Cl^- ions in the $AgCl$ based ChG glasses. Acting as a glass network terminal, Cl^- ions tend to substitute some bridging S to bond with As, and interrupt the glass network, resulting in the more open structure with the mixed $Ag_yAs [S_3]Cl_y$ pyramids [6]. Because of the larger bond strength of As-Cl ($D_{298} = 107$ kcal/mo1 [7]) than that of Ag-Cl ($D_{298} = 74.26$ kcal/mo1 [8]), the replacement of S by Cl is quite possible. Therefore decrease in the connectivity of the glass network consequently leads to an increase in crystallization tendency and a decrease in T_g [9].

The above structural changes are also characterized by Raman spectroscopy. As shown in Fig. 2, Raman spectra of all samples have been normalized with the main band at 375 cm^{-1} which corresponds to the asymmetric stretching vibration of As-S bonds with non-bridging S atoms in As_3S_6 rings structure [10,11]. Other bands include those at 335 cm^{-1} , 210 cm^{-1} and 135 cm^{-1} , respectively.

It is known from previously reported work that the Raman band at 335 cm^{-1} is due to the symmetrical bond stretching vibration of As-S bonds [10] with bridging S atoms while bands at 135 cm^{-1} and 210 cm^{-1} correspond to the vibration of Ag-Cl bonds [12]. For amorphous samples G40, G45 and G50, the intensity of all three bands decreases with the increasing $AgCl$ content, confirming the above reasoning that Cl^- ions substitute some bridging S to bond with As, and thus interrupt the pyramidal based glass network [6]. For the crystallized sample G55, however, two bands for Ag-Cl bonds become more intense whereas two bands for As-S bonds suffer obvious shifts towards lower wavenumbers. The former observation is in accordance with XRD results in Fig. 1 (a), indicating that the short range order in the present glasses actually consists of $AgCl$ molecular fragments which in the crystal structure are normally sharper than glassy phase with the same composition. The latter phenomenon most likely results from the effect of $AgCl$ crystals on the lengths of As-S bonds. According to Wilson's method, relationship of the bond force constant (K) or vibration frequency (ν) with the atomic distance of the bond can be expressed by the following formulas:

$$K = a(r - b)^{-3} \quad (1)$$

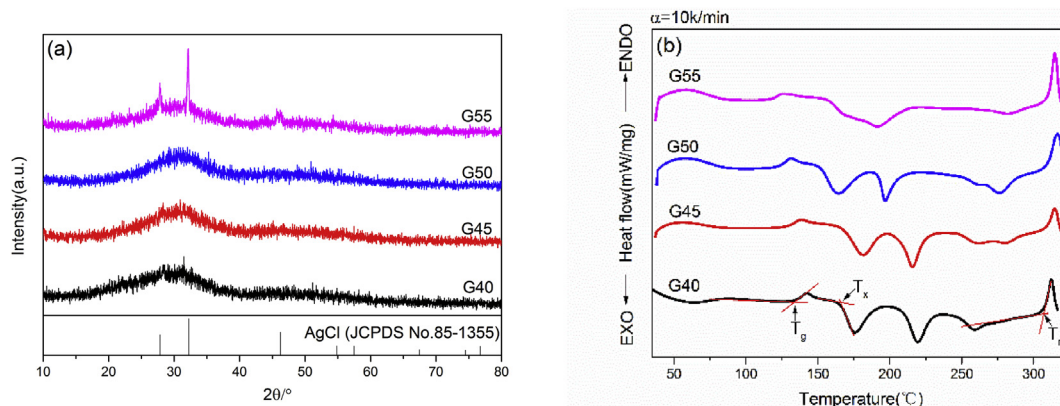


Fig. 1. XRD patterns (a) and DSC traces at the heating rate of 10 K/min (b) of samples.

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