

Formation, thermal, optical and physical properties of GeS₂–Ga₂S₃–AgCl novel chalcogenide glasses

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Abstract Novel GeS₂–Ga₂S₃–AgCl chalcogenide glasses had been prepared by melt-quenching technique, and the glass-forming region was determined by XRD, which indicated that the maximum of dissolvable AgCl was up to 65 mol%. Thermal and optical properties of the glasses were studied by differential scanning calorimetry (DSC) and Visible–IR transmission, which showed that most of GeS₂–Ga₂S₃–AgCl glasses had strong glass-forming ability and broad region of transmission (about 0.45–12.5 μm). With the addition of AgCl, the glass transition temperature, T_g decreases distinctly, and the short-wavelength cut-off edge (λ_{vis}) of the glasses also shifts to the long wavelength gradually. However, the glass-forming ability of the glass has a complicated evolutionary trend depended on the compositional change. In addition, the values of the Vickers microhardness, H_v , which decrease with the addition of AgCl, are high enough for the practical applications. These excellent properties of GeS₂–Ga₂S₃–AgCl glasses

make them potentially applied in the optoelectronic field, such as all-optical switch, etc.

Introduction

Chalcogenide glasses, due to their higher refractive indices, have exhibited larger third-order nonlinear susceptibility, $\chi^{(3)}$ [1]. Subsequently, after effective poling, large second-order nonlinear susceptibility, $\chi^{(2)}$, should be obtained through $\chi^{(2)} = 3\chi^{(3)}E_{DC}$, where E_{DC} is the frozen in electric field due to the poling procedure [2]. Comparing with the As and Se-containing chalcogenide glasses that suffered from the drawback of two-photon absorption (TPA) at the telecommunication wavelength of 1.3 μm [3]. GeS₂–Ga₂S₃-based glasses have become the hotspot by researchers due to their good glass-forming ability, low maximum phonon energy, wide and high Vis–IR transparency, large third/second-order nonlinear susceptibility, excellent ability as promising hosts for rare-earth (RE) doped matrix, etc [4–7]. Recently Kityk et al. [8], also discovered the excellent IR nonlinear optical properties in sulphide glass-ceramic with β -GeS₂ microcrystallites, which were due to the anharmonic electron-phonon interactions (EPI). Furthermore, because of the heavier atomic mass and large polarizability of Ag⁺ ion, it can be deduced that the addition of AgCl is promising to increase refractive index and get more excellent third/second-order nonlinear properties. And the addition of haloid atom, chlorine, would also be expected to improve the glass-forming ability and optical transmittance of the glasses. Therefore, we studied the glass-forming ability, thermal, optical and physical properties of pseudo-ternary GeS₂–Ga₂S₃–AgCl glasses in this work, which indicated that these glasses can be applied potentially in advanced techniques, such as all-optical switching, etc.

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Experimental

Homogeneous $\text{GeS}_2\text{-Ga}_2\text{S}_3\text{-AgCl}$ glasses were obtained by conventional melt-quenching technique using high-purity Ge, Ga, S (all of 5 N) and AgCl (3 N) as raw materials. The mixtures (2 g) were melted in silica ampoules at 1,200 K for 12 h and then quenched in ice water. Details of the preparations were similar to our previous work [9–11]. The $10 \times 10 \times 1 \text{ mm}^3$ glass plates were prepared from the bulk glasses and were optically polished.

Amorphous characteristics of the prepared samples were confirmed by X-ray diffraction with Cu K_α radiation (40 kV, 40 mA), which also determined the glass-forming region of the system. Samples with no diffraction peaks are labeled as glassy, samples with broad and weak peaks are labeled as partly crystalline and samples with narrow and strong peaks are labeled as crystalline.

The glass transition temperature, T_g and crystallization temperature, T_c (onset temperature of crystallization) were determined by differential scanning calorimetry (DSC, Netzsch STA 449 °C) at 10 °C min^{-1} heating rate with a precision of $\pm 1 \text{ °C}$.

Optical transmission was recorded with a spectrophotometer (Shimadzu UV-1601) in the visible and near-IR region (Vis–NIR) and a Fourier transform IR spectrometer (Nicolet 60-SXB) in the middle-IR region. The refractive index (n) was measured by spectroscopic ellipsometer (TP-77) in the range between 400 nm and 1,200 nm.

The Vickers microhardness, H_v , was measured by a Vickers HX-1000TM/LCD with a 25 g load during 20 s. A series of five measurements was carried out for each composition and the average value was calculated as the experimental H_v with an accuracy of $\pm 2\%$. And the density of samples was tested by the Archimedes method using CCl_4 as the immersed medium. The compositions of the prepared glasses were analyzed by electron probing micro analysis (EPMA, JXA-8800R), revealing that the difference between theoretical and real composition was within reasonable range ($\pm 1 \text{ atom.}\%$) except for the element of chlorine (losing almost 10 atom.% of the theoretical content), which is due to the light-induced decomposition of AgCl in the process of glass preparation.

Results and discussion

The glass-forming region

Figure 1 shows the glass-forming region of pseudo-ternary $\text{GeS}_2\text{-Ga}_2\text{S}_3\text{-AgCl}$ system determined by XRD according to the standard mentioned in Section “Experimental”. It can be seen that the relatively large glass-forming region obtained by quenching the melt (2 g) into 0 °C ice water in

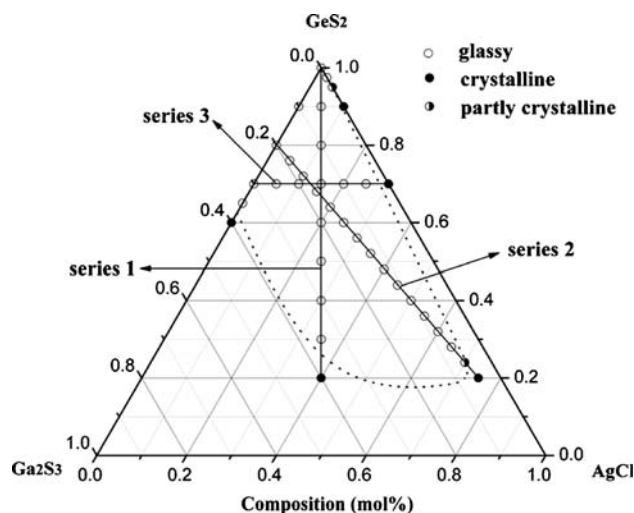


Fig. 1 Glass-forming region of pseudo-ternary $\text{GeS}_2\text{-Ga}_2\text{S}_3\text{-AgCl}$ system. Series 1: $(100-2x) \text{ GeS}_2-x \text{ Ga}_2\text{S}_3-x \text{ AgCl}$; Series 2: $0.8(100-x) \text{ GeS}_2-0.2(100-x) \text{ Ga}_2\text{S}_3-x \text{ AgCl}$; Series 3: $70 \text{ GeS}_2-(30-x) \text{ Ga}_2\text{S}_3-x \text{ AgCl}$

this system is mainly situated in the GeS_2 -rich region and extended from the GeS_2 -rich apex to the AgCl-rich region. It is obvious that no glass is obtained on $\text{Ga}_2\text{S}_3\text{-AgCl}$ side. The maximum of dissolvable AgCl on Series 2 (where the ratio of $\text{GeS}_2/\text{Ga}_2\text{S}_3$ maintains 4:1) is unexpectedly up to 65 mol% due to the addition of haloid atom, chlorine. In addition, the color of glasses changes from yellow to reddish slightly with the addition of AgCl.

Figure 2 shows the XRD patterns of some crystallized samples. In our previous research, samples with more than 35% Ga_2S_3 in the pseudo-binary $\text{GeS}_2\text{-Ga}_2\text{S}_3$ system have $\alpha\text{-Ga}_2\text{S}_3$ crystalline separate out [10]. Along the $\text{GeS}_2\text{-AgCl}$ system (see Fig. 1), sample only doping with 5% AgCl has the separation of crystalline GeS_2 . However, crystalline Ag_8GeS_6 is separated out when the addition of AgCl is up to 70% on Series 2 (sample B14 ($x = 70$)), and even on Series 1 that is characterized with $\text{Ga}_2\text{S}_3/\text{AgCl} = 1$, $\alpha\text{-AgGaS}_2$ is separated out also when the content of AgCl reaches 40% (sample A8 ($x = 40$)). That is to say, the addition of Ga_2S_3 has an important effect on the mitigation of phase separation in $\text{GeS}_2\text{-AgCl}$ system. Furthermore, according to our previous microstructure researches on $\text{GeS}_2\text{-Ga}_2\text{S}_3\text{-MCl}$ ($M=\text{K, Cs}$) ternary system [9, 11], it can be deduced that the formation of new $[\text{Ge}(\text{Ga})\text{S}_{4-x}\text{Cl}_x]$ mixed tetrahedral structural units (s.u.) would improve the glass-forming ability remarkably.

Thermal properties

A typical DSC curve of $\text{GeS}_2\text{-Ga}_2\text{S}_3$ -based glasses has been shown in our previous work [10]. Two typical characteristic temperatures investigated in the DSC curve are as

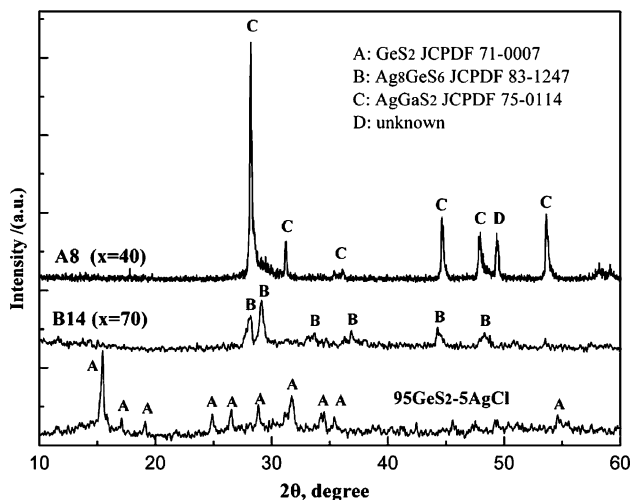


Fig. 2 XRD patterns of the crystallized samples. Letters A, B and C denote the characteristic peaks of GeS_2 , Ag_8GeS_6 and $\alpha\text{-AgGaS}_2$, respectively. Letters D denotes the unknown crystalline phase

follows: Firstly, every glass shows an endothermic step corresponding to its glass transition temperature, T_g ; Secondly, the crystallization process of the testing sample shows one or two exothermic peak corresponding to its crystallization temperature, T_c . The typical T_g and T_c of some glasses in $\text{GeS}_2\text{-Ga}_2\text{S}_3\text{-AgCl}$ ternary system are listed in Table 1 [11]. It is obvious that the values of T_g and T_c decrease with the addition of AgCl on all the three series. On the one hand, the descending of the glass former, GeS_2 would result in the decrease of T_g and T_c . On the other hand, it can be explained through the literature report by Heo et al. [12], indicating that a definite relationship between the crosslink density and the glassy transition temperature for the oxide glassy network. Therefore, it is reasonable to deduce that the value of T_g in the presented glasses should have an intimate relationship with the crosslink density and the network connectivity of the glasses. And the addition of the network terminating atoms, Cl, which are the nonbridging atoms compared with the bridging sulfur atoms, will induce the descending of the network connectivity and make the glass network more opened. Subsequently, the value of T_g will also decrease with the addition of AgCl gradually.

It is known that the criterion ΔT (the difference between T_c and T_g) is an critical parameter to evaluate the thermal stability and fiber-drawing property of a glass, and the glass with the value of $\Delta T > 100$ °C is usually considered to have the ability to be drawn into fibers. The values of ΔT for most glasses in the system are larger than 100 °C, making the glass show potential application in drawing fibers.

Besides the criterion ΔT , the Hruby criterion, H_r ($H_r = (T_c - T_g)/(T_m - T_c)$, where T_m is the melting point), is also a vital criterion used to evaluate the glass-forming ability of the amorphous materials. However, as a result of the high

volatility of chalcogenide glasses, the melting point could not be recorded precisely. Therefore, an alternative criterion, H' ($H' = (T_c - T_g)/T_g$) is used to evaluate the ability of a glass against crystallization [13]. The values of H' of some glasses are also listed in Table 1. Most of the H' values in the system are high, which indicates the strong glass-forming ability of $\text{GeS}_2\text{-Ga}_2\text{S}_3\text{-AgCl}$ glasses. And it can be deduced that the most stable glass composition in the presented glasses is $90\text{GeS}_2\text{-5Ga}_2\text{S}_3\text{-5AgCl}$, which exhibits the largest H' value (0.197).

Furthermore, it can be found that the value of H' enhances slightly with the moderate addition of AgCl and then decreases gradually while adding AgCl continuously on Series 2 and 3. However, the value of H' decreases monotonously with the addition of AgCl on Series 1. These interesting phenomena can be interpreted through the two inverse facets resulted from the addition of AgCl. On the one hand, the addition of the network terminating atoms, Cl, will induce the degradation of the connectivity of glass network and result in the decrease of glass-forming ability; On the other hand, it has been reported in our previous research that the addition of Ga_2S_3 will induce the formation of $[\text{GaS}_4]$ tetrahedral s.u. and force germanium (gallium) atoms to form $[\text{S}_3\text{Ge}(\text{Ga})\text{-Ge}(\text{Ga})\text{S}_3]$ ethane-like s.u. instead of corner-sharing $[\text{Ge}(\text{Ga})\text{S}_4]$ tetrahedral s.u. to compensate the shortage of sulfur atoms [14]. At the moment, the addition of AgCl will alleviate the shortage of sulfur atoms by providing Cl to form $[\text{Ge}(\text{Ga})\text{S}_{4-x}\text{Cl}_x]$ mixed tetrahedral s.u. instead of ethane-like s.u., which will improve the glass forming ability (H' value). On Series 1 where the ratio of $\text{Ga}_2\text{S}_3/\text{AgCl}$ maintaining 1:1, the ratio of $(\text{S} + 0.5\text{Cl})/(\text{Ge} + \text{Ga})$ is less than 2 on the whole series (see Table 1), i.e., the system is shortage of sulfur atoms and the shortage of sulfur atoms in the system cannot be mitigated with the addition of Ga_2S_3 and AgCl simultaneously with the ratio as 1:1, thereby, the first facet mentioned above will result in the decrease of H' value with the addition of AgCl on Series 1. While on Series 2 and 3, the system is shortage of sulfur atoms at the beginning, and the substitution of AgCl for Ga_2S_3 could provide Cl atoms to compensate the shortage of S atoms, improving the glass forming ability subsequently. After the ratio of $(\text{S} + 0.5\text{Cl})/(\text{Ge} + \text{Ga})$ is larger than 2, the system will be affluent with S(Cl) atoms, and the mitigating effect with the addition of AgCl will vanish. Inversely, the value of H' will decrease due to the addition of the network terminating atoms, Cl. Therefore, the interesting phenomena mentioned above could be explained successfully.

Optical properties

Figure 3 shows the Vis–NIR transmission spectra of $\text{GeS}_2\text{-Ga}_2\text{S}_3\text{-AgCl}$ glasses on Series 2. In this series, the molar

Table 1 Thermal and physical properties of GeS₂–Ga₂S₃–AgCl glasses

Samples	H_v (kg mm ⁻²)	T_g (°C)	T_c (°C)	ΔT^a (°C)	H'^b	(S + 0.5Cl)/(Ge + Ga)
Series 1: (100–2x) GeS _{2-x} Ga ₂ S _{3-x} AgCl						
A1(x = 5)	290.5	402.6	535.6	133	0.197^c	1.98^c
A2(x = 10)	262.4	380.3	498.2	117.9	0.180	1.95
A3(x = 15)	247.7	363.5	462.3	98.8	0.155	1.93
A4(x = 20)	239.4	356.8	440.9	84.1	0.134	1.90
A5(x = 25)	233.2	340.7	410.5	69.8	0.114	1.88
A6(x = 30)	228.4	–	–	–	–	1.85
Series 2: 0.8(100–x) GeS _{2-0.2(100-x)} Ga ₂ S _{3-x} AgCl						
B1(x = 5)	299.6	417.6	519.4	101.5	0.147	1.86
B2(x = 10)	275.7	371.5	488.1	116.6	0.181	1.88
B3(x = 15)	241.8	368.5	485.6	117.1	0.183	1.91
B4(x = 20)	232.2	359.2	469.9	110.7	0.175	1.94
B5(x = 25)	223.4	346	434.8	88.8	0.144	1.97
B6(x = 30)	215.8	–	–	–	–	2.01
Series 3: 70 GeS _{2-(30-x)} Ga ₂ S _{3-x} AgCl						
C1(x = 5)	271.4	409.2	521.4	112.2	0.164	1.81
C2(x = 10)	256.8	390.4	493.6	113.2	0.173	1.86
C3(x = 15)	247.7	363.5	462.3	98.8	0.155	1.93
C4(x = 20)	233.8	344.4	439.6	95.2	0.154	2.00
C5(x = 25)	222.4	337.3	419.5	82.2	0.135	2.09

^a $\Delta T = T_c - T_g$

^b $H' = (T_c - T_g)/T_g$

^c Overstriking words indicate that the system is shortage of S (Cl) atoms, i.e., (S + 0.5Cl)/(Ge + Ga) < 2

concentration ratio of GeS₂ to Ga₂S₃ is maintained 4: 1. These glasses begin to transmit at 440–480 nm, which is much shorter than As and Se-containing chalcogenide glasses [15]. And the short-wavelength cut-off edge (λ_{vis}), which is due to the electrical transition between valence bands and conduction bands shifts toward the long wavelength with the addition of AgCl. It can be interpreted from polarizability. Due to the higher polarizability of Ag⁺ ions compared with Ge⁴⁺ and Ga³⁺ ions, the distinct Red shift of λ_{vis} would occur. However, since Cl⁻ ions (polarizability: 3.05) are less polarizable than S²⁻ ions (polarizability: 7.25) and the addition of AgCl could alleviate the shortage of sulfur atoms by providing Cl to transform [S₃Ge(Ga)–Ge(Ga)S₃] ethane-like s.u. into [Ge(Ga)S_{4-x}Cl_x] mixed tetrahedral s.u., which will result in the Blue shift of λ_{vis} , it can be interpreted that the Red shift of λ_{vis} in the system is not very large with the addition of AgCl. And the shift of λ_{vis} on Series 1 and 3 is also slight with the compositional change. In addition, according to the K–K relationship for optical parameters [16], it can be deduced that the transmittance of the glasses would increase with the addition of AgCl, which can be confirmed in Fig. 3.

The IR transmission spectrum of the most stable compositional glass (90GeS₂–5Ga₂S₃–5AgCl) is shown in Fig. 4. The long-wavelength cut-off edge located near

800 cm⁻¹ (12.5 μm) is ascribed to the intrinsic multiphonon Ge–S and Ga–S vibrations [17], and it is not affected by the change of composition. The strong absorption bands at 2,500 cm⁻¹ and 3,200 ~ 3,600 cm⁻¹ are ascribed to S–H, and –OH impurities, respectively, and the minor absorption band at 1,300 cm⁻¹ is assigned to –OH and G–O impurities. The obvious absorption band sited at 1,060 cm⁻¹ is due to S–H and S=O impurities. The absorption bands in the spectrum are mainly due to extrinsic impurities, which are resulted from the surface oxidation of the raw materials and the hydroxide contamination originated from the small water during the glass preparation, and it is difficult to avoid forming the strong M–OH and M–SH bands in chalcogenide glasses, where M is a metallic cation. However, efforts should be devoted to removing these impurities as a result that the impurities are very harmful to the practical applications in the optoelectronic field. In addition, the absorption band at 3,200–3,600 cm⁻¹ becomes more obvious with the addition of AgCl, indicating that the water-resistance property drops when halides are associated with the sulfide glasses.

The refractive index, n of some GeS₂–Ga₂S₃–AgCl glasses collected as a function of wavelength at 400–1,200 nm is shown in Fig. 5. They follow as a typical dispersion curve of chalcogenide glasses. Due to the larger

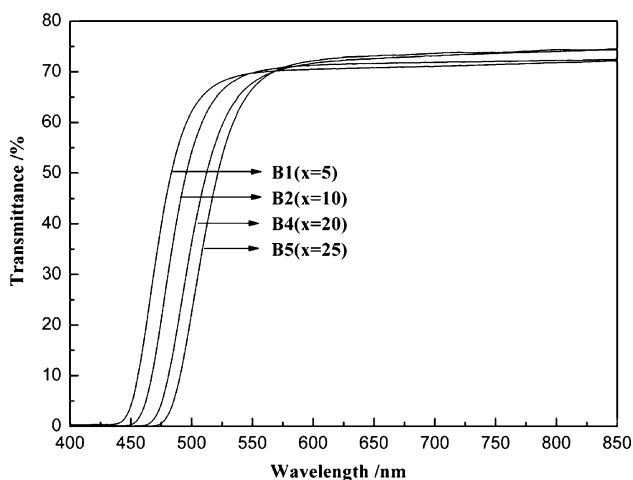


Fig. 3 Vis-NIR transmission spectra of $\text{GeS}_2\text{-Ga}_2\text{S}_3\text{-AgCl}$ glasses on Series 2: $0.8(100-x)\text{ GeS}_2\text{-}0.2(100-x)\text{ Ga}_2\text{S}_3\text{-}x\text{ AgCl}$

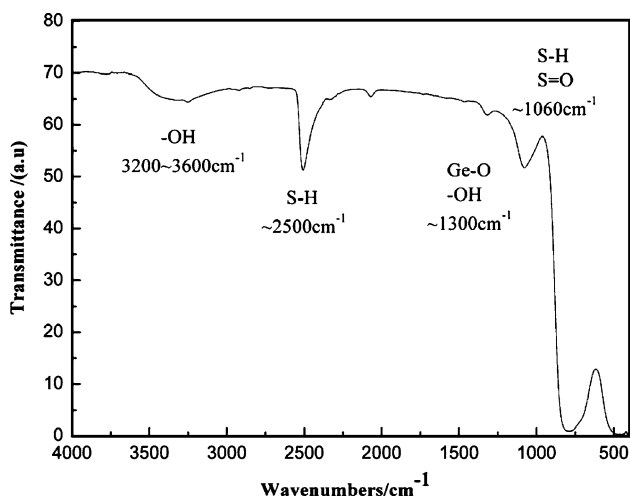


Fig. 4 IR transmission spectrum of the representative $90\text{GeS}_2\text{-}5\text{Ga}_2\text{S}_3\text{-}5\text{AgCl}$ glass

polarizability of Ga^{3+} ions compared with that of Ge^{4+} ions, refractive index should be increased with the addition of Ga_2S_3 . And the Ag^+ ions with larger atomic mass can also result in the augment of refractive index, n . Therefore, the refractive indices are relatively high, which are rather beneficial to the enhancement of optical nonlinear susceptibility and the applications in optoelectronic field.

Physical properties

The evolution of the Vickers microhardness, H_v , of $\text{GeS}_2\text{-Ga}_2\text{S}_3\text{-AgCl}$ glasses on Series 1, 2 and 3 is illustrated in Fig. 6. In this system, the values of H_v are in the range of $190\text{-}300\text{ kg mm}^{-2}$, which have a strong dependence on compositional change. It is obvious that the value of H_v decreases with the addition of AgCl . Cl, which is a non-

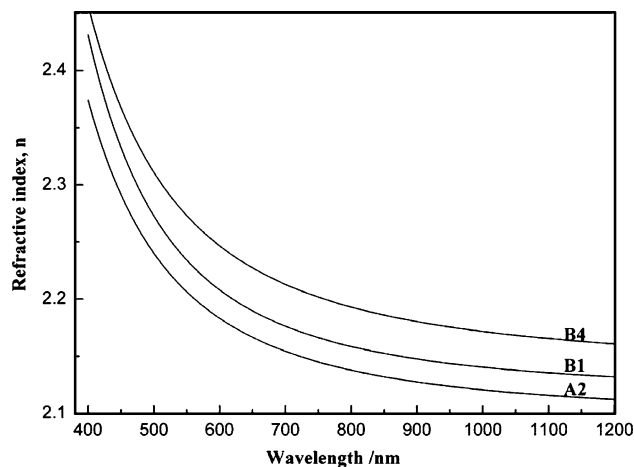


Fig. 5 Refractive index, n collected as a function of wavelength of $\text{GeS}_2\text{-Ga}_2\text{S}_3\text{-AgCl}$ glasses A2 ($80\text{GeS}_2\text{-}10\text{Ga}_2\text{S}_3\text{-}10\text{AgCl}$), B1 ($76\text{GeS}_2\text{-}19\text{Ga}_2\text{S}_3\text{-}5\text{AgCl}$) and B4 ($64\text{GeS}_2\text{-}16\text{Ga}_2\text{S}_3\text{-}20\text{AgCl}$)

bridging atom, plays the role as the glass network terminator and breaks M-S-M ($\text{M}=\text{Ge}$ and Ga) bonds to form M-Cl bonds. Thereby, the addition of AgCl into the system would provide the network terminating Cl and result in the decrease of the dimensionality of structural network. The interruption of the glass network should make the network more opened and decrease the rigidity of the glasses subsequently. However, when the ratio of $\text{AgCl}/\text{Ga}_2\text{S}_3 < 2$, i.e., $(\text{S} + 0.5\text{Cl})/(\text{Ge} + \text{Ga}) < 2$, the substitution of AgCl for Ga_2S_3 could alleviate the shortage of sulfur atoms by providing Cl to form $[\text{Ge}(\text{Ga})\text{S}_{4-x}\text{Cl}_x]$ tetrahedral s.u. instead of $[\text{S}_3\text{Ge}(\text{Ga})\text{-Ge}(\text{Ga})\text{S}_3]$ ethane-like s.u., which would mitigate the opening of structural network. Therefore, the obvious trend that the value of H_v decreased

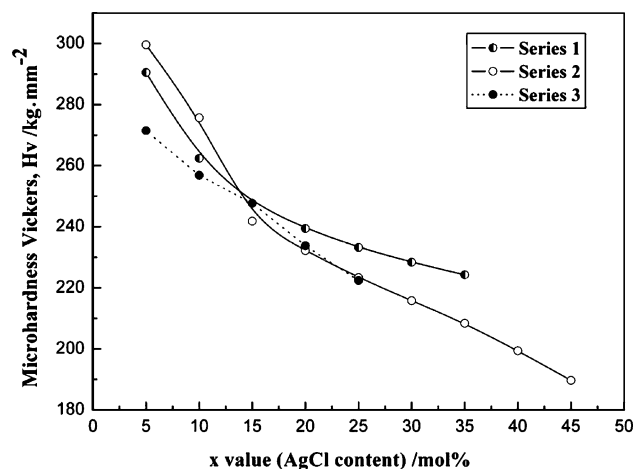


Fig. 6 Vickers microhardness, H_v , of $\text{GeS}_2\text{-Ga}_2\text{S}_3\text{-AgCl}$ glasses plotted as a function of the content of AgCl . Series 1: $(100-2x)\text{ GeS}_2\text{-}x\text{ Ga}_2\text{S}_3\text{-}x\text{ AgCl}$; Series 2: $0.8(100-x)\text{ GeS}_2\text{-}0.2(100-x)\text{ Ga}_2\text{S}_3\text{-}x\text{ AgCl}$; Series 3: $70\text{ GeS}_2\text{-}(30-x)\text{ Ga}_2\text{S}_3\text{-}x\text{ AgCl}$

slowly on Series 3 ($70\text{GeS}_2-(30-x)\text{Ga}_2\text{S}_3-x\text{AgCl}$) when the addition of AgCl less than 20 mol% (i.e., $(\text{S} + 0.5\text{Cl})/(\text{Ge} + \text{Ga}) < 2$), and then it decreased quickly by adding AgCl constantly would be explained successfully. This is due to the fact that the system will be affluent of S(Cl) atoms when the content of AgCl more than 20 mol% (i.e., $(\text{S} + 0.5\text{Cl})/(\text{Ge} + \text{Ga}) > 2$) on Series 3, and thus the mitigating effect on the opening of structural network with the addition of AgCl will vanish.

In addition, the density, ρ of the glasses in the system was also measured with the Archimedes method using CCl_4 as the immersed medium, which shows the values of ρ are in the range of 2.7–3.1 g/cm^3 , increasing with the addition of AgCl due to the large atomic mass of AgCl.

Conclusions

Pseudo-ternary $\text{GeS}_2\text{--Ga}_2\text{S}_3\text{--AgCl}$ chalcogenide glasses are systematically investigated in this work. The relatively large glass-forming region that is mainly situated in the GeS_2 -rich region is reported and the maximum of dissolvable AgCl is unexpectedly up to 65 mol%. The glass-forming ability of most $\text{GeS}_2\text{--Ga}_2\text{S}_3\text{--AgCl}$ glasses is excellent, and it exhibits a complicated evolutionary trend with the addition of AgCl due to the two inverse facets resulted from the addition of AgCl. These glasses have a broad region of transmission from 0.45 μm to 12.5 μm approximately, and the Vickers microhardness of most glasses is larger than 200 kg mm^{-2} . Based on the high thermal stability, relatively broad and high Vis–IR transparency, large refractive index and microhardness of these novel $\text{GeS}_2\text{--Ga}_2\text{S}_3\text{--AgCl}$ chalcogenide glasses, it can be

deduced that it is promising for them to be applied in the optoelectronic field, etc.

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