Preparation and properties of novel GeS₂-Ga(In)₂S₃-CuI chalcohalide glasses

X. ZHENG^{*}, F. CHEN^b, H. TAO, H. GUO^a, C. LIN^b, S. GU, X. ZHAO

Key Laboratory of Silicate Materials Science and Engineering (Wuhan University of Technology), Ministry of Education, China, 122 Luoshi Road, Hongshan District, Wuhan, Hubei 430070, P.R. China. ^aState Key Laboratory of Transient Optics and Photonic, Xi'an Institute of Optics and precision Mechanics, Chinese Academy of Science (CAS), Xi'an, Shanxi 710119, PR China. ^bCollege of Information Science and Engineering, Ningbo University, Ningbo 315211, PR China.

Novel GeS₂-Ga(In)₂S₃-Cul chalcohalide glasses were prepared successfully. These glasses have relatively high glass transition temperatures up to 452 °C but narrow glass-forming region, and a wide range of transmission approximately from 0.50 to 12.5µm. The structural evolvement of the glasses was studied by Raman spectroscopy. Finally, third-order optical nonlinearities were investigated utilizing Z-scan technique at the wavelength of 800nm. Both nonlinear refractive index n_2 and nonlinear absorption coefficient β show an increasing tendency with increasing Cul content or substituting In for Ga, and structural dependency of n_2 has also been discussed. A minimum figure of merit *FOM* = 2.237 was obtained.

(Received January 17, 2011; accepted January 26, 2011)

Keywords: Chalcohalide glasses, Raman spectroscopy, Z-scan, Nonlinear optics

1. Introduction

It is well known that chalcogenide and chalcohalide glasses have wide transparence in the mid-infrared, high optical nonlinearity, strong photosensitivity, and low phonon energies compared with oxide and fluoride glasses. So they received world-wide scientific interests for their great potential application in the area of optoelectronic and photonic devices [1-2]. Recently, Ga-containing GeS₂ based chalcohalide glasses have become one of the predominant candidates for ultra-fast all optical switching and rare-earth doped fiber amplifier applications at the telecommunication wavelength of 1.3µm due to their higher band-gap energy compared with As- and Se-containing chalcogenide glasses [3-4]. In addition, relatively large amounts of metal sulfides [5], metal halides [6] could be dissolved in Ga-containing GeS₂ based glasses, so the glass-forming ability and optoelectronic properties of these glasses could be tailored in a wide range by changing composition of these additives. Based on the similarity of chemical properties of Ga and In, it can be anticipated that In₂S₃-based

chalcohalide glasses could also be promising materials candidates in the above-mentioned fields.

To date, numerous Ga(In)₂S₃-containing GeS₂ based glassy systems have been studied chalcohalide systemically, mainly including GeS₂-Ga(In)₂S₃-MX (M=K, Cs, Ag, Cd, Pb, etc. X=Cl, Br, I) compositions. Among the different alkali or heavy-metal halides incorporated in such glasses, the silver chloride appears as an excellent candidate to adjust the optical properties of the based GeS₂-Ga₂S₃ glasses. Dong et al. [7-8] have demonstrated that high quantity of AgCl could be dissolved in GeS₂-Ga₂S₃ glasses, and obtained prominent optical properties including second- and third-order nonlinearity in GeS₂-Ga₂S₃-AgCl system. Recently, infrared transmitting glass ceramics containing nonlinear optical AgGaGeS₄ crystallites were fabricated by heat-treating of $30GeS_2 \cdot 35Ga_2S_3 \cdot 35AgCl$ chalcohalide glass [9], and intensive second harmonic generation was observed in these glass ceramics. The above results indicate that AgCl-containing chalcohalide glasses are materials candidates very suitable for the next generation of optoelectronic and photonic applications.

Both Cu and Ag belonging to Nobel-metals and Group I B, so GeS_2 -Ga $(In)_2S_3$ -CuX (X = Cl, Br, I) glasses are expected to have similar prominent optoelectronic properties compared with their AgX (X=Cl, Br, I) counterparts. However, to the author's best knowledge, there is little information available in literatures about the research of CuX (X=Cl, Br, I)-containing GeS₂ based chalcohalide glasses. Considering that CuI has best chemical stability in the metal halides of CuX (X=Cl, Br, I), so in the present work, we prepared the pseudo-ternary GeS₂-Ga(In)₂S₃-CuI novel chalcohalide glasses and investigated the glass-forming ability, thermal, physical, and optical properties. Their third-order optical nonlinearities were also studied through Z-Scan technique at the wavelength of 800nm.

2. Experiments

Homogeneous GeS_2 -Ga(In)₂S₃-CuI chalcohalide glasses (hereinafter labeled as GG(In)C) were obtained by conventional melt-quenching technique using high-purity Ge, Ga, In, S (all of 5N) and CuI (3N) as raw materials. The mixtures were reacted in sealed silica ampoules at 1250K for 12h and then quenched in mixed ice water. Details of the preparations were similar to our previous works [10]. The $8 \times 8 \times 1 \text{mm}^3$ glass plates were prepared from the bulk glasses and optically polished for both sides.

Non-crystalline characteristics of the prepared samples were confirmed by X-ray diffraction (XRD, X'pert PRO diffractometer) with Cu K_{α} radiation (40kV, 40mA). The glass transition temperature $T_{\rm g}$ and crystallization temperature $T_{\rm c}$ (onset temperature of crystallization) were determined by differential scanning calorimetry (DSC, Netzesh STA 449C) at a heating rate of 10°C/min with a precision of ±1°C.

Vickers microhardness H_v was measured by a Vickers HX-1000TM/LCD with a 25g load during 20s, and the accuracy is within $\pm 2\%$. Density ρ was calculated based on the accurate measurement of glass size and weight, and the error is about ± 0.05 g/cm³. The compositions and uniformity of the prepared glasses were analyzed by electron probing microanalysis (EPMA, JXA-8800R), and the error is within $\pm 1\%$.

Optical transmission was recorded with a spectrophotometer (Shimadzu UV-1601) in the visible and near-infrared region (Vis-NIR), and a Fourier transform IR spectrometer (Nicolet 60-SXB) in the middle-IR region. Refractive indices n_0 were measured using a Spectro-Ellipsometer (Woollam W-VASE32TM) between 400 and 1300nm wavelength, and the estimated error is ± 0.05 .

Raman spectra were measured at room temperature

using the back (180°) scattering configuration by the micro-Raman spectrometer (Renishaw RM-1000). For the avoidance of local laser damage, a He-Ne laser (λ =632.8nm) with a power less than 10mW was used as an excitation source. The error in the frequencies was ±1 cm⁻¹.

The third-order optical nonlinearities (including nonlinear refractive index n_2 and nonlinear absorption coefficient β) were determined on the bases of Z-scan measurement using pump laser beam of 200fs duration generated from a mode-locked Ti:Sapphire laser (Coherent Mira 900-D) at 800nm, the detailed experimental setup used has already been described in Ref.[11]. The close aperture transmittance of a tightly focus Gaussian beam through a finite aperture S (linear transmission, S=0.05) in the far field was measured as a function of the sample position z with respect to the focal plane, while the open aperture transmittance was obtained after removing the aperture. The estimated error of Z-scan results is within ±15%. All optical measurements above were operated at room temperature. No changes were observed under microscopy between the as-prepared samples and ones after laser irradiation, indicating that no obvious photo-induced phenomena occurred during the optical experiments.

3. Results

3.1. Glass formation, physical and thermal properties

The glass-forming region for the GG(I)C system is not depicted here, because the glasses could be manufactured only when the CuI content was less than 6 mol% and 12mol% for GGC and GIC systems, respectively, and when the quenching was performed into mixed ice water with small quantity of melt (2g). No glasses could be manufactured in GeS₂-CuI or Ga₂S₃-CuI pseudo-binary systems. The non-crystalline samples' colors varied from yellowish-brown to reddish-brown. Compared with the large glass-forming region of GeS₂-Ga₂S₃-AgX (X=Cl, Br, I) system, the glass-forming region of GG(I)C system is very small, this miserable glass-formation ability may due to the way in which Ag and Cu get into the GeS₂-Ga₂S₃ glass matrix and the resultant short-range order differ to a large extent [12-13].

Fig. 1 shows the XRD patterns of some crystallized samples. Along the GeS₂-CuI pseudo-binary system, sample only adding with 5% CuI has the separation of crystalline Cu₂GeS₃. Along the GGC system, sample adding with 7% has the separation of crystalline GeS₂ and

 Cu_2GeS_3 . Along the GIC system, sample adding with 13% has the separation of crystalline GeS_2 and Cu_8GeS_6 . That is to say, CuI plays a role of glass network destructor when introduced into GeS_2 glass. Glasses could be formed when a small content of CuI co-addition with Ga or In into GeS_2 system, however, further addition of CuI will results of the separation of crystallites in GG(I)C system.



Fig.1. XRD patterns of the crystallized samples. Letters a, b and c denote the characteristic peaks of GeS_2 , Cu_2GeS_3 and Cu_8GeS_6 , respectively.

To analyze the compositional dependence of relevant properties in GG(I)C system, among various compositions studied, $92.5\text{GeS}_2 \cdot 5\text{Ga}_2\text{S}_3 \cdot 2.5\text{CuI}$, $90\text{GeS}_2 \cdot 5\text{Ga}_2\text{S}_3 \cdot 5\text{CuI}$, and $90\text{GeS}_2 \cdot 5\text{In}_2\text{S}_3 \cdot 5\text{CuI}$ (all in mol%, hereinafter labeled as GGC2.5, GGC5 and GIC5, respectively) were chosen to be compositions of the samples for the following study. Analytical results obtained from EPMA reveal that the difference between theoretical and real composition of these glasses is within a reasonable range.

The density ρ , Vickers microhardness H_{ν} characteristic temperatures and glass-forming ability of GGC2.5, GGC5 and GIC5 glasses are summarized in Table 1. It is known that the criterion ΔT (the difference between T_c and T_g) and Hruby criterion H_w ($\Delta T/T_g$) are two critical parameters to evaluate the thermal stability of a glass, and glasses with the value of $\Delta T > 100^{\circ}$ C or high value of H_w are usually considered to have good thermal stability and suit for the fiber-drawing. However, the ΔT of GGC2.5, GGC5 and GIC5 are just 58°C, 40°C and 67°C, respectively, all of them below 100°C, and the values of H_w of three samples are relatively small. So the glasses of GG(I)C system have relatively weaker thermal stability, which is consistent with the above-mentioned poor glass-forming ability of GG(I)C system. As shown in Table 1, density ρ increasing with increasing the content of CuI (GGC2.5 \rightarrow GGC5) or substituting In for Ga (GGC5 \rightarrow GIC5), which is due to the larger atomic mass of I and In compared with S and Ga. However, the variation tendency of Vickers microhardness H_v reverses to that of density ρ , which is due to the decreased rigidity of the glass network with increasing addition of CuI or substituting In for Ga, these structural changes will be analyzed in the following Raman spectra.

Sample	ρ (g/cm ³)	H_v (kg/mm ²)	$T_g(^{\circ}C)$	$T_c(^{\circ}C)$	${}^{\vartriangle}T(^{\circ}C)^{a}$	H_w^{b}
GGC2.5	2.752	264.2	452.1	510.1	58	0.128
GGC5	2.811	258.6	441.1	481.1	40	0.091
GIC5	3.009	241.4	408.7	475.7	67	0.164
1	1	1			1	

Table 1. Physical and thermal properties of GG(I)C glass samples.

^a $\triangle T = T_c - T_g$ ^b $H_w = \triangle T / T_g$

3.2. Linear optical properties

Fig. 2 shows the transmission spectra of GGC2.5, GGC5 and GIC5 glasses in the mid-IR range. The absorption bands in the spectra are due to extrinsic impurities, which are result from the surface oxidation of raw material and the hydroxide contamination originated from water during the preparation. The strongest absorption bands at 2520cm⁻¹ and 3200~3650cm⁻¹ are ascribed to S–H, and H₂O impurities, respectively. The absorption band at 1320cm⁻¹ is assigned to Ge–O and S–O impurities. The absorption band at 1130cm⁻¹ is assigned to SO₂ impurities. Efforts should be devoted to removing these impurities which are very harmful to the practical applications in the optoelectronic field. The long-wavelength cut-off edge of these glasses sited near $800 \text{cm}^{-1}(12.5 \mu\text{m})$, which is due to the intrinsic multi-phonon absorption of Ge-S and Ga(In)-S bonds vibration[14], and it does not shift with the compositional variation in GG(I)C system. In addition, as shown in Fig. 2,

the intensity of absorption bands at 2520cm⁻¹ and $3200 \sim 3650$ cm⁻¹ of GIC5 are stronger than those of GGC5, which indicates that the water-resistance property drops when Ga is replaced by In in GG(I)C5 system.



Fig.2. IR transmission and Vis-NIR absorption (inset) spectra of glass samples

The linear optical absorption spectra of GGC2.5, GGC5, and GIC5 glasses in Vis-NIR region are shown in the inset of Fig. 2. It distinctly indicates that almost no absorption exists at the femtosecond laser operated wavelength of 800nm. In the spectra, it is obvious that the visible cutting-off edge of these glasses exhibit a red-shift with increasing addition of CuI or substituting In for Ga, this can be interpreted from polarizability. The short-wavelength absorption edge of the glass is ascribed to the electrical transition between valence bands and conduction bands [15-16]. Due to the higher polarizability of Cu^+ and I⁻ ions compared with Ge^{4+} and S^{2-} ion (GGC2.5 \rightarrow GGC5), and the higher polarizability of In³⁺ ions compared with Ga^{3+} ion (GGC5 \rightarrow GIC5), so required excitation energy of electronic transition is smaller, just showing distinct red shift of short-wavelength absorption cut-off edge.

In the high absorption region (where absorption is associated with interband transitions), the absorption coefficient α can be calculated from observed absorbance data using Beer Lambert's formula: $\alpha = 2.303A/d$, where A is the optical density and d is the thickness of the samples. The absorption coefficient is given by the following

quadratic equation according to the 'non-direct transition' model, which is normally called Tauc laws [17].

$$\alpha(h\nu) = B \frac{(h\nu - E_{opg})^2}{h\nu}$$
(1)

where *B* is a constant depending on the electronic transition probability, *hv* is the photon energy and E_{opg} is the Tauc optical band gap. The values of E_{opg} can be calculated from the $\alpha = 0$ intersects of $(\alpha hv)^{1/2}$ versus *hv* plots (see Fig. 3). The well fitted results indicates that 'non-direct transition' is certainly the mechanism responsible for the strong optical absorption spectra region of the GG(I)C glasses. The calculated E_{opg} of these glasses are listed in Table 2, it is obvious that the optical band gaps decrease when the content of CuI increases or Ga is replaced by In in GG(I)C system, this variation tendency is consistent with that of above-mentioned short-wavelength absorption cut-off edge.

Sample	n_0 (800nm)	$E_{opg}(eV)$	β (10 ⁻¹¹ m/W)	$n_2 (10^{-11} \text{ esu})$	FOM
GGC2.5	2.10	2.39	2.83	0.97	2.334
GGC5	2.12	2.30	6.08	1.32	3.727
GIC5	2.19	2.17	6.57	2.46	2.237

Table 2. Linear and nonlinear optical parameters of GG(I)C glass samples.



Fig.3. The absorption coefficient plotted as $(\alpha hv)^{1/2}$ versus the photon energy (hv) for glass samples.

3.3. Raman spectroscopy

Fig. 4 shows Raman spectra of GGC2.5, GGC5, and GIC5 glasses. The Raman spectra are dominated by a broad band between 250cm^{-1} and 450cm^{-1} that is composed of several overlapping bands. Four main bands (255, 340, 372, 432 cm⁻¹) have been shown in the spectra of all three glasses. The strongest peak at 340 cm⁻¹ is ascribed to the symmetrical stretching vibration (v_1) of [Ge(Ga)S_{4/2}] tetrahedra [18]. The shoulder sited at 372 cm⁻¹ is assigned to the companion (A^c) mode of [GeS_{4/2}] tetrahedra, and the band at around 255 cm⁻¹ is ascribed to the vibration of the [S_{3/2}Ge(Ga)-(Ga)GeS_{3/2}] ethane-like structural units due to the shortage of sulfur [19]. However, the ascription of the band at 432 cm⁻¹ is still controversial till now [19-20].

With increasing addition of CuI or substituting In for Ga in GG(I)C system, two obvious changes in the Raman spectra can be detected. Firstly, from GGC2.5 to GGC5, the peak of band at 255 cm^{-1} shifted slightly to a lower frequency and the intensity of band also enhanced a little. This change can be interpreted as follow: as the Ga₂S₃ contents in GGC2.5 and GGC5 are fixed, so addition of CuI into GeS₂-Ga₂S₃ glasses can provide more Γ to form [Ge(Ga)S_{4-x}I_x] mixed tetrahedral units instead of

 $[S_{3/2}Ge(Ga)-(Ga)GeS_{3/2}]$ ethane-like structural units. Due to the larger atomic mass of I comparing with that of S, the vibration frequency for I mixed tetrahedral units will become lower, which results in the slightly shifts of band towards lower frequency. Secondly, from GGC5 to GIC5, when Ga is replaced by In, there is another obvious shoulder emerged at 300cm⁻¹ in the Raman spectrum of GIC5 glasses. This shoulder is ascribed to the symmetric stretching vibration of $[InS_{4-x}I_x]$ mixed tetrahedral units [21].



Fig.4. Raman spectra of glass samples

Therefore, the structure of GG(I)C glasses can be described as follows: these glasses are mainly composed of $[MS_{4/2}]$ (M=Ge, Ga, In) tetrahedra and $[S_{3/2}M-MS_{3/2}]$ (M=Ge, Ga, In) ethane-like structural units, which form a three-dimensional glassy network through bridging sulfur bonds. The addition of CuI, which plays the role of sulfur compensator, involves the breaking of $[S_{3/2}M-MS_{3/2}]$ (M=Ge, Ga, In) ethane-like structural units to form $[MS_{4-x}I_x]$ (M=Ge, Ga, In) mixed tetrahedral units.

3.4. Third-order nonlinear optical properties

Fig. 5 and 6 show Z-scan signals of GGC2.5, GGC5 and GIC5 samples in the conditions of closed aperture (CA) and open aperture (OA) measurements, respectively. Here, the Z-scan measurements have been carried out at the power density of $I_0 \sim 2.9 \text{GW/cm}^2$ and the beam waist radius of $\omega_0 \sim 20 \mu \text{m}$. The experimental data in the case of CA and OA are fitted by the well-established Equations described below [22]:

$$T = 1 + \frac{4x}{(x^2 + 1)(x^2 + 9)} \Delta \phi_0$$
(2)

$$T = 1 - \frac{1}{\sqrt{2}(x^2 + 1)} \Delta \psi_0$$
(3)

where *x* is the relative distance from the focus point, and $x = z/z_0 = 2z/k\omega_0^2$. *z*, *z*₀, *k* and ω_0 are the distance from the focus point, the Rayleigh range of the light, the wavenumber of the light and the beam waist at the focal plane, respectively. From the fitting curves, we can get the transmittance changes, ΔT_v and ΔT_{p-v} , then the nonlinear absorption β and the nonlinear refractive index n_2 related with the phase changes due to nonlinear absorption ($\Delta \psi_0$) and nonlinear refraction ($\Delta \Phi_0$) are given by:

$$\Delta T_{\rm v} = \Delta \psi_0 = \beta I_0 L_{\rm eff} / 2 \tag{4}$$

$$\Delta T_{p-v} = 0.406(1-S)^{0.25} \left| \Delta \Phi_0 \right|$$
 (5)

$$n_2 = \frac{\lambda \Delta I_{p-\nu}}{0.812\pi (1-S)^{0.25} I_0 L_{eff}}$$
(6)

where *S* is the aperture linear transmittance, and $L_{\text{eff}} = [1 - \exp(-\alpha L)]/\alpha$ is the effective length of the sample with the sample length *L* and the linear absorption coefficient α . The calculated values of β and n_2 of GGC2.5, GGC5 and GIC5 glasses are summarized in Table 2.



Fig.5. Z-scan signals of glass samples in the conditions of close aperture measurement. The solid lines are theoretical fits.



Fig.6. Z-scan signals of glass samples in the conditions of open aperture measurement. The solid lines are theoretical fits.

4. Discussion

As shown in Table 2, both β and n_2 increase from GGC2.5 to GGC5, or from GGC5 to GIC5. This indicates that the addition of CuI or substitute In for Ga in GG(I)C system have positive effects on the values of β and n_2 .

Since the linear absorption spectra of glass samples show intense bands in the 450~550nm region, the main source of nonlinear absorption at wavelength of around 800nm is recognized as two photo absorption (TPA). Aversa [23] had shown that TPA coefficient is related to the ratio of incident photo energy *hv* to E_{opg} . According to KK relation [24], TPA in semiconductors can be enhanced when *hv*/ E_{opg} approach 0.7. The values of *hv*/ E_{opg} for GGC2.5, GGC5 and GIC5 glasses are 0.65, 0.67 and 0.71, respectively. So the values of β increase from GGC2.5 to GGC5 and from GGC5 to GIC5.

According to the semiempirical Miller' rule [25], it is possible to estimate the third-order optical nonlinear susceptibility $\chi^{(3)}$, of a material from the linear refractive index, n_0 ,

$$\chi^{(3)} \propto \left[(n_0^2 - 1)/4\pi \right]^4 \times 10^{-10} \tag{7}$$

From which, a large $\chi^{(3)}$ is expected in glass with large n_0 .

In present case, the values of n_0 of GGC2.5, GGC5 and GIC5 glasses are listed in Table 2. From GGC2.5 to GGC5, the increase of n_0 was due to the larger polarizability of Cu⁺ and I⁻ ions compared with Ge⁴⁺ and S^{2-} ion, and Γ ions with larger atomic mass also result in the augment of n_0 . From GGC5 to GIC5, the increase of n_0 was due to the larger polarizability and atomic mass of In^{3+} ions compared with that of Ga^{3+} ion. The variation tendency of the n_0 is consistent with that of n_2 , which indicates that the Z-scan results in GG(I)C system are following the Miller's rule.

Based on the above-mentioned analysis of Raman spectra, the structural dependence of third-order optical nonlinearities in GG(I)C system could also be deduced. From GGC2.5 to GGC5, with the addition of CuI, part of $[S_{3/2}Ge(Ga)-(Ga)GeS_{3/2}]$ ethane-like structural units transformed to $[Ge(Ga)S_{4-x}I_x]$ mixed tetrahedral units. From GGC5 to GIC5, [GaS_{4-x}I_x] mixed tetrahedral units are replaced by [InS4-xIx] mixed tetrahedral units. This reveals that [MS_{4-x}I_x] (M=Ge, Ga, In) mixed tetrahedral units play an important role in the third-order optical nonlinearities of GG(I)C glasses. Due to the larger atomic radii, mass and electronegativity of In and I compared with Ga and S, [MS_{4-x}I_x] (M=Ge, Ga, In) mixed tetrahedral units with higher hyperpolarizability will induce a larger electron cloud's distortion degree under femtosecond laser irradiation, which make greater contribution to the enhancement of n_2 . In addition, optical and structural properties are drastically changed even by addition of low Cu content into chalcogenide glasses as discussed in Ref. [26]. So the addition of CuI modifier into GeS₂-Ga(In)₂S₃ based glasses might also play an important role on third-order optical nonlinearities intrinsically, which should be studied systematically in the future.

Generally, figure of merit $FOM = 2\beta\lambda/n_2$ is considered to be a criterion to analyze the suitability of a non-linear material for all-optical switching devices, and FOM < 1 is expected. As seen in Table 2, the values of FOM for GGC2.5, GGC5 and GIC5 glasses are larger than 1, which due to the strong nonlinear absorption at wavelength of 800nm. However, previous studies have indicated that the value of FOM is highly dependent on the wavelength of laser and always drop drastically with the wavelength increasing. For example, the value of FOM for As₄₀Se₆₀ glass is 5.3 at 1064nm but only 0.03 at 1430nm [2]. Therefore, FOMs < 1 are expected for GG(I)C chalcohalide glasses at infrared optical telecommunication wavelengths.

5. Conclusion

summary, new chalcohalide glasses in In GeS₂-Ga(In)₂S₃-CuI pseudo-ternary system were prepared and investigated systematically in this work. These glasses have relative broad and high Vis-IR transparency, narrow glass-forming region, large refractive index and microhardness. Their third-order optical nonlinearities were studied using Z-san method with femtosecond laser pulse at the wavelength of 800nm. Both nonlinear refractive index n_2 and nonlinear absorption β increase with increasing CuI content or substituting In for Ga. The structural dependency of β and n_2 of these glasses reveals that [MS_{4-x}I_x] (M=Ge, Ga, In) mixed tetrahedral units which possess high hyperpolarizability may do great contribution to the enhancement of third-order optical nonlinearities. These results suggest a potential application of the present CuI-containing chalcohalide glasses in the infrared optoelectronic and photonic field, such as all-optical switching devices.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (NSFC, No. 51032005, 60807034, 60907039 and 60808024), the Fundamental Research Funds for the Central Universities (Wuhan University of Technology), the Natural Science Foundation of Hubei province (2010CDB00601), the Opening Research Fund of State Key Laboratory of Transient Optics and Photonics, and the "Hundreds of Talents Programs" from the Chinese Academy of Sciences.

References

- K. Tanaka, Curr. Opin. Solid State Mater. Sci. 1, 567 (1996).
- [2] C. Quemard, F. Smektala, V. Couderc, A. Barthélémy, J. Lucas, J. Phys. Chem. Solids 62, 1435 (2001).
- [3] X. F. Wang, S. X. Gu, J. G. Yu, C. L. Liu, X. J. Zhao, H. Z.Tao, Mater. Chem. Phys. 83, 284 (2004).
- [4] K. Ogusu, J. Yamasaki, S. Maeda, M. Kitao, M. Minakata, Opt. Lett. 29, 265 (2004).

- [5] X. F. Wang, S. X. Gu, J. G. Yu, X. J. Zhao, H. Z. Tao, Solid State Commun. **130**, 459 (2004).
- [6] H.Z. Tao, X.J. Zhao, C.B. Jing, Solid State Commun. 133, 327 (2005).
- [7] G.P. Dong, H.Z. Tao, X.D. Xiao, C.G. Lin, X.J. Zhao, J. Mater. Sci. 42, 9632 (2007).
- [8] G.P. Dong, H.Z. Tao, X.D. Xiao, C.G. Lin, Y.Q. Gong, X.J. Zhao, S.S. Chu, S.F. Wang, Q.H. Gong, Opt. Express 15, 2398 (2007).
- [9] X.L. Zheng, H.Z. Tao, C.G. Lin, S.X. Gu, G.P. Dong, X.J. Zhao, Opt. Mater. 31, 1434 (2009).
- [10] H.Z. Tao, X.J. Zhao, C.B. Jing, J. Mol. Struct. 697, 23 (2004).
- [11] Y.F. Chen, Q.H. Nie, T.F. Xu, S.X. Dai, X.S. Wang, X. Shen, J. Non-Cryst. Solids 354, 3468 (2008).
- [12] K. Ramesh, S. Asokan, K.S. Sangunni, E.S.R. Gopal, J. Phys. Chem. Solids 61, 95 (2000).
- [13] X.J. Zhao, L.Y. Xu, H.B. Yin, S. Sakka, J. Non-Cryst. Solids 167, 70 (1994).
- [14] B. Frumarova, V. Smrcka, J. Oswald, P. Krecmer, M. Frumar, V. Cerny, Opt. Mater. 6, 217 (1996).
- [15] G. Tang, Z.Y. Yang, L. Luo, W. Chen, J. Alloy. Compd. 459, 472 (2008).

- [16] C.M. Liu, G. Tang, L. Luo, W. Chen, J. Alloy. Compd. 474, 468 (2009).
- [17] J. Tauc, Amorphous and Liquid Semiconductors, Plenum Press, New York (1974).
- [18] G. Lucovsky, F.L. Galeener, R.C. Kezer, R.H. Geils, H.A. Six, Phys. Rev. B 10, 5134 (1974).
- [19] J. Heo, M.Y. Joong, S.Y. Ryou, J. Non-Cryst. Solids 238, 115 (1998).
- [20] J.E. Griffiths, J.C. Phillips, G.P. Espinosa, J.P. Remeika, Phys. Rev. B 26, 3499 (1982).
- [21] H.Z. Tao, S. Mao, G.P. Dong, H. Xiao, X.J. Zhao, Solid State Commun.137, 408 (2006).
- [22] M. Sheik-Bahae, A.A. Said, T.H. Wei, D.J. Hagan, E.W. Van Stryland, IEEE J. Quantum Electron. 26, 760 (1990).
- [23] C. Aversa, J.E. Sipe, M. Sheik-Bahae, E.W. Van Stryland, Phys. Rev. B 50, 18073 (1994).
- [24] K. Tanaka, J. Non-Cryst. Solids 534, 338 (2004).
- [25] R.C. Miller, Appl. Phys. Lett. 5, 17 (1964).
- [26] K. Ogusu, S. Maeda, M. Kitao, H. Li, M. Minakata, J. Non-Cryst. Solids 347, 159 (2004).

*Corresponding authors: zhengxl0615@hotmail.com