

Freely adjusted properties in Ge–S based chalcogenide glasses with iodine incorporation

Minming Zhu, Xunsi Wang, Chen Jiang, Huijuan Xu, Qihua Nie, Peiquan Zhang, Shixun Dai, Xiang Shen, Tiefeng Xu, Guangming Tao, et al.

► **To cite this version:**

Minming Zhu, Xunsi Wang, Chen Jiang, Huijuan Xu, Qihua Nie, et al.. Freely adjusted properties in Ge–S based chalcogenide glasses with iodine incorporation. *Infrared Physics and Technology*, Elsevier, 2015, 69, pp.118–122. 10.1016/j.infrared.2015.01.015 . hal-01220891

HAL Id: hal-01220891

<https://hal-univ-rennes1.archives-ouvertes.fr/hal-01220891>

Submitted on 4 Nov 2015

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

1 Freely Adjusted Properties in Ge-S based Chalcogenide 2 Glasses with Iodine Incorporation

3 Minming Zhu^a, Xunsi Wang^{a,*}, Chen Jiang^a, Huijuan Xu^a, Qihua Nie^a, Peiquan Zhang^a,
4 Shixun Dai^a, Xiang Shen^a, Tiefeng Xu^a, Guangming Tao^b, and Xianghua Zhang^c

5 ^aLaboratory of Infrared Material and Devices, Ningbo University, Ningbo, Zhejiang 315211,
6 China

7 ^bCREOL, The College of Optics & Photonics, University of Central Florida, Orlando, FL 32816
8 United State

9 ^cLaboratory of Glasses and Ceramics, UMR 6226 CNRS-University of Rennes 1, Rennes Cedex
10 135042, France

11
12 **Abstract:** In this study, we examined the function of halogen iodine acting as a glass network
13 modifier in green chalcogenide glasses based on the Ge-S system. We obtained a series of Ge-S-I
14 glasses and determined their glass-forming region. We then recorded the physical, thermal, and
15 optical properties and studied the effect of halogen iodine on Ge-S-I glasses. Results show that
16 these glasses have relatively wide optical transmission window for infrared (IR) applications.
17 The softening temperature of Ge-S-I glasses varies from 210.54°C to 321.63°C, this temperature
18 fits well with some kinds of high-temperature polymers, such as PES and PEI, the polymers
19 serve as protective layers with high strength and flexibility, thus simplifying the fabrication
20 processes of IR chalcogenide glass fiber. Finally, we performed a purification process to
21 eliminate impurities and to improve optical spectra.

22 **Key words:** Chalcogenide glass; Purification; Optical fiber.

23

24 1. Introduction

25 Halide and chalcogenide glasses have attracted considerable attention as potential candidates
26 for material transmission in the mid-infrared (IR) region [1-3]. Halide glasses have ultra-low loss
27 in mid-IR but have poor chemical resistance [4]. Chalcogenide glasses have high transition
28 temperature (T_g), as well as good chemical and thermal stability. However, high optical
29 transmission loss limited the application of chalcogenide glasses in long-distance fiber
30 communication or fiber sensing because of several intrinsic defects in their net-structure [5].
31 Therefore, a type of chalcogen halide glass (CHG) with the integrated advantages of low-loss halide
32 glass fiber, high chemical stability, and good anticrystallization was developed. CHG can
33 enhance the compactness of the glass network, improve glass anticrystallization, and
34 significantly increase glass-forming capability. Moreover, halogen or halide with low melting
35 temperature and low refractive index can be introduced into chalcogenide glasses to improve the
36 glass and optical spectra properties [4]. Numerous studies have reported on the advantages of
37 CHGs [4, 6-8], particularly rare earth-doped CHGs. However, few studies have been conducted
38 on the CHG fiber and its fabrication processes.

39 Arsenic sulfide has outstanding properties in terms of fiber drawing feasibility but is
40 environmentally toxic. Ge-S glass is good for the environment, has high chemical and
41 mechanical stability, and is easy to prepare with high purity [9]. Ge-S has a strong crystallization
42 tendency. In addition, As_2Se_3 and As_2S_3 glasses are suitable for polyethersulfone or
43 polyetherimide [10]. However, high-temperature polymers that fit chalcogenide glasses are
44 difficult to find, especially for Ge-S based glasses, because of their relatively high T_g . We

45 prepared Ge-S based CHGs with halogen iodine to fabricate low-loss CHG fiber. We then
46 investigated the effect of halogen on the chemical, physical, thermal, and optical properties of
47 CHGs in Ge-S-I systems in detail.

48 A wide range of unique devices have been developed with the use of a special optical fiber
49 or through the same fiber-forming strategy of combining multiple materials with disparate
50 optical, electronic, and thermomechanical properties monolithically. These methods suggest new
51 ways to leverage the fiber drawing process as a fabrication methodology[11]. This method
52 includes the investigation of the nonlinear characteristics of a new class of robust, multimaterial,
53 and all-solid chalcogenide nanotapers prepared from high-index-contrast chalcogenide fibers.
54 Another step is the generation of the IR super continuum extending over more than one octave of
55 bandwidth, produced in a single spatial mode from a robust, compact, and composite
56 chalcogenide glass nanotaper and zero-GVD, high-index contrast, all-solid CHG fibers for IR
57 nonlinear fiber optics. The process of rolling and covering glasses with high-strength polymer
58 strengthens fragile CHG glass fibers. Glass and polymer stick together tightly under a
59 high-temperature and vacuum environment, thereby removing water in the process. Hence,
60 additional work has to be performed to decrease the glass softening temperature (T_p) to fit
61 high-strength polymer. This process provides protection for the fiber and increases the feasibility
62 of CHG fiber fabrication.

63 2. Experimental

64 Bulk glasses were prepared by using a traditional melt-quenching method. Elemental raw

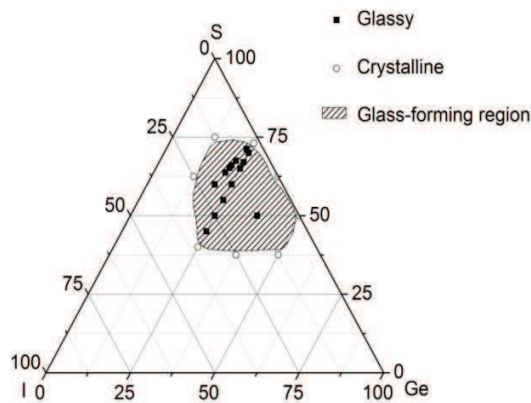
65 materials of high-purity Ge and S(99.99%) and I(99.9%) were carefully weighed and transferred
66 into quartz ampoules that were then sealed under a vacuum of air pressure (2×10^{-3} Pa). The
67 investigated compositions in this glass system are as follows: series A, $\text{Ge}_{25}\text{S}_{75-x}\text{I}_x$
68 ($x=2,5,8,10,15,20,25,30$); series B, $(\text{GeS}_3)_{100-x}\text{I}_x$ ($x=5,10,12,13,15,20$). Iodine is volatile at room
69 temperature. Hence, the materials in the ampoules should be cooled by liquid nitrogen during the
70 vacuum evacuation process. The quartz ampoules containing the raw materials were heated
71 slowly in a rocking furnace to 800°C at a rate of 5Kmin^{-1} and maintained at this temperature for
72 24h. Then the ampoules were quenched in water and swiftly moved to a preheated furnace to
73 anneal at 10°C below T_g for 4h to minimize inner tension. Glass rods were taken from the
74 ampoules, cut into disks, and then polished for testing. The melting and fabricating conditions
75 are nearly the same, and all of the samples were processed into 2mm with precise polishing.

76 All optical tests were conducted at room temperature. Densities were measured according to
77 the Archimedes principle, and the accuracy was $\pm 0.001\text{ g/cm}^3$. T_g and T_p were determined in the
78 temperature range of 40°C to 450°C at a heating speed of 4°C/min using Netzsch DIL402
79 thermal dilatometer, and the accuracy was $\pm 1.0^\circ\text{C}$. The visible absorption spectra of glass
80 samples were recorded in the range of 400nm to 2500nm using Perkin-Elmer Lambda 950
81 UV-Vis-NIR spectrophotometer. The IR transmission spectra of glass samples were obtained in
82 the range of 4000cm^{-1} to 400 cm^{-1} using the Nicolet 380 Fourier Infrared spectrophotometer.
83 SAIRON SPA4000 Prism coupling instrument was used to measure the refractive index of the
84 glasses.

85

86 **3. Results and discussions**87 *3.1 Glass-forming region*

88 On the basis of the two glass-forming regions (GFRs) of Ge-S_{1.31-1.50} and Ge-S_{2.0-9.0} in the
 89 Ge-S binary system of Kawamoto and Tsuchihashi[12], we obtained an expanded ternary GFR
 90 of the Ge-S-I system by quenching a series of 8g melts in water (**Fig.1**). The results show a
 91 limited but detailed distribution of GFR in the Ge-S-I system. Iodine was added as a substitute
 92 for sulfur. Therefore, some of the bridging sulfur chains are released and self-polymerized to
 93 form S₈ rings[7]. Ge₂₅S_{75-x}I_x glasses are formed together stability. The GFR also presents the
 94 states of anticrystallization while iodine content is 2 and 30. Meanwhile, an optimized
 95 glass-forming line is found in the GFR with good glass stability and anti-hygroscopicity, as
 96 shown in glass series B [(GeS₃)_{100-x}I_x].

97
98 **Fig.1** GFR in the Ge-S-I ternary99 *3.2 Physical properties*

100 **Table 1** lists the components and physical properties of the analyzed glass samples. The

101 measured density(ρ) of the glasses increases linearly as the iodine content in series A and B
 102 increases. The observed density increase in both systems is primarily attributed to the large
 103 difference in atomic mass between sulfur and iodine. An increase in total mass by the
 104 substitution of relatively light sulfur atoms with heavy halogen atoms results in a variation of the
 105 dominant glass network structure. The atomic weights of Ge, S, and I are 72.6, 32, and 127,
 106 respectively. Thus, the increase in iodine content is responsible for the increase in glass density.
 107 The density of a given composition can be calculated by using the following formula:

$$\rho = \sum_i M_i / V_m \quad (1)$$

108 Where M_i denotes the molar mass of the glass, $M_i = C_i A_i$ (C_i is the molar concentration, and A_i is
 109 the molecular weight of the component).

111 **Table 1** Physical and thermal properties of Ge-S-I glasses

Composition	n , 632.8nm	n , 1310nm	n , 1550nm	T_g (°C)	T_p (°C)	ρ (g/cm ³)
(GeS ₃) ₉₅ I ₅	2.0891	2.0186	2.0122	250.23	321.63	2.7616
(GeS ₃) ₉₀ I ₁₀	2.0782	2.0071	2.0066	208.82	269.05	2.9317
(GeS ₃) ₈₈ I ₁₂	2.0752	2.0046	2.0034	195.24	277.34	3.0193
(GeS ₃) ₈₇ I ₁₃	2.0690	1.9962	1.9864	178.63	246.46	3.0852
(GeS ₃) ₈₅ I ₁₅	2.0630	1.9898	1.9791	166.62	221.14	3.2003
(GeS ₃) ₈₀ I ₂₀	2.0494	1.9685	1.9604	141.35	204.13	3.4325
Ge ₂₅ S ₇₀ I ₅	2.0911	2.0891	2.0814	285.53	337.25	2.8139
Ge ₂₅ S ₆₇ I ₈	2.0826	2.0630	2.0593	245.53	300.01	2.9547
Ge ₂₅ S ₆₅ I ₁₀	2.0785	2.0586	2.0541	220.21	271.23	3.0021
Ge ₂₅ S ₆₀ I ₁₅	2.0653	2.0332	2.0251	196.62	256.36	3.2519
Ge ₂₅ S ₅₅ I ₂₀	2.0561	1.9875	1.9805	183.99	235.73	3.3538
Ge ₂₅ S ₅₀ I ₂₅	2.0484	1.9772	1.9770	179.78	210.54	3.5466

112 3.3 Thermal properties

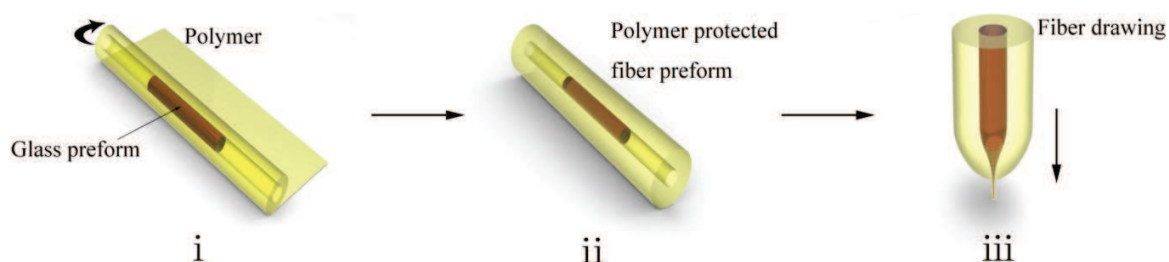
113 We investigated the thermal characteristics of glass samples by using a thermal dilatometer.

114 **Table 1** lists the T_g and T_p values. We observed and recorded two main trends according to series

115 A and B. All glasses were found to exhibit a single glass transition and a single crystallization
116 peak, which exhibited good unit in coordination with the chemically bonded phases of Ge, S, and
117 I in terms of synthesizing glass. The addition of iodine decreased T_g for all glass systems. Thus,
118 T_g and T_p gradually decreased as iodine increased because of the low melting point of halogen
119 iodine.

120 Iodine ions have the effect of terminating the network, decreasing the average bond strength
121 in the glasses. The amount of bridging sulfur would reduce because of the formation of new Ge-I
122 bonds, and the amorphous network would start to lose its three-dimensional connectivity. A
123 larger number of substitutions occurred as more iodine was eventually added. This result gave
124 rise to a novel form of chain-structured[6] glass network and improved glass thermostability.
125 Therefore, the physical and chemical properties of the glasses are determined by the rate of Ge-S,
126 and the glass-forming capability is based on the iodine content of in Ge-S-I glasses.

127 The free adjustment of T_g and T_p with iodine incorporation provides facilitates the
128 exploration of high-strength chalcogenide glass fibers with a protective polymer jacket. **Table 2**
129 presents a series of Ge-S-I glasses that fits commercial polymers. The chalcogenide glass fiber is
130 easily prepared and has an extended application because it is protected by a matching
131 high-strength polymer. **Fig.2** shows the polymer rolling and fiber drawing processes, and Refs.
132 [10, 13] discuss the details.



133

134 **Fig.2** Main processes for the fabrication of polymer-protected fiber preform and fiber drawing135 **Table 2** Thermal properties of glasses with matching polymers

Polymer	Temperature (°C)	Matched glasses
Polyimide(PI)	250–340(T_g)	$\text{Ge}_{25}\text{S}_{67}\text{I}_8, (\text{GeS}_3)_{95}\text{I}_5$
Polyethersulfone(PES)	225(T_g)	$\text{Ge}_{25}\text{S}_{65}\text{I}_{10}$
Polyetherimide(PEI)	217(T_g)	$\text{Ge}_{25}\text{S}_{65}\text{I}_{10}$
Polysulfone(PSU)	190(T_g)	$(\text{GeS}_3)_{88}\text{I}_{12}, \text{Ge}_{25}\text{S}_{60}\text{I}_{15}$
Poly(etherketone) (PEK)	162(T_g)	$(\text{GeS}_3)_{85}\text{I}_{15}$
Polycarbonate(PC)	150(T_g)	$(\text{GeS}_3)_{80}\text{I}_{20}$
Polyetheretherketone (PEEK)	148(T_g)	$(\text{GeS}_3)_{80}\text{I}_{20}$
PTFE	332(T_p)	$(\text{GeS}_3)_{95}\text{I}_5$
cPTFE	316(T_p)	$(\text{GeS}_3)_{95}\text{I}_5$
FEP	270(T_p)	$(\text{GeS}_3)_{88}\text{I}_{12}, \text{Ge}_{25}\text{S}_{65}\text{I}_{10}$
PFA	306(T_p)	$\text{Ge}_{25}\text{S}_{67}\text{I}_8$
ETFE	257(T_p)	$\text{Ge}_{25}\text{S}_{60}\text{I}_{15}$
PVDF	177(T_p)	—
PVF	196(T_p)	$(\text{GeS}_3)_{80}\text{I}_{20}$
Cyclic olefin copolymer (COC)	70–155(T_g)	$(\text{GeS}_3)_{80}\text{I}_{20}$

136

137

138 **3.4 Refractive index**

139 The refractive index of glasses is measured using SPA4000 Prism coupling instrument at

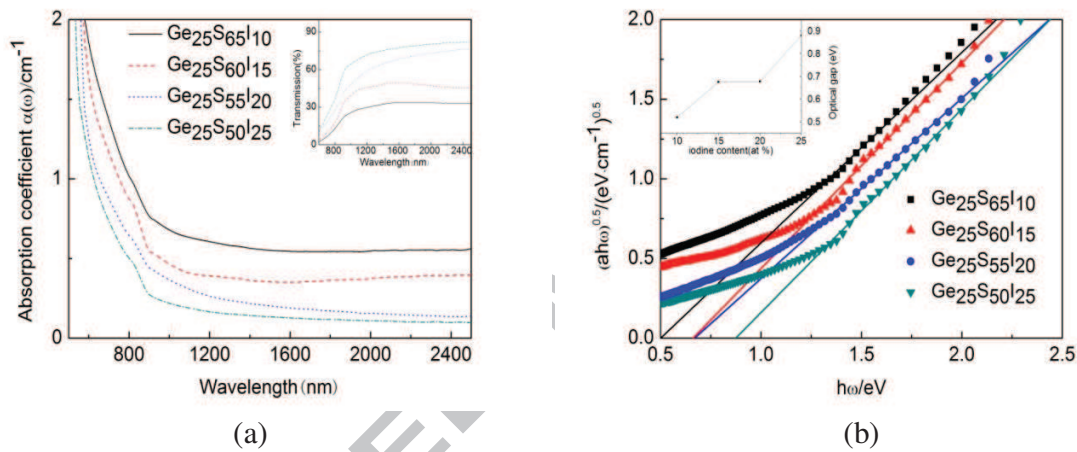
140 632.8, 1310, and 1550nm. The refractive index n is generally determined by the ionic

141 polarization and the density of the glass. Ionic polarization occurs as light is transmitted through

142 the glass. Such transmission consequently affects the speed of light, which determines the

143 refractive index of the glasses. The refractive index of the glasses decreases as iodine atoms are
 144 added into the Ge-S systems. This effect decreases glass network connectivity because of the
 145 incorporation of network-terminating iodine atoms[14, 15], which weaken the average bond
 146 strength of the glasses. In addition, the density of glass affects the refractive index. The glass
 147 refractive index gradually decreases as iodine under a same type of glass host increases.

148 3.5 Vis-NIR absorption edges and optical band gap



149
 150 (a) Near-IR absorption spectra of the Ge-S-I glass samples. (b) Relationship between
 151 $ah\omega^{0.5}$ and $h\omega$ for glass samples; upper-left inset shows the relationship between indirect optic
 152 gap E_{opt} and iodine content.

154 **Fig.3(a)** illustrates the Vis-NIR absorption spectra for the glasses with different iodine
 155 contents. **Fig.3(a)** insert shows the dependence of short-wave cutoff edge (λ_{vis}) on heavy metal
 156 halide content for $Ge_{25}S_{75-x}I_x$ glasses. λ_{vis} gradually shifts to a shorter wavelength as iodine
 157 increases. Some sulfur ions at the end of the Ge-S netchain are replaced by iodine ions. A higher
 158 excitation energy of light is needed for a stronger binding energy between cation and anion ions.
 159 Hence, the optical cut off edge is shorter. Iodine can cause the lower sideband of the valance

160 band to drift directly toward a lower energy band because it is negatively charged and
 161 electrophilic. **Table 3** shows that the optical band gap energy increases as iodine content
 162 increases although the conduct band changes insignificantly.

163

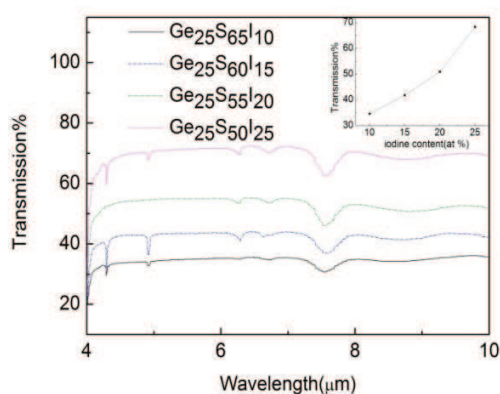
164 **Table 3** Indirect optical gap and IR transmission of $\text{Ge}_{25}\text{S}_{75-x}\text{I}_x$ glasses

Glasses	Indirect optical gap(eV)	Transmission(%) at $9\mu\text{m}$
$\text{Ge}_{25}\text{S}_{65}\text{I}_{10}$	0.520	34.36
$\text{Ge}_{25}\text{S}_{60}\text{I}_{15}$	0.676	41.95
$\text{Ge}_{25}\text{S}_{55}\text{I}_{20}$	0.678	50.07
$\text{Ge}_{25}\text{S}_{50}\text{I}_{25}$	0.880	68.08

165 *3.6 IR optical transmission*

166 **Fig.4** shows the IR transmission spectra of some typical glass samples. These samples have
 167 excellent transparency in the IR region wavelength. The IR transmittance ratio changes
 168 considerably as the iodine content varies. The phonon energy depends on the strength of the
 169 chemical bond and the weight of the atoms. Iodine can open the structure of $\text{Ge}_{25}\text{S}_{75-x}\text{I}_x$ glasses.
 170 Hence, the highest transmission ratio can be achieved with the $\text{Ge}_{25}\text{S}_{50}\text{I}_{25}$ composition. The
 171 decrease in refractive index can slightly improve the transmission ratio. However, Fig.4 shows
 172 that other reasons, such as the effect of reflection, scatter, absorption, and other factors in IR
 173 transmission, should be present. The most important reason may be the improvement of the glass
 174 network with iodine, which serves as an adjuster to decrease the defect of glass network and to
 175 cut down the value of the weak absorption tail of glass gradually. The available transmission IR
 176 cut off waveleng this generally determined by the molecular vibrational spectroscopy of glass
 177 network formers, which is called glass phonon energy. Owing to the glass network former[16] of

178 Ge-S and the addition of iodine (some sulfur is partly replaced by iodine), glass network
 179 connectivity is significantly strengthened. Thus, optical transparency is improved while keeping
 180 a nearly similar IR cutoff wavelength under nearly the same phonon energy.

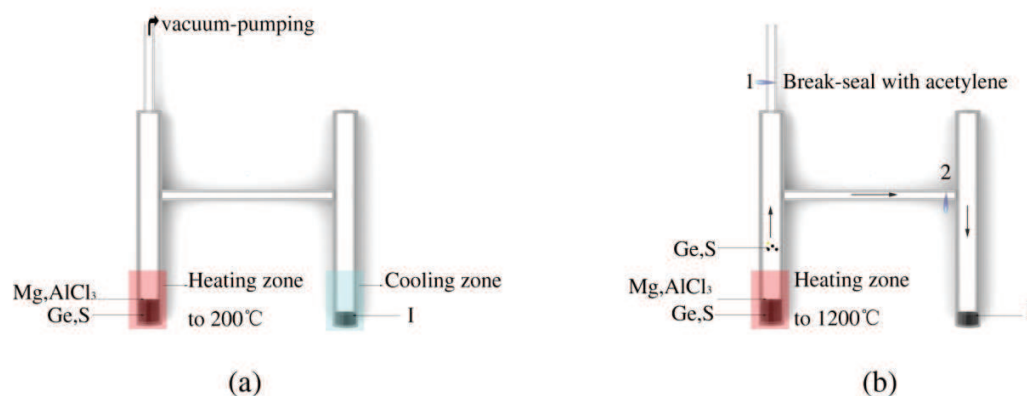


181
 182

183 **Fig.4** IR transmission spectra of some Ge-S-I glasses

184 We performed an additional purification process to improve the quality of glass $\text{Ge}_{25}\text{S}_{60}\text{I}_{15}$.
 185 We heated the selected glass composition and its raw materials at to 200°C to be under an
 186 evacuated vacuum condition to remove reduced water, as shown in **Fig.5(a)**. Ge and S, Mg, or
 187 AlCl_3 were all placed into the left quartz tube to remove impurities, where as I was placed in the
 188 right quartz tube under liquid N_2 cooling during the vacuum evacuation process. The middle of
 189 the quartz tube was welded using anoxy-acetylene flamer and formed an H-shaped silica vessel
 190 after the raw materials transferred into the quartz tube. Then the H-shaped tube was sealed under
 191 a vacuum of $2 \times 10^{-3} \text{Pa}$ at the point of 1, as shown in **Fig.5(b)**. The left quartz tube was heated to
 192 1200°C with a fast-heating furnace. The raw materials of Ge and S or glasses were distilled into
 193 the right quartz tube gradually with the help of high temperature. Oxide and other particles
 194 remained in the left tube, and then the tube was sealed by oxy-acetylene flamer at point 2, as

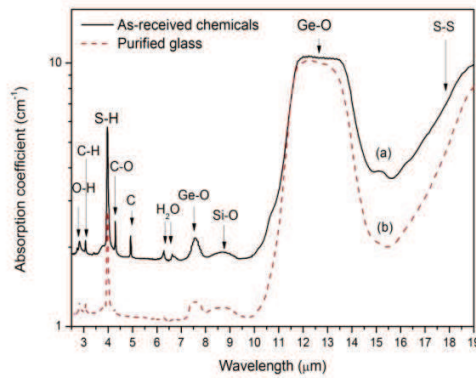
195 shown in **Fig.5(b)**. Finally, the quartz tube was heated slowly at 800°C in a rocking furnace at a
 196 rate of 5Kmin⁻¹, as mentioned previously.



198 **Fig.5** Purification processes of Ge-S-I glasses:(a) evacuation process and(b) seal and purification
 199 processes

200 **Fig.6** shows the comparisons between the bulk glass synthesized with as-received chemicals
 201 and the purified glass. **Table 4** shows that impurity losses attributed to the fundamental H-S
 202 vibrational band (3.96 μ m)[17], H-S combinational bands(3.78 μ m)[18], and carbon impurity
 203 (4.92 μ m)[18] are noticeable in the low purity glass. **Fig.6(b)** shows that impurity-related
 204 vibrational H₂O (6.32 μ m) and C absorption bands (4.92 μ m)are eliminated effectively by using
 205 purified chemicals because the raw materials in the process of vacuum evacuation can not be
 206 heated because of the volatility of iodine[19]. Moreover, the absorption peak of S-H, Ge-H, and
 207 Ge-O has a clear improvement. The absorbance coefficients of S-H, Ge-H, and Ge-O are lower
 208 (more transparent) than that of the original. This method can compensate for the shortage of
 209 liquid N₂ during the cooling condition in the vacuum evacuation process. This method will also
 210 keep all the extracted water as solid ice mixed with glass raw material. However, more

211 purification processes are needed to remove other impurities as well as the unbound water of the
 212 glass. Multiple distillations of the chemicals are also necessary to reduce the extrinsic scattering
 213 centers and to absorb impurities further. Therefore, this method provides a high probability for
 214 the fabrication of high-purity chalcogenide optical glass or fiber.



215
 216 **Fig.6** Absorbance coefficient plot for (a) glass $\text{Ge}_{25}\text{S}_{60}\text{I}_{15}$ made from as-received chemicals and (b)
 217 glass $\text{Ge}_{25}\text{S}_{60}\text{I}_{15}$ made from partially purified chemicals with 500ppm Mg as an oxide scavenging
 218 agent.

219 **Table 4** Extrinsic absorption bands of selected oxides and hydride impurities

Impurities	Absorption wavelength(μm)	Reference
O-H	3.06m, 2.82m	[18]
H ₂ O	6.62w, 6.28m	[18]
S-H	3.96vs, 3.78m	[17]
Si-O	8.7m	Fundamental
Ge-O	12.5vs	Fundamental[20]
Ge-O	7.5s	Over stone
C	4.92s	[18]
C-O	4.29s	[18]
C-H	3.07m	[18]
S-S	19sh	Multi-phonon absorption

220 Intensity of absorption bands: vs,very strong; s,strong; m,middle; w,weak; sh,absorption shoulder.

221

222 4. Conclusions

223 In this study, we prepared a series of Ge-S-I CHGs and investigated some key properties.

224 Density increases while T_g , T_p , and refractive index n decrease gradually as iodine increases. The

225 short wavelength of λ_{vis} shifts to shorter wavelength gradually as the halogen content increases

226 for $Ge_{25}S_{75-x}I_x$ glasses. Iodine can open the structure of Ge-S, and $Ge_{25}S_{50}I_{25}$ has the highest

227 transmission. The indirect optical gap and the cut off edge at $9\mu m$ increase as iodine increases

228 from 10 to 25 for the $Ge_{25}S_{75-x}I_x$ glasses. These glasses have excellent transmission property in

229 the IR region and possess great potential for future IR application. Moreover, a purification

230 process was verified to eliminate the impurities effectively, particularly the unbound water and

231 carbon particles of the glass. All this work significantly improved optical transmission. Owing to

232 the freely adjusted thermal properties with the addition of iodine, commercial polymer can be

233 adopted to protect chalcogenide glass-based fibers effectively because of the perfect suitability of

234 these materials.

235

236 Acknowledgments

237 This work was financially supported by the National Program on Key Basic Research Project

238 (973 Program) (Grant No. 2012CB722703), the Natural Science Foundation of China (Grant Nos.

239 61377099 and 61177087), the Scientific Research Fund of Zhejiang Provincial Education

240 Department (R1101263), the Natural Science Foundation of Ningbo (Grant No. 2013A610118),

241 the Teaching and Research Award Program for Outstanding Young Teachers in Higher Education
242 Institutions of MOE, PRC, the Ningbo optoelectronic materials and devices creative team
243 (2009B21007), the Scientific Research Foundation of Graduate School of Ningbo University,
244 and the K. C. Wong Magna Fund in Ningbo University.

245

246 **References and links**

247 1. R. M. Almeida and J. D. Mackenzie, "The effects of oxide impurities on the optical properties
248 of fluoride glasses," *Journal of Non-Crystalline Solids* **56**(1), 63-68 (1983).

249 2. M. G. Drexhage, M. Tomozawa, and R. Doremus, *Treatise on materials science and
250 technology, Vol (26)* Academic Press, New York, 1985).

251 3. M. Poulain, "Halide glasses," *Journal of Non-Crystalline Solids* **56**(1), 1-14 (1983).

252 4. J. Sanghera, J. Heo, and J. Mackenzie, "Chalcohalide glasses," *Journal of non-crystalline
253 solids* **103**(2), 155-178 (1988).

254 5. D. Lezal, J. Pedlikova, and J. Zavadil, "Chalcogenide glasses for optical and photonics
255 applications," *J. Optoelectron. Adv. Mater* **6**(133-137 (2004).

256 6. J. Heo and J. D. Mackenzie, "Chalcohalide glasses: I. Synthesis and properties of Ge-S-Br and
257 Ge-S-I glasses," *Journal of non-crystalline solids* **111**(1), 29-35 (1989).

258 7. J. Heo and J. D. Mackenzie, "Chalcohalide glasses: II. Vibrational spectra of G- S-Br glasses,"
259 *Journal of non-crystalline solids* **113**(1), 1-13 (1989).

260 8. A. Kut'in, A. Plekhovich, A. Vel'muzhov, and M. Churbanov, "Chemical and physical
261 transformations in Ge-SI glass preparation," *Inorganic Materials* **48**(4), 428-432 (2012).

- 262 9. J. Kirchhof, J. Kobelke, M. Scheffler, and A. Schwuchow, "As-S based materials and fibres
263 towards efficient 1.3 μm fibre amplification," *Electronics Letters* **32**(13), 1220-1221 (1996).
- 264 10. G. Tao, S. Shabahang, E.-H. Banaei, J. J. Kaufman, and A. F. Abouraddy, "Multimaterial
265 preform coextrusion for robust chalcogenide optical fibers and tapers," *Optics letters* **37**(13),
266 2751-2753 (2012).
- 267 11. G. Tao, A. M. Stolyarov, and A. F. Abouraddy, "Multimaterial fibers," *International Journal*
268 *of Applied Glass Science* **3**(4), 349-368 (2012).
- 269 12. Y. Kawamoto and S. Tsuchihashi, "Glass Forming Regions and Structure of Glasses in the
270 System Ge-S," *Journal of the American Ceramic Society* **52**(11), 626-627 (1969).
- 271 13. E. Pone, C. Dubois, N. Gu, Y. Gao, A. Dupuis, F. Boismenu, S. Lacroix, and M. Skorobogatiy,
272 *Drawing of the hollow all-polymer Bragg fibers* (2006).
- 273 14. J. Heo, H. Nasu, and J. D. Mackenzie, "Infrared transmitting chalcogenide glasses," in *30th*
274 *Annual Technical Symposium*, (International Society for Optics and Photonics, 1986), 85-91.
- 275 15. B. J. Riley and W. C. Lepry, *Initial Assessment of the Consolidation of Chalcogels into a*
276 *Viable Waste Form* (Pacific Northwest National Laboratory, 2012).
- 277 16. A. Seddon and M. Hemingway, "Thermal properties of chalcogenide-halide glasses in the
278 system: Ge-SI," *Journal of Thermal Analysis and Calorimetry* **37**(9), 2189-2203 (1991).
- 279 17. S. Shibata, Y. Terunuma, and T. Manabe, "Sulfide glass fibers for infrared transmission,"
280 *Materials Research Bulletin* **16**(6), 703-714 (1981).
- 281 18. T. Kanamori, Y. Terunuma, S. Takahashi, and T. Miyashita, "Chalcogenide glass fibers for
282 mid-infrared transmission," *Lightwave Technology, Journal of* **2**(5), 607-613 (1984).

- 283 19. S. DAI, B. PENG, and X. SHEN, "Elimination of Impurities in Ge-Se-Sb Glass [J]," Acta
284 Photonica Sinica **37**(S1), 1-7 (2008).
- 285 20. D. Lezal, "Chalcogenide glasses-survey and progress," Journal of Optoelectronics and
286 Advanced Materials **5**(1), 23-34 (2003).

ACCEPTED MANUSCRIPT