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Composition dependences of refractive index and thermo-optic coefficient in Ge-As-Se chalcogenide glasses

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ABSTRACT

The refractive indices (n) and thermo-optic coefficients (ζ) of $Ge_{14}As_xSe_{86-x}$ and $Ge_xAs_{12}Se_{88-x}$ glasses are measured in the 2–12 μm mid-infrared range. The composition dependences of the two parameters are investigated and strategies for tailoring them are proposed. The density (d) shows a maximum at the stoichiometric composition when Ge content is fixed; while it exhibits a minimum at the mean coordination number ($<r>$) of 2.67 when As concentration is fixed. The volume thermal expansion coefficient (β) broadly decreases with increasing $<r>$. Two semi-empirical relations are used to predict n and ζ from the glass composition. The n of a Ge-As-Se glass could be predicted with an error of <1% from the d of the glass and the molar refractivity (R_i) of the constituent elements. The estimated values of R_i for Ge, As and Se between 2 and 12 μm range from 10.12–10.52, 11.71–11.91, and 11.17–11.25 cm^3/mol, respectively. The ζ of a Ge-As-Se glass could be forecasted with an error of <6 ppm/K from the β of the glass and the thermal coefficients of the molar refractivity (φ_i) of the constituent elements. The estimated values of φ_i for Ge, As and Se between 2 and 12 μm range from 26.2–26.7, 54.9–55.7 and 85.4–86.8 ppm/K, respectively.

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1. Introduction

Chalcogenide glasses (ChG) [1–12] have been extensively studied for applications in the areas of infrared (IR) technology, integrated optics and nonlinear optics because of their excellent IR transparency, high linear and nonlinear refractive indices, and ease of processing. For example, IR lenses made of Ge-As-Se and Ge-Sb-Se glasses have been used in night vision systems [1,2]; integrated devices based on ChG have been developed for telecommunications and optical sensing [3–5]; and dispersion engineered optical waveguides have been designed and fabricated for mid-IR supercontinuum sources, and Raman or Brillouin lasers [6–12]. For the optical designs of glass lenses, the linear refractive index n and its thermo-optic coefficient ζ ($\zeta = dn/dT$) are crucial parameters. Hence, knowledge of n and its variation with wavelength and temperature is highly desirable for the designs of IR optical systems. However, limited n data of ChG are available in the literature [13–16], except for those of a few commercial compositions such as As_2S_3, As_2Se_3, $Ge_{33}As_{12}Se_{55}$, and $Ge_{28}Sb_{12}Se_{60}$, and reported data of ζ are even fewer. In this paper, a systematic investigation of the composition dependences of n and ζ in the Ge-As-Se system is conducted. Compositional factors influencing n and ζ are identified and semi-empirical method are proposed to tailor these two parameters. The Ge-As-Se system was chosen for this investigation because it has a large glass-forming region [17], so that a large number of chemical compositions with broadly different properties can be tested. In addition, Ge-As-Se glasses have superior thermal and mechanical properties, as well as relatively high laser damage threshold, and therefore are popular optical materials for IR lenses and nonlinear waveguides [1,18].

2. Experimental procedures

To conduct a systematic investigation of the composition dependence of n and ζ in the Ge-As-Se glass system, two groups of glasses with different compositional features were prepared: (i) $Ge_{14}As_xSe_{86-x}$, x = 4, 8, 12, 16, 20, 23.2, 28, and 32; (ii) $Ge_xAs_{12}Se_{88-x}$, x = 17, 21, 23.3, 25, 27.5, 29 and 33. These glasses were selected to cover the Se-rich, stoichiometric, and Se-deficient compositions, as well as to cover a large mean coordination number (MCN or $<r>$) range of 2.32–2.78, which includes the two topological transition points of $<r> = 2.4$ [19] and $<r> = 2.67$ [20]. Table 1 lists the compositions and their chemical and topological parameters. The *dSe* represents the departure from stoichiometry of the composition. It is quantified as the degree to which the glass is Se-rich or Se-deficient and is calculated by $dSe\ (\%) = (100 - x - y) - 2x - 1.5y = 100 - 3x - 2.5y$ for $Ge_xAs_ySe_{100-x-y}$. The $<r>$ defines the average number of covalent bond per atoms, and is

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Table 1
Composition, respective departure from stoichiometry (*dSe*) and mean coordination number (<*r*>), refractive index at 10 μm ($n_{10\ \mu m}$) at 25 °C, measured ($\zeta_{10\ \mu m}$) and calculated ($\zeta_{10\ \mu m}^{*}$) thermo-optic coefficients at 10 μm, density (*d*), and volume thermal expansion coefficient (β) for Ge-As-Se glasses.

Composition	*dSe* (%)	<*r*>	$n_{10\ \mu m}$ (±0.0005)	$\zeta_{10\ \mu m}$ (±6 ppm/K)	$\zeta_{10\ \mu m}^{*}$ (ppm/K)	*d* (±0.005 g/cm^3)	β (±1.5 ppm/K)
$Ge_{14}As_4Se_{82}$	48	2.32	2.4461	−17	-20	4.380	83.4
$Ge_{14}As_8Se_{78}$	38	2.36	2.4722	−8	-5	4.406	76.5
$Ge_{14}As_{12}Se_{74}$	28	2.40	2.4891	0	6	4.432	71.4
$Ge_{14}As_{16}Se_{70}$	18	2.44	2.5194	16	18	4.455	66.3
$Ge_{14}As_{20}Se_{66}$	8	2.48	2.5510	28	26	4.475	62.4
$Ge_{14}As_{23.2}Se_{62.8}$	0	2.512	2.5628	42	45	4.479	55.5
$Ge_{14}As_{28}Se_{58}$	−12	2.56	2.5588	38	39	4.467	56.1
$Ge_{14}As_{32}Se_{54}$	−22	2.60	2.5761	35	32	4.458	57.1
$Ge_{33}As_{12}Se_{55}$	−29	2.78	2.4991	71	72	4.411	37.2
$Ge_{29}As_{12}Se_{59}$	−17	2.70	2.4482	65	66	4.369	40.2
$Ge_{27.5}As_{12}Se_{60.5}$	−12.5	2.67	2.4346	63	68	4.357	39.9
$Ge_{25}As_{12}Se_{63}$	−5	2.62	2.4347	51	46	4.363	49.6
$Ge_{23.3}As_{12}Se_{64.7}$	0	2.586	2.4506	40	36	4.386	54.7
$Ge_{21}As_{12}Se_{67}$	7	2.54	2.4628	32	30	4.404	58.6
$Ge_{17}As_{12}Se_{71}$	19	2.46	2.4895	24	21	4.432	64.2

calculated as the sum of the products of individual element molar fractions and respective covalent coordination numbers [19,21].

The Ge-As-Se glasses were synthesized by melting mixtures of high-purity germanium (5 N), arsenic (6 N) and selenium (6 N) elements in evacuated (<10^{-5} mbar) and flame-sealed quartz tubes in a rocking furnace. Arsenic was pretreated under vacuum at 320 °C for 1 h to remove high-vapor-pressure oxide impurities. The material weighing and loading process were conducted in a glove box filled with dry nitrogen to avoid contamination from the ambient environment. The mixture in the quartz tube was homogenized at 850 °C for more than 12 h. After that, the temperature of the furnace was lowered to 650–700 °C and the tube was held at this temperature for another 2 h. In the end, the melt in the tube was quenched in water to form a glass and the resulting glass was annealed to remove the internal stresses.

The *n* of the glasses at different temperatures were measured on single-side polished discs using an IR variable angle spectroscopic ellipsometer (IR-VASE, J. A. Woollam, Lincoln, NE) equipped with a temperature controllable sample chamber. The incident light (1.7–30 μm) which was emitted from a glow bar and collimated using a set of mirrors had a spot size of ~9 mm in diameter. The light reflected by the sample was detected by a deuterated tri-glycine sulfate (DTGS) detector. The values of *n* were obtained by analyzing the polarization change (amplitude ratio) and the phase difference of the reflected light [22]. Each sample was measured more than three times, and the variation of measured *n* for each sample was within ±0.0005. The densities (*d*) of the glasses were measured using the Archimede's method. The *d* was calibrated using a Ge single crystal whose *d* is 5.765 g/cm^3. Each sample was measured more than six times, and the error was less than ±0.005 g/cm^3. The thermal expansion curves of the glasses were measured on glass rods (Ø 9 mm × 20 mm) using a DIL 402C dilatometer (NETZSCH, Germany) at a heating rate of 5 °C/min, and the linear thermal expansion coefficients (α) ranging from 30 to 100 °C were determined from the curves. Each sample was measured three times, and the variation of measured α was within $\pm 5 \times 10^{-7}$/K.

3. Results

The measured *n* of the Ge-As-Se glasses at different wavelengths are summarized in Tables 2 and 3. It is found that *n* decreases with increasing wavelength for each glass. This is in agreement with the dispersions of optical glasses in their transparent windows [14]. The *n* shows the same composition dependence at different wavelengths. The values of *n* at a specific wavelength (e.g. 10 μm) are therefore used to demonstrate the evolution of the *n* with the chemical or topological parameter (e.g. *dSe* or <*r*>). Overall, the variation of *n* does not show a universal dependence on *dSe* or <*r*> (see Fig. 1). However, if the two groups of glasses are considered separately, the *n* broadly decreases with increasing *dSe* (see Fig. 1a) or decreasing <*r*> (see Fig. 1b) when the atomic concentration of Ge is fixed at 14%; while it shows a broad minimum between *dSe* = −5% and *dSe* = −12.5% (see Fig. 1a) or between <*r*> = 2.62 and <*r*> = 2.67 (see Fig. 1b) when As content is fixed at 12%.

The measured ζ at 10 μm of the investigated glasses are listed in Table 1. Here, ζ is the average value between 25 and 100 °C, and the measurement error is about ±6 ppm/K. The dependence of ζ on *dSe* and <*r*> are plotted in Fig. 2a and b, respectively. The ζ shows a well-defined dependence on <*r*> on the whole (see Fig. 2b), that is the ζ

Table 2
Measured (n_{mea}) and calculated (n_{cal}) refractive indices at 2, 4 and 6 μm at 25 °C for Ge-As-Se glasses.

Composition	Refractive index at 2 μm			Refractive index at 4 μm			Refractive index at 6 μm		
	n_{mea}	n_{cal}	δ (%)	n_{mea}	n_{cal}	δ (%)	n_{mea}	n_{cal}	δ (%)
$Ge_{14}As_4Se_{82}$	2.4747	2.4634	−0.46	2.4585	2.4507	−0.32	2.4540	2.4467	−0.30
$Ge_{14}As_8Se_{78}$	2.4976	2.4925	−0.20	2.4834	2.4786	−0.19	2.4794	2.4743	−0.21
$Ge_{14}As_{12}Se_{74}$	2.5204	2.5226	0.09	2.5034	2.5074	0.16	2.4984	2.5027	0.17
$Ge_{14}As_{16}Se_{70}$	2.5492	2.5515	0.09	2.5337	2.5350	0.05	2.5288	2.5300	0.05
$Ge_{14}As_{20}Se_{66}$	2.5845	2.5814	−0.12	2.5668	2.5635	−0.13	2.5614	2.5581	−0.13
$Ge_{14}As_{23.2}Se_{62.8}$	2.6026	2.5934	−0.35	2.5801	2.5746	−0.21	2.5737	2.5689	−0.19
$Ge_{14}As_{28}Se_{58}$	2.6005	2.6019	0.05	2.5769	2.5819	0.19	2.5702	2.5759	0.22
$Ge_{14}As_{32}Se_{54}$	2.6127	2.6097	−0.11	2.5919	2.5887	−0.12	2.5862	2.5825	−0.14
$Ge_{33}As_{12}Se_{55}$	2.5398	2.5179	−0.86	2.5173	2.4961	−0.84	2.5107	2.4895	−0.85
$Ge_{29}As_{12}Se_{59}$	2.4852	2.4882	0.12	2.466	2.4686	0.10	2.4600	2.4625	0.10
$Ge_{27.5}As_{12}Se_{60.5}$	2.4756	2.4797	0.17	2.4537	2.4608	0.29	2.4470	2.4549	0.32
$Ge_{25}As_{12}Se_{63}$	2.4732	2.4824	0.37	2.4525	2.4642	0.48	2.4462	2.4587	0.51
$Ge_{23.3}As_{12}Se_{64.7}$	2.4901	2.4966	0.26	2.4694	2.4787	0.38	2.4630	2.4732	0.41
$Ge_{21}As_{12}Se_{67}$	2.4962	2.5073	0.45	2.4791	2.4900	0.44	2.4736	2.4847	0.45
$Ge_{17}As_{12}Se_{71}$	2.5200	2.5240	0.16	2.5038	2.5078	0.16	2.4988	2.5028	0.16

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