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Lasing transition ($^4F_{3/2} \rightarrow {^4I_{11/2}}$ at 1.06 μm) lifetimes and non-linearity characteristics of Nd^{3+}-doped chalcogenide glasses

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Abstract

Optical properties such as the radiative lifetimes (T_m) of the lasing transition $^4F_{3/2} \rightarrow {^4I_{11/2}}$ at 1.06 μm, the absorption coefficients (β) for the hypersensitive transition ($^4G_{5/2} \leftarrow {^4I_{9/2}}$) in the wavelength region 560–590 nm and also certain non-linearity characteristic parameters such as ϑ_d, n_2, γ and $\chi^{(3)}_{1111}$ were determined for eleven newly developed Nd^{3+}-doped chalcogenide glasses. These laser optical materials were significantly influenced in their properties by irradiations carried out with an argon ion laser (488, 514 nm) and a UV source (254 nm).

Keywords: Chalcogenide glasses; Optical properties; Lasing transition lifetimes

1. Introduction

Glasses containing one or more of the chalcogen elements (S, Se or Te) together with one or more elements such as Ge, Si, P, As, Sb and a number of others, have been identified as chalcogenide glasses. The extended IR transmission (8–12 μm) of the chalcogenide glasses makes them effective and useful for different commercial applications as IR optical materials [1–4]. Earlier, we have carried out extensive spectroscopic analyses on a variety of HMF (ZrF_4, InF_3)-based optical component materials for 7–8 μm IR transmitting optical device applications [5–8]. The present study was aimed at the characterization of another new family of materials known as chalcogenide glasses developed on the basis of chalcogens (Se and Te) used together with Ge, As and Sb doped with the promising lasing Nd^{3+} ions.

2. Experimental studies

2.1. Preparation of chalcogenide glasses

Raw materials of GeO_2, TeO_2, Se_2O_3, Sb_2O_3, As_2O_3 and Nd_2O_3 were purchased from Aldrich (Canada). All chemicals were of high purity. Table 1 gives the chemical compositions of the glasses used. The chemicals were weighed, following the table, collected in silica ampoules separately for each glass batch, evacuated and then sealed before melting in the temperature range 900–1000 °C in a rotating furnace. The melts thus became homogenized in the ampoule. The melts from the ampoules were quenched in cool water to obtain transparent optical glasses.

When compared with the HMF glasses that were developed and characterized by us earlier [5–8], the present glasses were found to be of good stability and chemical durability as they resist the moisture in the

Table 1
Composition of glasses (%)

Glass	Ge	Sb	Se	As	Te	Nd
Cg-1	0.1	0.1	0.79	–	–	0.01
Cg-2	0.1	0.2	0.69	–	–	0.01
Cg-3	0.2	0.1	0.69	–	–	0.01
Cg-4	0.2	0.2	0.59	–	–	0.01
Cg-5	0.2	0.3	0.49	–	–	0.01
Cg-6	0.3	0.2	0.49	–	–	0.01
Cg-7	0.28	–	0.6	0.11	–	0.01
Cg-8	0.28	0.12	0.55	–	0.04	0.01
Cg-9	–	–	0.6	0.39	–	0.01
Cg-10	0.28	–	0.55	0.12	0.04	0.01
Cg-11	0.31	–	0.51	0.12	0.05	0.01

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laboratory atmosphere. The chalcogenide glasses showed extended IR transmission up to 12 μm by observation of IR spectrophotometric absorption spectral profiles.

2.2. Densities and refractive indices

The densities of the glasses were measured by the use of the traditional method of Archimedes principle with xylene as an immersion liquid, and were in the range 4.5–4.9 g cm^{-3}. The refractive indices were measured at three different wavelengths ($\lambda_F = 489$ nm, $\lambda_d = 589.3$ nm, $\lambda_c = 656.3$ nm) with a precision refractometer. These measured data (n_F, n_d, n_c) agreed well with the results from reflected spectral recordings in the wavelength range 400–700 nm. The refractive indices (n_d) obtained at $\lambda_d = 589.3$ nm for the chalcogenide glasses were found to be greater (in the range 1.6–1.7) than those of the HMF glasses (1.5), which could be due to the availability of the chalcogens (Se, Te) and the other elements (Ge, Sb, As) in their glass matrices.

2.3. Radiative lifetimes

The radiative lifetimes (T_m μs) of the lasing transition $^4F_{3/2} \rightarrow {}^4I_{11/2}$ at 1.06 μm of the Nd^{3+} – chalcogenide glasses were measured with an argon ion laser (488 nm) of 1.5 W as an excitation source. In order to obtain satisfactory and repeatable data, a suitable chopper was employed in the path of the laser beam. A spectrofluorimeter has coupled to a Model 5120 lock-in amplifier (0.5 Hz–120 kHz), a transient recorder and a Nicolet Model 1070 signal averager arranged to collect lifetime values for the prominent emission transition $^4F_{3/2} \rightarrow {}^4I_{11/2}$ of the Nd^{3+}-doped optical materials.

2.4. Absorption coefficients

It is well known that Nd^{3+}-doped materials absorb more light in the wavelength range 560–590 nm, wherein there is a bright hypersensitive transition $^4I_{9/2} \rightarrow {}^4G_{5/2}$. Therefore, in this wavelength range, a special effort was made to measure absorption coefficient (β) for all eleven Nd^{3+}–chalcogenide glasses. By employing the photopyroelectric spectroscopic technique (PPES), as described in an earlier paper [9], the absorption coefficients (β) were evaluated.

We observed the effect of radiation on the densities, refractive indices, lifetimes and absorption coefficients of the eleven Nd^{3+}–chalcogenide glasses with a 1.5 W argon ion laser source (488 nm, 514 nm) and with a 1000 W arc lamp (254 nm) UV source. For the first time we made an effort to elucidate the effect of radiation on the absorption coefficients of the materials.

3. Results and discussion

It is considered necessary, in assessing optical quality, to understand the non-linear properties of materials. According to the literature [10–12], an optical material should possess a minimum value of its non-linear refractive index (n_2) for its use as an efficient laser material or a good optical fibre. Non-linearity properties of the glass samples could be studied through their Abbé number (ϑ_d) which could be obtained from the measured refractive indices:

$$\vartheta_d = \frac{(n_d - 1)}{(n_F - n_c)}$$

where n_d is the refractive index at $\lambda_d = 589.3$ nm, n_F at $\lambda_F = 486.1$ nm and n_c at $\lambda = 656.3$ nm.

The non-linear refractive indices (n_2) of the glasses were estimated from the equation [12]

$$n_2\ (10^{13}\ \text{esu}) = \frac{68(n_d - 1)(n_d^2 + 2)^2}{\vartheta_d \left[1.517 + \dfrac{(n_d + 1)(n_d^2 + 2)\vartheta_d}{6n_d}\right]^{1/2}}$$

Once this n_2 has been evaluated, it is easy to determine the non-linear refractive index coefficient (γ) [13]:

$$\gamma\ (\text{cm}^2\ \text{W}^{-1}) = \left(\frac{4\pi \times 10^7}{c n_d}\right) n_2\ (\text{esu})$$

The non-linear susceptibility ($\chi^{(3)}_{1111}$) factors for all the glass samples were calculated in terms of linear (n_d) and non-linear (n_2) refractive indices [14] by the expression

$$\chi^{(3)}_{1111} = \left(\frac{n_d}{12\pi}\right) n_2\ (\text{esu})$$

The refractive indices (n_F, n_d, n_c), Abbé number (ϑ_d), non-linear refractive index (n_2), non-linear refractive index coefficient (γ) and non-linear susceptibility ($\chi^{(3)}_{1111}$) of the unirradiated Nd^{3+}–chalcogenide glasses are given in Table 2. The glasses that have lower non-linear refractive indices with lower dispersion in the visible wavelength range could become valuable optical materials. Tables 2–5 clearly illustrate how the glass compositions could effect the non-linear properties (n_2, γ, $\chi^{(3)}_{1111}$) of the glasses. Among the several glasses investigated, the two Nd^{3+}–chalcogenide glasses Cg-6 (0.3Ge–0.2Sb–0.49Se) and Cg-9 (0.6Se–0.39As) have the lowest non-linear property values, encouraging us to suggest these two optical materials as ideal systems for further improvement in the design and development of bulk materials for obtaining lasing action at 1.06 μm from the transition $^4F_{3/2} \rightarrow {}^4I_{11/2}$. The measured radiative lifetimes (T_m) for this lasing transition and the absorption coefficients (β) for the hypersensitive transition $^4I_{9/2} \rightarrow {}^4G_{5/2}$ of the eleven Nd^{3+}–chalcogenide

Table 2
Measured values of refractive indices (n_F at 489.0 nm, n_d at 589.3 nm, n_c at 656.3 nm), Abbé numbers (ϑ_d), non-linear refractive indices ($n_2 \times 10^{13}$ esu), its coefficient ($\gamma \times 10^{16}$ cm^2 W^{-1}) and non-linear susceptibilities ($\chi^{(3)}_{1111} \times 10^{15}$ cm^2) of unirradiated Nd^{3+}–chalcogenide glasses

Glass	n_F	n_d	n_c	ϑ_d	n_2	γ	$\chi^{(3)}_{1111}$
Cg-1	1.645	1.640	1.636	71	1.414	3.614	6.150
Cg-2	1.629	1.625	1.620	69	1.416	3.652	6.102
Cg-3	1.624	1.620	1.615	69	1.397	3.613	5.999
Cg-4	1.605	1.600	1.596	67	1.379	3.613	5.852
Cg-5	1.597	1.590	1.586	54	1.849	4.872	7.793
Cg-6	1.596	1.592	1.589	85	0.957	2.518	4.038
Cg-7	1.634	1.630	1.626	79	1.1734	3.017	5.071
Cg-8	1.668	1.660	1.653	44	3.045	7.6862	13.402
Cg-9	1.654	1.650	1.647	93	0.971	2.467	4.249
Cg-10	1.709	1.700	1.694	47	3.067	7.560	13.824
Cg-11	1.702	1.695	1.690	58	2.214	5.472	9.948

Table 3
Measured values of refractive indices (n_F at 489.0 nm, n_d at 589.3 nm, n_c at 656.3 nm), Abbé numbers (ϑ_d), non-linear refractive indices ($n_2 \times 10^{13}$ esu), its coefficient ($\gamma \times 10^{16}$ cm^2 W^{-1}) and non-linear susceptibilities ($\chi^{(3)}_{1111} \times 10^{15}$ cm^2) of Nd^{3+}–chalcogenide glasses irradiated with an argon ion laser (488 nm)

Glass	n_F	n_d	n_c	ϑ_d	n_2	γ	$\chi^{(3)}_{1111}$
Cg-1	1.572	1.569	1.563	63	1.382	3.692	5.751
Cg-2	1.559	1.552	1.550	61	1.379	3.723	5.675
Cg-3	1.554	1.548	1.545	61	1.363	3.689	5.593
Cg-4	1.536	1.529	1.527	59	1.351	3.704	5.479
Cg-5	1.528	1.520	1.518	52	1.586	4.373	6.374
Cg-6	1.528	1.521	1.519	58	1.352	3.756	3.454
Cg-7	1.564	1.557	1.556	70	1.140	3.069	4.707
Cg-8	1.596	1.585	1.582	42	2.648	7.001	11.129
Cg-9	1.582	1.575	1.574	72	1.153	3.005	4.815
Cg-10	1.635	1.625	1.621	45	2.677	6.911	11.533
Cg-11	1.627	1.620	1.617	58	1.638	4.238	7.037

Table 4
Measured values of refractive indices (n_F at 489.0 nm, n_d at 589.3 nm, n_c at 656.3 nm), Abbé numbers (ϑ_d), non-linear refractive indices ($n_2 \times 10^{13}$ esu), its coefficient ($\gamma \times 10^{16}$ cm^2 W^{-1}) and non-linear susceptibilities ($\chi^{(3)}_{1111} \times 10^{15}$ cm^2) of Nd^{3+}–chalcogenide glasses irradiated with an argon ion laser (514 nm)

Glass	n_F	n_d	n_c	ϑ_d	n_2	γ	$\chi^{(3)}_{1111}$
Cg-1	1.563	1.556	1.553	56	1.585	4.269	6.540
Cg-2	1.549	1.542	1.539	54	1.604	4.366	6.560
Cg-3	1.544	1.539	1.533	49	1.837	5.002	7.497
Cg-4	1.526	1.519	1.516	52	1.581	4.362	6.368
Cg-5	1.517	1.510	1.506	51	1.582	4.391	6.335
Cg-6	1.516	1.510	1.506	51	1.582	4.391	6.335
Cg-7	1.553	1.546	1.543	55	1.580	4.283	6.478
Cg-8	1.586	1.575	1.571	38	2.984	7.940	12.463
Cg-9	1.572	1.565	1.564	71	1.143	3.061	4.743
Cg-10	1.624	1.613	1.610	44	2.676	6.953	11.447
Cg-11	1.618	1.615	1.607	56	1.880	4.878	8.050

Table 5
Measured values of refractive indices (n_F at 489.0 nm, n_d at 589.3 nm, n_c at 656.3 nm), Abbé numbers (ϑ_d), non-linear refractive indices ($n_2 \times 10^{13}$ esu), its coefficient ($\gamma \times 10^{16}$ cm^2 W^{-1}) and non-linear susceptibilities ($\chi^{(3)}_{1111} \times 10^{15}$ cm^2) of Nd^{3+}–chalcogenide glasses irradiated with a UV source (254 nm)

Glass	n_F	n_d	n_c	ϑ_d	n_2	γ	$\chi^{(3)}_{1111}$
Cg-1	1.701	1.693	1.692	77	1.443	3.572	6.478
Cg-2	1.684	1.677	1.675	75	1.493	3.597	6.400
Cg-3	1.679	1.673	1.670	75	1.424	3.567	6.318
Cg-4	1.660	1.651	1.650	65	1.662	4.219	7.277
Cg-5	1.650	1.641	1.639	58	1.917	4.896	8.342
Cg-6	1.650	1.642	1.641	71	1.422	3.629	6.191
Cg-7	1.689	1.683	1.681	85	1.213	3.020	5.413
Cg-8	1.725	1.717	1.709	45	3.418	8.341	15.560
Cg-9	1.710	1.704	1.702	88	1.216	2.754	5.495
Cg-10	1.767	1.758	1.751	47	3.550	8.463	16.549
Cg-11	1.760	1.755	1.749	69	1.989	4.748	9.254

Table 6
Measured lifetimes (T_m) for the lasing transition $^4F_{3/2} \rightarrow {}^4I_{11/2}$ and absorption coefficients (β) for the hypersensitive transition $^4I_{9/2} \rightarrow {}^4G_{5/2}$ of Nd^{3+}–chalcogenide glasses

Glass	T_m μs	β (10^3 cm^{-1}) [a]			
		1	2	3	4
Cg-1	170	2.15	2.05	2.03	2.47
Cg-2	170	2.13	2.04	2.00	1.45
Cg-3	170	2.12	2.04	2.01	2.43
Cg-4	170	2.10	2.03	1.98	2.33
Cg-5	170	2.10	2.03	1.97	2.30
Cg-6	170	2.09	2.00	1.94	2.25
Cg-7	200	2.25	2.16	2.12	2.59
Cg-8	200	2.17	2.08	2.07	2.41
Cg-9	200	2.30	2.21	2.17	2.55
Cg-10	190	2.16	2.07	2.05	2.27
Cg-11	190	2.14	2.04	2.03	2.25

[a] 1 = unirradiated; 2 = irradiated with an argon ion laser (488 nm); 3 = irradiated with argon ion laser (514 nm); 4 = irradiated with a xenon arc lamp (254 nm).

glasses are listed in Table 6. It can be seen that sample Cg-9 has higher values of T_m and β than the other glasses.

There are some interesting observations (Tables 3–5) relevant to the glasses arising from the irradiation with an argon ion laser source (488 nm, 514 nm) and a UV source (254 nm). The results indicate that the non-linearity properties of the Nd^{3+}–chalcogenide glasses display variations due to the irradiation in a random manner. However, it is observed that the properties of the unirradiated glasses changes in an orderly fashion. The lifetimes of the lasing transition did not show variations due to irradiation from the argon ion laser or UV source. The absorption coefficients decreased when the samples were irradiated with an argon ion laser and increased when exposed to a UV source.

From the results in Tables 2–6 for refractive indices (n_d, n_F, n_c), non-linearity properties, the lifetimes (T_m) of the lasing transition $^4F_{3/2} \rightarrow {}^4I_{11/2}$ at 1.06 μm and absorption coefficients (β) concerning the hypersensitive transition wavelength region, it is concluded that these glasses could be suggested as good candidates for use as IR optical devices both in glass laser technology and in optical communications.

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References

[1] J.A. Savage, *J. Non-Cryst. Solids, 47* (1982) 101.
[2] X.H. Zhang, G. Fontenean and J. Locus, *J. Non-Cryst. Solids, 104* (1988) 38.
[3] J.S. Sanghera, J. Heo and J.D. Mackenzie, *J. Non-Cryst. Solids, 103* (1988) 155.
[4] G. Fuxi, *J. Non-Cryst. Solids, 140* (1992) 184.
[5] M. Hanumanthu, K. Annapurna and S. Buddhudu, *Solid State Commun., 80* (1991) 315.
[6] K. Annapurna, M. Hanumanthu and S. Buddhudu, *Spectrochim. Acta, Part A, 48* (1992) 791.
[7] K. Annapurna and S. Buddhudu, *J. Phys. D., 25* (1993) 302.
[8] K. Annapurna and S. Buddhudu, *Spectrochim. Acta, Part A, 49* (1993) 73.
[9] A. Mandelis, J. Vanniasinkam and S. Buddhudu, *Phys. Rev. B, 48* (1993) 6808.
[10] M.J. Weber, in D.C. Brown (ed.), *High Peak Power Nd:Glass Laser Systems,* Springer, Berlin, 1981.
[11] M.J. Weber, *CRC Handbook of Laser Sciences and Technology,* CRC Press, Boca Raton, FL, 1991.
[12] N.L. Boling, A.J. Glass and A. Owyoung, *IEEE J. Quantum Electron., 14* (1978) 601.
[13] K. Annapurna and S. Buddhudu, *J. Solid State Chem., 93* (1991) 454.
[14] S.H. Kim, T. Yoko and S. Sakka, *J. Am. Ceram. Soc., 76* (1993) 865.