



ELSEVIER

Journal of Alloys and Compounds 216 (1994) 281–283

Journal of
ALLOYS
AND COMPOUNDS

Non-linearity–elastic properties and lifetimes of the lasing transition (${}^4F_{3/2} \rightarrow {}^4I_{11/2}$) of Nd^{3+} -doped semiconducting glasses

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Received 13 April 1994; in final form 13 May 1994

Abstract

This paper reports the preparation and characterization of three new series of Nd^{3+} -doped optical glasses based on GeO_2 , TeO_2 and V_2O_5 . By the measurement of refractive indices (n_F , n_d , n_C) and ultrasonic velocities (V_l , V_t), non-linearity and elastic properties of the glasses have been studied. By the use of an Ar^+ laser (488 nm), the lifetimes of the lasing transition (${}^4F_{3/2} \rightarrow {}^4I_{11/2}$) at $1.06 \mu m$ have been determined for the semiconducting laser glasses.

Keywords: Non-linearity; Elastic properties; Semiconducting glasses

1. Introduction

Previously from our laboratories we have reported the optical properties of certain IR-transmitting optical glasses based on ZrF_4 and InF_3 doped with Nd^{3+} and Eu^{3+} ions as the luminescent centres [1–4]. Recently there has been an article published [5] describing the IR transmission abilities of GeO_2 -, TeO_2 - and V_2O_5 -based semiconducting glasses. The purpose of the present work is to prepare, characterize and examine Nd^{3+} -doped glasses to assess their optical performance by measuring their various non-linearity properties, ultrasonic velocities, IR spectra and lifetimes of the lasing transition.

2. Experimental details

Table 1 lists the three new series of Nd^{3+} -doped semiconducting glasses prepared by the quenching technique [1–5] from the melts (900–1000 °C) by sandwiching between two well-polished brass plates to obtain circular-shaped optical materials for their characterization.

The raw chemicals used in the present work have been procured from Aldrich of Toronto, Canada. The high quality semiconducting laser glasses thus prepared have been labelled as SG-1 (A–C); SG-2 (A–C) and SG-3 (A–C) for convenience of representation.

Table 1
Composition of Nd^{3+} -doped semiconducting glasses

Glass type	GeO_2	TeO_2	V_2O_5	Li_2O	Na_2O	Nd_2O_3
SG-1A	50		49.9			0.1
SG-1B		50	49.9			0.1
SG-1C	25	25	49.9			0.1
SG-2A	30		49.9	20		0.1
SG-2B	30		49.9		20	0.1
SG-2C	30		49.9	10	10	0.1
SG-3A		30	49.9	20		0.1
SG-3B		30	49.9		20	0.1
SG-3C		30	49.9	10	10	0.1

Archimedes' principle was the basis behind the measurement of the densities of the glasses, with xylene as the immersion liquid. The refractive indices of the glasses were determined on a precision refractometer at three different wavelengths ($\lambda_F = 486$ nm, $\lambda_d = 589$ nm and $\lambda_C = 656$ nm). By using a Matec Model 6600 pulse modulator with a piezoelectric transducer, an electric pulse was generated. This transducer was coupled to one of the faces of the glass; the pulse was reflected on the opposite face and back detected by the same transducer. The pulse transit time t (s) was measured with a Hewlett–Packard Model 174/A oscilloscope and the ultrasonic velocity V ($m s^{-1}$) was

Table 2
IR cut-off wavelength of Nd³⁺-doped semiconducting glasses

Glass type	IR cut-off wavelength (μm)
SG-1A	5.1
SG-1B	5.8
SG-1C	5.3
SG-2A	5.1
SG-2B	5.2
SG-2C	5.3
SG-3A	5.9
SG-3B	5.9
SG-3C	6.0

Table 3
Average molecular weight (\bar{M}), density (d), rare earth ion concentration (N) and molar refractivity (R_M) of Nd³⁺-doped semiconducting glasses

Glass	\bar{M} (g)	d (g cm ⁻³)	N (10 ²² ions cm ⁻³)	R_M (cm ³)
SG-1A	143.39	5.16	2.167	10.223
SG-1B	170.89	5.85	2.062	14.164
SG-1C	157.14	5.62	2.154	12.043
SG-2A	128.45	4.47	2.095	10.164
SG-2B	134.87	4.52	2.019	10.496
SG-2C	131.66	4.49	2.056	10.315
SG-3A	144.95	5.16	2.143	11.859
SG-3B	151.37	5.21	2.073	12.213
SG-3C	148.16	5.18	2.106	12.032

evaluated by the equation

$$V = \frac{2L}{t}$$

where L (m) is the sample length. Depending upon the transducer used, the longitudinal (V_l) or transverse (V_t) velocities were measured. Before measuring the lifetimes of the lasing transition of these Nd³⁺-doped

glasses, their IR transmission ability was examined primarily on a Pye–Unicam IR spectrophotometer. The IR cut-off wavelengths of all nine glasses are listed in Table 2 for comparison within each of the three series investigated.

An Innova Ar⁺ laser (488 nm) with a 1.5 W power was the source of excitation used to measure the radiative lifetime T_m (μs) of a strong emission transition (⁴F_{3/2} → ⁴I_{11/2}) at 1.06 μm. In order to obtain satisfactory and repeatable data, a suitable chopper was employed in the path of the laser beam. The fluorescence spectrophotometer was coupled to a Lockin Model 5210 amplifier (0.5 Hz–120 kHz), a transient recorder and a Nicolet 1070 signal averager in order to collect the data on the lifetimes of the prominent fluorescent transitions of the various glasses.

3. Results and discussion

Using the measured density (d) and refractive index (n_d) values of the glasses of the present work, various other physical properties have also been evaluated (Table 3) in order to facilitate an understanding of the glass compositional effects on the reported results. The theoretical procedures used to obtain these factors are given in our previously published papers [6,7]. Table 4 describes the non-linearity properties of the glasses. For an ideal optical material the non-linearity properties are expected to be minimum according to the literature [8–10]. This requirement is met by the glasses such as SG-1A, SG-2A and SG-3A. These ideal optical glasses have higher values for their ultrasonic velocities compared with those of the other two materials in each of the three series, as seen in Table 5. The formulae needed to evaluate the elastic properties of the glasses have been used in a straightforward way as reported in the literature [11–16]. Table 6 reveals that the elastic properties such as longitudinal modulus, shear modulus, bulk modulus, Young modulus and Poisson ratio take lower values for lower ultrasonic velocities of the glasses.

Table 4
Refractive indices n_F (at $\lambda_F=486$ nm), n_d (at $\lambda_d=589$ nm) and n_C (at $\lambda_C=656$ nm), Abbe number (v_d), non-linearity refractive index (n_2), non-linearity coefficient (r) and non-linear susceptibility ($\chi_{111}^{(3)}$) of Nd³⁺-doped semiconducting glasses

Glass	n_F	n_d	n_C	v_d	n_2 (10 ¹³ e.s.u.)	r (10 ¹⁶ C m ² W ⁻¹)	$\chi_{111}^{(3)}$ (10 ¹⁵ e.s.u.)
SG-1A	1.662	1.657	1.6538	80	1.239	3.133	5.444
SG-1B	1.9677	1.9555	1.9457	43	6.377	13.664	33.063
SG-1C	1.816	1.8082	1.8031	63	2.590	6.002	12.417
SG-2A	1.6296	1.625	1.621	73	1.302	3.357	5.609
SG-2B	1.6282	1.6213	1.6161	51	2.199	5.684	9.453
SG-2C	1.629	1.622	1.618	57	1.867	4.823	8.029
SG-3A	1.798	1.786	1.773	31	7.053	16.548	33.400
SG-3B	1.810	1.782	1.765	17	17.052	40.099	80.571
SG-3C	1.800	1.783	1.766	23	10.891	25.596	51.489

Table 5

Measured longitudinal (V_l) and transverse (V_t) velocities and calculated mean sound velocity (V_m) and compressibility (C) of Nd³⁺-doped semiconducting glasses

Glass	V_l (m s ⁻¹)	V_t (m s ⁻¹)	V_m (m s ⁻¹)	C (10 ⁸ m ² kg ⁻¹)
SG-1A	3400	1900	2115	2.189
SG-1B	3950	2180	2429	1.420
SG-1C	3740	2050	2286	1.642
SG-2A	3000	1800	1991	3.407
SG-2B	3280	1920	2129	2.767
SG-2C	3100	1870	2068	3.184
SG-3A	3450	1870	2087	2.090
SG-3B	3680	2195	2429	1.933
SG-3C	3500	2010	2232	2.093

Table 6

Estimated longitudinal modulus (L), shear modulus (G), bulk modulus (B), Young modulus (Y) and Poisson ratio (σ) of Nd³⁺-doped semiconducting glasses

Glass	L (GPa)	G (GPa)	B (GPa)	Y (GPa)	σ
SG-1A	596.5	186.3	456.8	474.2	0.27
SG-1B	912.7	278.0	704.2	712.2	0.28
SG-1C	786.1	236.2	608.9	607.1	0.29
SG-2A	402.1	144.8	293.5	352.8	0.22
SG-2B	486.4	166.7	361.4	413.1	0.24
SG-2C	432.0	151.2	314.1	381.6	0.21
SG-3A	613.8	180.3	478.6	465.9	0.29
SG-3B	705.5	251.0	517.3	614.4	0.22
SG-3C	634.7	209.3	477.7	524.9	0.25

Table 7

Measured lifetime T_m of lasing transition (⁴F_{3/2} → ⁴I_{11/2}) of Nd³⁺-doped semiconducting glasses

Glass type	T_m (μ s)
SG-1A	90
SG-1B	93
SG-1C	93
SG-2A	90
SG-2B	90
SG-2C	92
SG-3A	96
SG-3B	96
SG-3C	100

Although there are significant variations in non-linearity and elastic properties, the lifetime values (Table 7) of the lasing transition (⁴F_{3/2} → ⁴I_{11/2}) of the Nd³⁺-doped glasses have been found to be approximately the same for all nine glasses studied.

It has thus been established that the presence of a TeO₂ content enhances the IR transmission of the glasses from 5.1 up to 6.0 μ m. It has thus been demonstrated that the optical performance of the glasses is encouraging. However, the light dispersion (non-linearity) characteristics that have been found (Tables 4 and 5) prevent these TeO₂-based glasses from being laser optical glasses. The glasses not containing TeO₂, however, do display low dispersion and are ideal laser optical glasses.

Summing up the various results given in Tables 3–7, it now becomes possible to declare at least one glass from each the three new series of glasses as ideal and suitable optical materials.

Acknowledgements

We are grateful to Professor S.V.J. Lakshman for his kind encouragement. We are thankful to the Departments of Chemistry, Metallurgy and Materials Science and the Ontario Laser Light Research Center of the University of Toronto, Toronto, Canada for their technical cooperation. One of us (K.A.) would like to thank the CSIR, New Delhi for the award of a senior research fellowship.

References

- [1] M. Hanumanthu, K. Annapurna and S. Buddhudu, *Solid State Commun.*, **80** (1991) 315.
- [2] K. Annapurna and S. Buddhudu, *J. Phys. D: Appl. Phys.*, **26** (1993) 302.
- [3] K. Annapurna, M. Hanumanthu and S. Buddhudu, *Spectrochim. Acta A*, **48** (1992) 791.
- [4] K. Annapurna and S. Buddhudu, *Spectrochim. Acta*, **49** (1993) 73.
- [5] S.H. Kin, T. Yoko and S. Sakka, *J. Am. Ceram. Soc.*, **76** (1993) 865.
- [6] K. Annapurna and S. Buddhudu, *Mater. Res. Bull.*, **27** (1992) 1107.
- [7] K. Annapurna and S. Buddhudu, *J. Solid State Chem.*, **93** (1991) 454.
- [8] R.N. Brown and M.J. Suscavage, *J. Non-Cryst. Solids*, **89** (1987) 282.
- [9] M.J. Weber, *J. Non-Cryst. Solids*, **123** (1990) 208.
- [10] E.M. Vogel, M.J. Weber and D.M. Kral, *Phys. Chem. Glasses*, **32** (1991) 231.
- [11] H. Mitsunaga and N. Vesugi, *J. Luminesc.*, **48–49** (1991) 459.
- [12] E.N. Bous and N.J. Kreidl, *J. Can. Ceram. Soc.*, **41** (1972) 83.
- [13] J. Wong and C. Angell, *Glass Structure by Spectroscopy*, Dekker, New York, 1976.
- [14] R.F. Bartholomew, *J. Non-Cryst. Solids*, **56** (1983) 331.
- [15] K.V. Damodaran, U. Selvaraj and K.J. Rao, *Mater. Res. Bull.*, **23** (1988) 1151.
- [16] M.C. Goncalves, R.M. Almeida, A.J. Delben and M.A. Aegtr, *J. Non Cryst. Solids*, **140** (1990) 52.