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Optical spectra of Nd^{3+}:CaO–La_2O_3–B_2O_3 glasses

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Abstract

This paper reports on different physical and absorption spectral properties of Nd^{3+}-doped calcium lanthanum borate glasses with and without Ta_2O_5 content to understand its influences on the hypersensitive absorption band intensities. From the recorded absorption spectra, Judd–Ofelt intensity parameters (Ω_λ, λ=2, 4, 6) have been calculated and are used to compute the radiative properties of the Nd^{3+}:glasses. The calculated Judd–Ofelt parameters are found to be increasing with the increased substitution of calcium for lanthanum in the glass composition, which may be due to the increase of Nd–O bond covalency. The glass with the tantalum (Ta^{5+}) as one of the constituent, has displayed a significant increase in the intensity of the hypersensitive transition ($^4I_{9/2}\rightarrow{}^4G_{5/2}$, $^2G_{7/2}$) of Nd^{3+} ions which is attributed to the asymmetry around the rare earth ion site aroused due to the occurrence of structural changes in the glass network and as well as mixed cationic effect with the addition of Ta^{5+} ions. Besides the spectral property analysis, different important physical properties have also been investigated from the measured density and refractive indices. The substitution of lanthanum with calcium increases the optical basicity of the glass with an increase in the oxide ion polarisability.

Keywords: Glasses; Non-crystalline materials; Optical properties

1. Introduction

The glasses containing rare earths in various forms such as network formers, modifiers or luminescent ions are of great deal of interest for their unique optical, thermal, electrical and magnetic properties [1]. Among the conventional glasses, borate glasses have been known to be the excellent host matrices for the rare earth oxides because of their good glass forming nature compared to several other conventional systems. The lanthanum borate glasses are considered as the new generation of optical glasses with a high refractive index and a low mean dispersion for their use in the design of optical devices [2]. The alkaline earth lanthanum borate glasses possess improved durability, high glass transition temperatures, low electrical conductivities and gas diffusivities towards high temperature hermetic sealing application [3,4]. Lanthanide borate glasses with good magneto-optical properties are frequently used materials as optical isolators in the high power laser systems and sensors of magnetic fields [5]. These glasses also exhibit nonlinear optical properties with considerable large third order nonlinear susceptibility and high response times. Hence these glasses are extensively used in the ultra-fast all optical switching in the field of optical communications [6,7]. Further recently, second harmonic generation (SHG) has been observed from the thermally poled lanthanum borate glasses, which can find application in electro-optic devices such as optical switches and modulators [8]. Due to the presence of rare earths as modifiers in the glass network, these glasses could accommodate more dopant luminescent ions without any fluorescence quenching that makes them as more suitable for laser active medium [9]. The extensive studies on the glass forming and structural details of the binary lanthanum borate and ternary alkaline earth lanthanum borate glasses establish

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that, the lanthanum borate glasses having near metaborate compositions (LnB_3O_6) possess $(B_3O_6)_\infty$ chains composing of BO_3 and BO_4 units in 2:1 ratio with each BO_4 tetrahedron is bonded to four BO_3 triangles at its corners. The lanthanum (La^{3+}) and alkaline earth (R^{2+}) cations sit in the 10 and 8 coordinate polyhedra respectively in between the boron chains by interconnecting them at BO_4 units just like in their crystalline counter parts [10–12]. In all these papers reported in the literature so far, deal with Raman, IR and ^{11}B NMR spectral studies for structural investigation of binary or ternary lanthanum borate glasses. Brow et al., have reported the glass formation zones of magnesium, calcium, barium lanthanum borate ternary systems revealing the wider range of homogenous glass formation could occur in CaO system and a narrow range of glass formation could take place in BaO system [13]. It is also observed that the, glass formation in all these three alkaline earth lanthanum borate glass systems has been found to be centered around the metaborate compositions. In the present investigation, few calcium lanthanum metaborate glass compositions have been chosen to dope with Nd^{3+} ions and to study their spectral properties as a function of glass host by interpreting with the IR, Raman, and ^{11}B NMR results of these glasses already available in the literature [12,13]. In one particular selected glass composition where Ca/La ratio is equivalent to 0.5, lanthanum has partially be replaced by tantalum (Ta) ion order to examine the structural changes in the glass network took up in the present work. It is a powerful tool upon the usage of rare earth ions as structural probes in order to study the local fields surrounding the individual rare earth sites within the glass matrix. There are numerous reports made available in literature on the rare earth ions as structural probes for the study of glass and crystal structures [14–16]. Due to the effective shielding of 4f shell by fully filled 5s and 5p orbitals, electronic cloud of trivalent lanthanide ions experience very weak ligand field influence. Although weak, this perturbation is responsible for the 4f intra-configurational electric dipole transitions, which are otherwise forbidden under Laporte's Rule. Hence intensities of these forced electric dipole 4f transitions reflect the interaction of rare earth ion with its nearest neighbors. Judd and Ofelt independently proposed a theory for the quantitative estimate of the forced electric dipole transition intensities [17,18]. Among the rare earth ions Nd^{3+} could be used as probe and also as an efficient laser active ion with its emission at 1.06 μm. In the present work, optical absorption spectra of Nd^{3+} doped calcium lanthanum borate glasses without and with tantalum have been measured and analyzed on the application of Judd–Ofelt theory in evaluating the three phenomenological J–O intensity parameters Ω_λ (λ=2, 4, 6). These were later used to estimate radiative properties of the emission transitions to examine the glass matrix suitability as a laser host. In addition to the spectral property evaluation, few important physical, optical and nonlinear optical properties have also been determined for the Nd^{3+} doped lanthanum calcium (tantalum) borate glasses.

2. Experimental

The glasses containing Nd^{3+}in the $CaO–La_2O_3–B_2O_3$ system have been prepared by adopting the quenching technique and their chemical compositions in mole percent are given below in the following table:

Glass identification	Chemical composition (mol%)					[O]/[B] ratio	Ca/La ratio
	B_2O_3	CaO	La_2O_3	Ta_2O_5	Nd_2O_3		
1. Nd^{3+}:CLB1	72.75	4.50	22.37	–	0.38	2	0.1
2. Nd^{3+}:CLB5	66.75	16.50	16.42	–	0.33	2	0.5
3. Nd^{3+}:CLB25	57.25	35.50	7.00	–	0.25	2	2.5
4. Nd^{3+}:CLTB5	69.80	15.00	10.40	4.50	0.33	2	0.5*

* Ca/(La+Ta) ratio.

In these glasses the dopant (Nd_2O_3) concentration has been fixed as 1 wt.% uniformly, hence there appear small variations when represented in mole fractions as shown in the above table. The four Nd^{3+}doped lanthanum calcium borate glasses are labeled as Nd^{3+}:CLB1, Nd^{3+}:CLB5, Nd^{3+}:CLB25 and Nd^{3+}:CLTB5 for convenience. The numbers in the designations refer to Ca/La ratios, which are equal to 0.1, 0.5, 2.5 and Ca/(La+Ta) equal to 0.5 respectively. The raw chemicals used were H_3BO_3 (EMerck, 99.99%), $CaCO_3$ (Fluka, 99.99%), Ta_2O_5, La_2O_3 (IREL, 99.99%), and Nd_2O_3 (IREL, 99.99%). The appropriate amounts of chemicals were weighed and mixed thoroughly in an Agate mortar and thus obtained batch mixer was charged in a pure platinum crucible at 1180 °C temperature in an electrically heated resistance furnace with a microprocessor control. The chemical batches were charged at this temperature to allow them to fuse at once and thereby limiting the evaporation losses. After the complete digestion of batch, the melt temperature has been raised to 1300 °C and kept for 1 h. The melt was homogenized by an intermittent stirring with a silica rod. The homogenized melt was poured on to a graphite mould that was heated at 650 °C to form the glasses. The glass blocks thus resulted were immediately transferred to the annealing furnace that