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# Influence of intermediates on the optical and theoretical parameters of $xLa_2O_3$-(10-x) $Y_2O_3$ -15SrO-15CaO -$10B_2O_3$-$10Al_2O_3$-$40SiO_2$ ($2 \leq x \leq 8$) glasses

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ABSTRACT

In the present investigation, an attempt has been made to study the effect of $La_2O_3/Y_2O_3$ (X) ratio on the optical properties of the novel glass series $xLa_2O_3$-(10-x)$Y_2O_3$ -15SrO-15CaO -$10B_2O_3$-$10Al_2O_3$-$40SiO_2$ (x = 2, 4, 6, 8). The glasses have been prepared via melt quenching route. Fourier transform infrared spectroscopy (FTIR) has been done to obtain the band positions and functional groups for all the pristine as well as heat treated glasses, respectively. UV-visible spectroscopy has been performed to obtain the band gap, Urbach energy and refractive indices for all the pristine as well as heat treated glasses. The parameters like density/molar volume have been calculated with the varying $La_2O_3/Y_2O_3$ (X) ratio. Also, some theoretical parameters like electronegativity of metal ion/oxide ion, interionic distance, ionic concentration, optical basicity and polarizability have been calculated. The parameters like average cross link density, average force stretching constant, bulk modulus and number of network bonds per unit volume have also been calculated. Furthermore, electron paramagnetic resonance (EPR) spectra have also been obtained for all the glass samples to determine the magnetic behavior as well as g values (spin Hamiltonian parameters). The optical basicity of all the glasses lies within the range of 0.621–0.631. All the pristine glasses exhibit band gap energy ranging from 5.80 to 5.89 eV.

## 1. Introduction

Glass and glass ceramics are the most acknowledged class of materials among the various scientific communities these days. The use of glasses and their associated parts in daily life makes them potential to accomplish various purposes in optical, mechanical, electrical, thermal, chemical and electronic fields [1–3]. Although, the structure of glass lacks long range order, the absence of grain boundaries in glasses makes them transparent, thus, leading to numerous optical applications. It is possible to alter local glass structure by tailoring its properties i.e. by addition of modifiers or intermediates or by providing controlled heat treatment to the glass and converting it to a glass ceramic [4–5]. Basically, the change in the local structure and properties of the glass by substitution of modifiers and intermediates depends on their amount, distribution and role played by them in the glass network [6].

Many studies have been carried out on the changes in properties of the glasses upon substitution of different constituents (modifiers or intermediates) in them [7–9]. The alkaline earth borosilicate glasses have also been a specific field of interest for researchers due to their strong structural linkage and high chemical durability [10]. Schwickert et al. reported that the glasses based on hexagonal structure oxides like $La_2O_3$ and $Y_2O_3$ have been special area of interest due to their versatile properties, like increasing mechanical strength and melting point of the glasses [11]. The introduction of lanthanum oxide ($La_2O_3$) to the glass network not only enhances its chemical durability but optical properties as well [12]. The optical glasses developed by CSIR-CGCRI contain $La_2O_3$ and are called as the new generation optical glasses [13]. The importance of these lanthanum based optical glasses is that it reduces the image distortion and optical astigmatism for an enlarged viewing fields, without optical recalculations, decreases the weight of optical systems and efficiently suppress the chromatic/spherical aberration. The structural and physical properties of heavy metal oxide, yttrium oxide ($Y_2O_3$), such as high refractive index, high density, good thermal conductivity, high thermal expansion and remarkable infrared transmission makes it attractive material to be used in modifying the glass properties [14]. The addition of $Y_2O_3$ in the glass structure makes the

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glass resistant to heat and shock [15–16]. Moreover, $Y_2O_3$ when introduced in the glass network leads to the formation of non-bridging oxygen, giving rise to different structural groups and hence, changes the structural and optical characteristics of the glasses [17–18]. Our group has already investigated the influence of modifier ratio on optical properties of strontium based alumino borosilicate glasses [19]. Therefore, the aim of present work focuses on the impact of intermediates on optical and theoretical properties of the present glasses.

Based on these objectives, the influence of $La_2O_3/Y_2O_3$ (X) ratio on the optical properties of $xLa_2O_3$-(10-x)$Y_2O_3$ -15SrO-15CaO-10$B_2O_3$-10$Al_2O_3$-40$SiO_2$ (x = 2,4,6,8) glasses have been studied using different characterization techniques like Fourier transform infrared spectroscopy (FTIR) and UV-Visible spectroscopy of the pristine as well as heat treated glasses. FTIR is performed to determine the functional groups and band positions. The band gap, Urbach energy and refractive index for all the pristine as well as heat treated glasses have been determined. The results of various physical and chemical properties of glasses like density, molar volume, ionic concentration, interatomic distance, optical basicity as well as oxide ion polarizability have been discussed by correlating these parameters in light of non-bridging oxygens. In addition to this, electron paramagnetic resonance (EPR) studies have been performed to determine magnetic behavior, g values, resonance magnetic field and line width of the present glasses. In order to deduce information about the glass structure, theoretical parameters like average cross link density, number of network bonds per unit volume ($n_b$) and average stretching force constant have also been determined. Structure–properties correlation has been established by studying the optical properties thoroughly.

## 2. Experimental techniques

### 2.1. Glass synthesis

The glass series $xLa_2O_3$-(10-x)$Y_2O_3$ -15SrO-15CaO -10$B_2O_3$-10$Al_2O_3$-40$SiO_2$ (x = 2, 4, 6, 8) chosen for the present study with sample labels and corresponding $La_2O_3/Y_2O_3$ (X) ratio are shown in Table 1 [20]. The glasses were prepared by taking required stoichiometric amounts of different constituent oxides or carbonates of 99.9% purity. Each batch was prepared using mortar and pestle by mixing an appropriate mole fraction of desired oxide ingredients in acetone medium. The powder obtained was put in alumina crucible and melted at 1550 °C in high resistance furnace and copper plates were used for quenching the melt in air. The internal stresses were removed by annealing the quenched glasses at 500 °C in preheated furnace. The glass samples (bulk pieces) were then heat treated at 850 °C for 200 h in muffle furnace in order to study the optical behavior of glass ceramics. The density of glasses was measured by Archimedes principle using o-xylene (99.9%) pure as immersion solution.

### 2.2. X-ray diffraction

The XRD studies of powdered glass samples were performed at voltage of 45 kV, $CuK_a$ radiation (λ = 1.5406 A°) using high-resolution XRD in a Bruker D8 X-ray diffractometer. The beam current was 40 mA and the pattern was recorded with scan time per step of 600 s.

**Table 1**
– Composition (mol %) of glasses constituents along with sample labels.

| Sample Name | $La_2O_3$ | $Y_2O_3$ | $Al_2O_3$ | $SiO_2$ | $B_2O_3$ | CaO | SrO | X = $La_2O_3/Y_2O_3$ |
|---|---|---|---|---|---|---|---|---|
| 2 LaY | 2 | 8 | 10 | 40 | 10 | 15 | 15 | 0.25 |
| 4 LaY | 4 | 6 | 10 | 40 | 10 | 15 | 15 | 0.66 |
| 6 LaY | 6 | 4 | 10 | 40 | 10 | 15 | 15 | 1.5 |
| 8 LaY | 8 | 2 | 10 | 40 | 10 | 15 | 15 | 4 |

### 2.3. Molar volume and density

The molar volume ($V_m$) and density of all the present glass compositions can be deduced by using the relation [21]:

$$V_m = M/\rho \quad (1)$$

where M denotes the molar mass and ρ is the density of all the glasses, respectively.

### 2.4. FTIR measurements

The glass powder was dispersed in KBr pellets. 2.0 mg from each sample was mixed with 100 mg of KBr in an agate mortar and pressed into pellets. Infrared transmission spectra using Bruker alpha FTIR-spectrophotometer from 600 to 4000 nm at room temperature was recorded.

### 2.5. UV measurements

The optical transmission spectra of the glasses (powdered) were recorded using a double beam UV-Vis spectrophotometer (Model: U-3900H, Hitachi) in the wavelength range of 200–800 nm at room temperature.

### 2.6. EPR measurements

The EPR spectra of powdered glass samples at room temperature were recorded by Varian E-109 EPR spectrometer in the X-band (< 9.3 GHz) and using 10.0 mW microwave power. The standard *g* marker for the determination of magnetic field used was Diphenyl picryl Hydrazyl (DPPH).

## 3. Results and discussion

### 3.1. X-Ray diffraction

The XRD of all the as prepared glasses is shown in Fig. 1. The amorphous nature of the glasses is indicated by absence of the crystalline phases. A broad hump is obtained between 25 and 35°, for all the glasses.

### 3.2. Molar volume and density

The density of a glass is an important parameter, which depends upon its structure indispensably. A slight change in the glass structure, changes the density markedly [21]. On the other hand, a more useful tool to describe the glass structure, other than density is molar volume. The spatial distribution of ions forming the glass structure is dependent

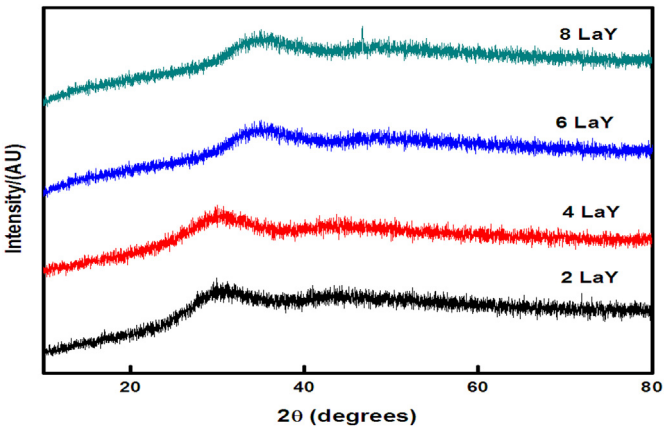


**Fig. 1.** XRD graphs for all the pristine glasses.