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# Dielectric properties of $(100-x)Li_2B_4O_7$–$x(Ba_5Li_2Ti_2Nb_8O_{30})$ glasses and glass nanocrystal composites

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ABSTRACT

Transparent glasses of various compositions in the system $(100-x)(Li_2B_4O_7)$–$x(Ba_5Li_2Ti_2Nb_8O_{30})$ ($5 \le x \le 20$, in molar ratio) were fabricated by splat quenching technique. The glassy nature of the as-quenched samples was established by differential thermal analyses (DTA). X-ray powder diffraction studies confirmed the as-quenched glasses to be amorphous and the heat-treated to be nanocrystalline. Controlled heat-treatment of the as-quenched glasses at 500 °C for 8 h yielded nanocrystallites embedded in the glass matrix. High Resolution Transmission Electron Microscopy (HRTEM) of these samples established the size of the crystallites to be in the nano-range and confirmed the phase to be that of $Ba_5Li_2Ti_2Nb_8O_{30}$ (BLTN) which was, initially, identified by X-ray powder diffraction. The frequency, temperature and compositional dependence of the dielectric constant and the electrical conductivity of the glasses and glass nanocrystal composites were investigated in the 100 Hz to 10 MHz frequency range. Electrical relaxations were analyzed using the electric modulus formalisms. The imaginary part of electric modulus spectra was modeled using an approximate solution of Kohlrausch–Williams–Watts relation. The frequency dependent electrical conductivity was rationalized using Jonscher's power law. The activation energy associated with the dc conductivity was ascribed to the motion of $Li^+$ ions in the glass matrix. The activation energy associated with dielectric relaxation was almost equal to that of the dc conductivity, indicating that the same species took part in both the processes.


## 1. Introduction

Transparent glasses comprising ferroelectric oxide crystals in the nano/micrometer range have received considerable attention, in the last few years, due to the ease with which these could be fabricated apart from their interesting electrical and optical properties which find applications in microwave, pyroelectric and piezoelectric devices [1,2]. The properties of these materials could be controlled by the appropriate choice of the glass composition and the heat-treatment conditions. We have been making attempts to design and fabricate borate and tellurite based materials in amorphous/glass phase for possible applications that include capacitor, pyroelectric, ferroelectric and nonlinear-optic devices [3,4].

One of the families of ferroelectric oxides that we have attempted belong to tetragonal tungsten bronze (TTB) which have been studied extensively owing to their interesting electro-optic, nonlinear-optic and pyroelectric properties and these attractive features make them potentially important for various device applications. The $Ba_5Li_2Ti_2Nb_8O_{30}$ (BLTN), which is a TTB structured material, in the powder form has been investigated for its electric conductivity, permittivity and nonlinear-optical properties [5–7]. It undergoes a ferroelectric to paraelectric phase transition ($T_c$) at 370 °C. In BLTN crystals the six 15CN and 12CN sites are only partially filled by the five barium atoms. Thus, one of them and the four 9CN (CN—coordination number) sites are available for the two lithium atoms. Consequently, the 9CN sites are thus only partially filled (no more than half), leading to an ionic conduction in these crystals. It is required to grow large single crystals of these materials (TTB) for many device applications. It is known that the process of growing large single crystals of device quality is expensive and time consuming. Therefore, it was felt that dispersing these crystallites at nano/micrometer level in transparent (to visible light) glass matrices is one of the alternative and effective approaches to obtain optically clear transparent composites. In this paper, we report the thermal and electrical transport properties of $(100-x)(Li_2B_4O_7)$–$x(Ba_5Li_2Ti_2Nb_8O_{30})$ ($5 \le x \le 20$, in molar ratio) glasses and glass nanocrystal composites. Electrical modulus ($M^* = 1/\varepsilon^*$, where $\varepsilon^*$ is the complex dielectric constant) formalism which has been a common method of describing the features of the frequency dependence of ionic conduction in glasses [8–10] has been employed to rationalize the dielectric properties. The reason

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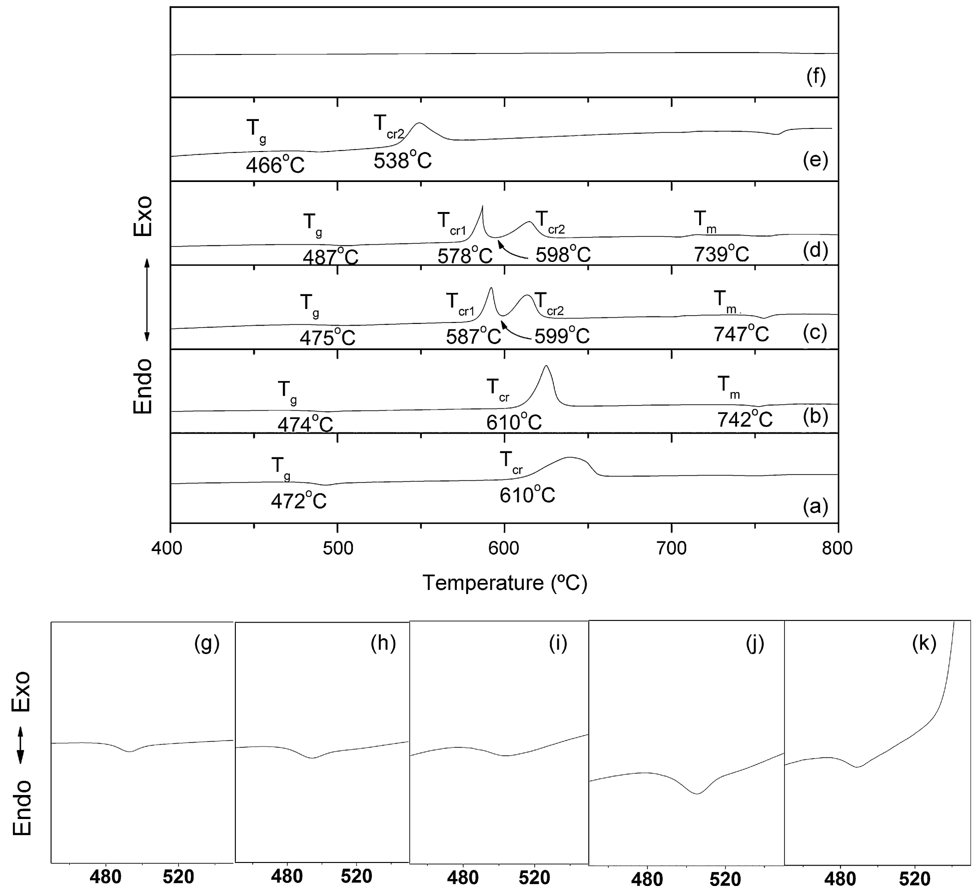


**Fig. 1.** DTA curves of the as-quenched glass samples for various compositions: (a) $x = 5$, (b) $x = 10$, (c) $x = 15$ and (d) $x = 20$ along with (e) 500 °C/8 h and (f) 550 °C/8 h heat-treated samples corresponding to the composition $x = 15$. DTA curves showing glass transition ($T_g$) for as-quenched glass samples corresponding to the compositions: (g) $x = 5$, (h) $x = 10$, (i) $x = 15$ and (j) $x = 20$ along with (k) 500 °C/8 h heat-treated samples corresponding to the composition $x = 15$.

for selecting $M^*$ for describing electrical relaxation in glasses is that electrode effects which may interfere with the bulk behavior of a specimen are suppressed in this representation [11].

## 2. Experimental

Glasses of different compositions in the system $(100 - x)$ $(Li_2B_4O_7)$–$x(Ba_5Li_2Ti_2Nb_8O_{30})$ $(5 \le x \le 20$, in molar ratio) were fabricated via the melt quenching technique using $Li_2B_4O_7$ (LBO) and pre-reacted $Ba_5Li_2Ti_2Nb_8O_{30}$ (BLTN) powders (size ≈ 5 μm). In order to obtain these powders, reagent grade $BaCO_3$, $Li_2CO_3$, $TiO_2$ and $Nb_2O_5$ were ground with pestle and mortar and calcined at 1000 °C for 4 h in air with one intermediate grinding. The formation of monophasic BLTN was confirmed by X-ray powder diffraction (Phillips diffractometer) studies. The pre-reacted BLTN powder was mixed thoroughly with pre-reacted $Li_2B_4O_7$ powder in appropriate ratio and melted at 1000 °C for 30 min. The melt was then quenched in air between two stainless steel plates that were preheated to about 200 °C.

X-ray powder diffraction (XRD) studies were performed at room temperature on the as-quenched and heat-treated samples to confirm their amorphous and crystalline states, respectively. The glassy state of the as-quenched samples was established by subjecting the powders (weighing ≈ 20 mg) to differential thermal analyses (DTA, TA instruments) in the 50–800 °C temperature range. A uniform heating rate of 10 °C/min was employed for this purpose. The values of the glass transition temperature ($T_g$) and the temperature of onset of crystallization ($T_{cr}$) were evaluated based on the DTA traces. High resolution transmission electron microscopic (HRTEM, Technai) studies were carried out on the samples to confirm the presence of crystallites and their dimensions.

The capacitance and dielectric loss ($D$) measurements on gold electroded as-quenched and heat-treated samples (at 500 °C/8 h) were carried out in the frequency range 100 Hz to 10 MHz with a signal strength of 0.5 $V_{rms}$ at various temperatures (50–600 °C). Silver epoxy was used to bond the leads to the samples which were of typical dimensions: 4 mm × 4 mm × 1 mm. A computer controlled HP 4194A impedance/gain phase analyzer (HP 4194A) in conjunction with a high temperature programmable furnace was used to collect the capacitance and dielectric loss data as functions of both frequency and temperature. The dielectric constants were calculated based on the capacitance ($C$), electroded area ($A$) and sample thickness ($d$) measurements according to the formula:

$$C = \frac{\varepsilon_o \varepsilon_r A}{d} \quad (1)$$

where $\varepsilon_o$ is the permittivity of free space, $8.854 \times 10^{-12}$ F/m.

## 3. Results and discussion

### 3.1. Thermal studies

The as-quenched samples were subjected to DTA to assess the glass transition ($T_g$) and crystallization ($T_{cr}$) temperatures. The DTA curves that were obtained for the as-quenched glass pieces of all the compositions are shown in Fig. 1(a)–(d). The DTA curves that are depicted in Fig. 1(a) and (b) correspond to the compositions $x = 5$ and 10, respectively. An endotherm around (472 °C) followed by an exotherm around 610 °C in Fig. 1(a) and (b) correspond to