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Dielectric properties and relaxation dynamics in $PbF_2-TeO_2-B_2O_3-Eu_2O_3$ glasses

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Abstract: Frequency and temperature dependent dielectric dispersion of $20PbF_2-20TeO_2-(60-x)B_2O_3-xEu_2O_3$($x$=0 to 2.5, mole fraction, %) glasses prepared by the melt−quenching technique were investigated in the frequency range 1 Hz−10 MHz and temperature range 313−773 K. Dielectric relaxation dynamics was analyzed based on the electric modulus behavior. Dielectric losses (tan δ) are found to be negligibly small in the temperature range 313−523 K, proving good thermal stability of the glasses. The present Eu_2O_3-doped oxyfluroborate glasses showed low dielectric loss at higher frequency and lower temperature, proving their suitability for nonlinear optical materials.

Key words: doped glass; dielectric spectroscopy; electric modulus; AC conductivity; activation energy; Arrhenius equation

1 Introduction

The competition of speed, cost and reliability of opto-electronic devices in various applications has led to the research for new materials which can meet the distinct requirement. The rare earth(RE)-doped borate glasses are among those materials which have a number of optics and photonics applications. The contribution of these glasses in the last decade is highly promising that the research over various REs and their suitable host material has been studied. From this point of view, borate-based glasses are the best choice, which more clearly shows the relationship between glass structure and optical properties of RE ions. An interesting characteristic of the borate glass is the appearance of variations in its structural properties when RE cations are introduced [1−3]. The structure of the borate glasses is not a random distribution of BO_3 triangles and BO_4 tetrahedra, but a gathering of these units to form well-defined and stable borate groups such as diborate, triborate, tetraborate, that constitute the random three-dimensional network [1]. These units make the borate glasses as one of the best choices for RE doping. Borate glass is a suitable optical material for RE ions with high transparency, low melting point, high thermal stability, good RE ion solubility [2] and shows more clear relationship between glass structure and physical properties. The addition of fluoride content to borate glasses decreases the phonon energy and increases the moisture resistance and transparency in the visible region, which in turn contribute to the reduction in the non-radiative losses. A large glass forming region also exists in the oxyfluoride systems with good and easy glass formation [3]. Lead fluoride gives some special significance with a good ability to form stable glasses over a wide range of concentrations due to dual role as glass modifier and glass former. PbF_2 is a conditional glass former, B_2O_3 is a glass forming oxide and with these two chemicals in the glass matrix, low rate of crystallization, moisture resistance, stable and transparent glasses have been achieved [3].

Among the possible REs, europium (Eu^{3+}) is one of the most investigated and also one of the best optically active elements [1−3]. Eu^{3+} is the most suitable rare earth element for investigating the inhomogeneities amongst the sites of the borate glass host because of its simpler electronic levels and glass network [4]. In particular, the addition of high field strength modifier, promoting the increase of the NBO species in the glass matrix, leads to the general depolymerisation of the network that can be related to the modifications of the optical and physical properties [3]. The trivalent Eu^{3+} ion is much favored among the RE elements because of its great importance

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in various applications such as laser materials, sensors, high density frequency-domain optical memory, amplifiers for fiber optical communications active and inactive components in optical and photonic devices [5]. Due to technological importance of europium ion (Eu^{3+}) and the advantages of above research, Eu_2O_3-doped lead fluoroborate glasses have been synthesized and investigated. A survey of literature shows that there are many reports available on quaternary borate glasses. The study of dielectric properties such as dielectric constant (ε'), loss tangent ($\tan\delta$) and conductivity ($\sigma(\omega)$) over a wide range of frequency and temperature of the glass materials not only helps in assessing the insulating characteristics and understanding the conduction phenomenon but also throws light on the structural aspects of the glasses to a large extent.

The purpose of the present work is to study the electrical conductivity and dielectric properties over a wide frequency range from 1 Hz to 10 MHz and a temperature range from 313 to 773 K for $20PbF_2$−$20TeO_2$−$(60−x)B_2O_3$–xEu_2O_3 glasses with various contents of Eu_2O_3 (0.1%−2.5%).

2 Experimental

2.1 Sample preparation

A series of Eu^{3+}-doped lead fluoroborate glasses $20PbF_2$−$20TeO_2$−$(60−x)B_2O_3$–xEu_2O_3 (where x=0−2.5) were prepared by the melt-quenching technique. The chemical powders were procured through Sigma Aldrich with purity<99%. These powders were thoroughly mixed in an agate mortar and pestle with respect to their glass compositions. The chemical compositions of the glasses with the name of samples are summarized in Table 1.

The thoroughly mixed chemical powders in the porcelain crucible were then kept for melting in an Indfurr electric furnace at 980 °C for 1.30 h. After the retirement of melting period, the molten mass is quenched rapidly on a stainless steel mould maintained at 200 °C. The glasses thus obtained were found to be clear, bubble free, transparent and yellowish in color. These samples were annealed at 200 °C for 3 h to remove induced residual thermal or mechanical stresses caused due to rapid quenching. Samples were then polished with different grain size emery polishing sheets. A thin coating of silver paint was applied on both sides of the sample to serve the purpose of dielectric measurement. The physical parameters like density, refractive of these glasses are given in Table 2.

Table 1 Chemical compositions of glasses

Glass code	$x(Eu_2O_3)$/%	Glass composition
Eu_0	0	$20PbF_2$–$20TeO_2$–$60B_2O_3$
Eu_1	0.1	$20PbF_2$–$20TeO_2$–$59.9B_2O_3$–$0.1Eu_2O_3$
Eu_2	0.5	$20PbF_2$– $20TeO_2$–$59.5B_2O_3$–$0.5Eu_2O_3$
Eu_3	1.0	$20PbF_2$–$20TeO_2$–$59B_2O_3$–$1.0Eu_2O_3$
Eu_4	1.5	$20PbF_2$–$20TeO_2$–$58.5B_2O_3$–$1.5Eu_2O_3$
Eu_5	2.0	$20PbF_2$–$20TeO_2$–$58B_2O_3$–$2Eu_2O_3$
Eu_6	2.5	$20PbF_2$–$20TeO_2$–$57.5B_2O_3$–$2.5Eu_2O_3$

Table 2 Density, molecular mass and refractive of PbF_2−TeO_2−B_2O_3−Eu_2O_3 glasses

Glass code	Molecular mass/(g·mol^{-1})	Density, ρ/(g·cm^{-3})	Refractive index n
Eu_0	122.7309	3.8561	1.6254
Eu_1	123.0132	3.8638	1.6875
Eu_2	124.1424	3.8921	1.7112
Eu_3	125.5539	3.9289	1.7460
Eu_4	126.9655	3.9689	1.7511
Eu_5	128.3770	4.0122	1.7567
Eu_6	129.7886	4.0410	1.7690

2.2 X-ray diffraction

Powder X-ray diffraction (XRD) patterns for all the glass samples in the present investigation were recorded at room temperature using a Rigaku Miniflex 600 X-ray diffractometer with Cu K_α radiation (40 kV and 15 mA) and a graphite monochromator with 2θ from 10° to 90°. XRD patterns of all glass samples are shown in Fig. 1.

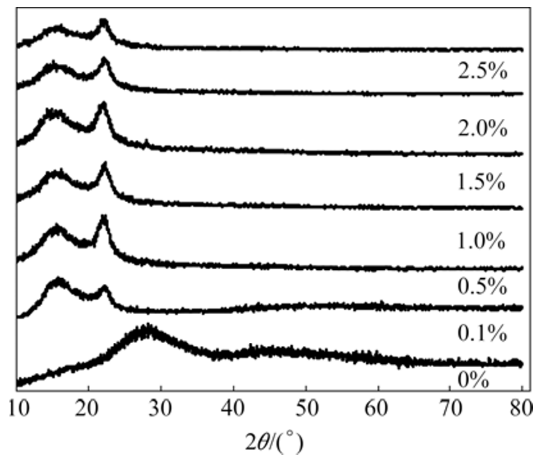

Fig. 1 XRD patterns of powdered samples of PbF_2−TeO_2−B_2O_3−Eu_2O_3 glass

2.3 Conductivity, impedance and dielectric measurement

The conductivity $\sigma(\omega)$, impedance (Z^*), dielectric constant (ε') and dielectric loss ($\tan\delta$) measurements on the as-quenched (annealed) polished glass plates that