ABSTRACT

The physical properties of borate-based glasses comprising crystallites of inorganic materials (polar) at different length scales have become increasingly important owing to their importance in the design and fabrication of composites for multifarious applications. Though ceramics of polar materials meet industrial demands to a great extent, they suffer from higher levels of porosity accompanied by grain boundary related problems which affect their physical properties. One of the diligent ways to circumvent this problem would be to adopt technologically viable alternate routes to fabricate ceramics. Among many others, glass-ceramic route could be effectively used to fabricate nearly pore-free structured ceramics. Indeed, this route provides with greater flexibility to obtain glasses with varied crystallite sizes via devitrification process at appropriate temperatures and duration of heat-treatment. Glass nanocrystal composites (GNC) form a subset of well-known class of materials, glass-ceramics. Therefore, it was in order, to disperse/embed nano crystallites of polar materials in appropriate glass matrices and visualize their physical properties that were of prime academic/technological interest. Barium sodium niobate (BNN) has a filled tungsten bronze structure associated with the general formula (A1)2(A2)4(C)4(B1)2(B2)8O30. It is known to be an interesting material especially from its electro-optic and non-linear optic properties viewpoint. Since growing single crystals of the desired size and shape of BNN is cumbersome, we thought that it was worth attempting to obtain equally transparent (optically) glasses containing nano/micro crystallites of BNN and visualize their physical properties while we are well aware that these properties would be inferior to that of their single crystalline counterparts. However, the challenge lies in tailoring glass nanocrystal composites with the desired microstructures for specific applications.

In the present investigations refractive index and band gap tunability have been accomplished by exercising a strict control over the crystallite sizes of Barium Sodium Niobate (BNN) in borate glass matrix. The frequency and temperature independent dielectric characteristics were demonstrated over a wide range of frequencies and temperatures. An attempt has been made to understand the origin of intense photoluminescence exhibited by these samples particularly at nanoscale. White light emitting phosphor materials have been fabricated by doping Barium Sodium Niobate (Ba2NaNb5O15) ceramics with Er3+. Strontium equivalent *i.e.* Sr2NaNb5O15 to BNN associated with improved piezo properties has been synthesized by adding MnO2 as a sintering aid. An attempt has been made to understand the origin of relaxor behavior of tetragonal tungsten bronze family of oxides. The results that are obtained in the present investigations have been classified into the following chapters. Each chapter is provided with conclusions and a list of references.

Chapter 1 gives a brief exposure to the tetragonal tungsten bronze structured materials. The emphasis has been on the optical, dielectric, ferroelectric and piezoelectric applications of these materials. A preamble to glasses, thermodynamic aspects of glass formation and fabrication of glass-ceramics are also included. The origin of photoluminescence in nano structured materials besides the tunability of their optical properties are included.

Chapter 2 deals with the detailed description concerning various experimental techniques that are employed to synthesize and characterize the materials under investigations.

Chapter 3 includes the details about the evolution of nanocrystalline Ba2NaNb5O15 phase in 2BaO-0.5Na2O-2.5Nb2O5-4.5B2O3 glass system and its refractive index and band gap tunability. Monophasic Ba2NaNb5O15 was crystallized at nanometer scale (12-36 nm) in 2BaO-0.5Na2O-2.5Nb2O5-4.5B2O3 glass system. To begin with, optically transparent glasses in this system were fabricated via the conventional melt- quenching technique. The amorphous and glassy characteristics of the as-quenched samples were respectively confirmed by X-ray powder diffraction and differential thermal analyses. Nearly homogenous distribution of Ba2NaNb5O15 (BNN) nanocrystals associated with tungsten bronze structure akin to their bulk parent structure was accomplished by subjecting the as-fabricated glasses to appropriate heat-treatment temperatures. Indeed, Transmission Electron Microscopy (TEM) carried out on these samples corroborated the presence of BNN nanocrystals dispersed in a continuous glass matrix. The as-quenched glasses were ~75% transparent in the visible range of the electromagnetic spectrum. The optical band gap and refractive index were found to have strong crystallite size (at nano scale) dependence. The optical band gap increased with the decrease in crystallite size. The refractive indices of the glass nanocrystal composites as determined by Brewster angle method were rationalized using different empirical models. The refractive index dispersion with wavelength of light was analyzed by invoking the Sell Meier relations. At room temperature under UV excitation (355 nm), these glass nanocrystal composites displayed violet-blue emission which was ascribed to the presence of defect states.

Chapter 4 comprises the temperature (300-973 K) and frequency (100 Hz-10 MHz) response of the dielectric and impedance characteristics of 2BaO-0.5Na2O-2.5Nb2O5- 4.5B2O3 glasses and glass nanocrystal composites that were studied. The dielectric constant of the glass was found to be almost independent of frequency (100 Hz-10 MHz) and temperature (300-600 K). The temperature coefficient of dielectric constant was 8±3 ppm/K in the 300-600 K temperature range. The relaxation and conduction phenomena were rationalized using modulus formalism and universal AC conductivity exponential power law respectively. The observed relaxation behavior was found to be thermally activated. The complex impedance data were fitted using the least square method. Dispersion of Barium Sodium Niobate (BNN) phase at nanometer scale in a glass matrix resulted in the formation of space charge around crystal-glass interface, leading to a high value of effective dielectric constant especially for the samples heat-treated at higher temperatures. 7ªe fabricated glass nanocrystal composites exhibited *P vs. E* hysteresis loops at room temperature and the remnant polarization (*Pr*) increased with the increase in crystallite size.

Chapter 5 describes the synthesis of fine powders comprising nano crystallites of barium sodium niobate, Ba2NaNb5O15 (BNN) via citrate assisted sol-gel route at much lower temperature than that of conventional solid-state reaction route. The phase evolution of BNN as a function of temperature was investigated by thermo gravimetric analysis (TGA), differential thermal analysis (DTA), Fourier transform infrared spectroscopy (FTIR) and X-ray powder diffraction (XRD). DTA data followed by XRD studies confirmed the BNN formation temperature to be around 923

K. The as-synthesized powders heat-treated at 923 K/10h attained orthorhombic structure akin to that of parent BNN phase. Transmission Electron Microscopy revealed the presence of dislocations in nano crystallites. The optical band gap was calculated using Kubelka-Munk function. These nano crystallites exhibited strong visible photoluminescence (PL) at room temperature. The PL mechanism was explained by invoking the dielectric confinement effect, defect states and generation of self-trapped excitons.

Chapter 6 illustrates the synthesis of Erbium (Er3+) doped nanocrystalline barium sodium niobate (Ba2Na1-3xErxNb5O15 where x=0, 0.02, 0.04 and 0.06) via citrate-based sol-gel route. The desired phase formation was confirmed by X-ray powder diffraction followed by FT-IR studies. The high-resolution transmission electron microscopy facilitated the establishment of the structure of nano crystallites and their morphology. Kubelka-Munk function was employed to obtain the optical band-gap based on diffused reflectance studies carried out on nano sized crystallites. The synthesized samples (x=0.02, heat-treated at 1023 K/2h) exhibited room temperature white light (blue, red and green) emission at a CIE coordinate (0.34, 0.40) and a color temperature ~5280 K, (cool white) under the excitation radiation of 355 nm. The blue (408 nm), green (524, 547 nm) and red (672 nm) emission bands were having their origin in Er3+-*ions*.

Chapter 7 deals with the fabrication of high temperature lead-free ferroelectric ceramics (Sr2NaNb5O15 + x wt% MnO2 (SNN-x Mn)) by conventional solid-state reaction route. Effects of MnO2 addition on the microstructure and electrical properties of Sr2NaNb5O15 ceramics were investigated for different x values (0≤x≤0.5). The microstructural, dielectric, ferroelectric and piezoelectric properties were studied. The MnO2-added SNN based ceramics were found to have tetragonal tungsten bronze structure at room temperature. Nearly equiaxed grains were obtained and the grains became larger with the increase of MnO2 addition up to x=0.25. The Curie temperature *TC* was found to increase with the increase of MnO2 addition besides an enhancement in the dielectric, Polarization *vs.* Electric field (*P–E* hysteresis loop) and strain *vs.* electric field characteristics. For instance, improved polarization performance (2*Pr* =10.78 □C/cm2 and 2*Ec* of 28.06 kV/cm) was obtained for the SNN-0.25 wt% MnO2 added ceramics. It was apparent that the MnO2 added SNN ceramics could show restrained cracks and enhanced piezoelectric properties. These results indicate that the SNN–x Mn ceramics (as lead-free piezoceramics) are promising for piezoelectric based device applications. The details pertaining to the synthesis and fabrication of high-density tungsten bronze Sr2NaNb5-yTayO15 (0≤y≤1.5) ceramics are also reported in this chapter. The effects of Ta5+ substitution on the microstructure and physical properties of the ceramics were systematically investigated. The XRD analyses revealed a decrease in lattice parameter on increasing Ta5+ substitution level. With the increasing of Ta5+ substitution, the orthorhombic– tetragonal transition temperature *TO−T* and the Curie temperature *TC* decreased monotonically. For the ceramics corresponding to y=1.5 the Curie temperature was found to be 273 K, *i.e.* the material is paraelectric at room temperature. Under systematic optimization of the substitution level, improved overall electrical properties *i.e. d33*=71 pC/N, *S*=0.033%, *TC*= 503 K, 2*Pr*=11.96 □C/cm2 and 2*Ec*=28.55 kV/cm were obtained for ceramics corresponding to the composition y (Ta5+)=0.05.

The thesis ends with an overall summary and conclusions followed by the vistas ahead.