ABSTRACT

The design, fabrication and application of materials that are of dimension(s) in the nanoscale form the basis of nanotechnology. Nanotechnology thrives owing to the anomalous, unique or even at times, extraordinary physical properties exhibited by nanomaterials as compared to their bulk counterparts. Also, modern technological advancements in the form of miniaturized instruments and sensors facilitate the use of several forms of nanomaterials. Nanostructures are of different types – nanoparticles/crystals, nanorods and nanowires, thin films, and bulk materials comprising nanoscale structures, etc. Various techniques are employed to synthesize nanomaterials.

They are categorized into two types – top-down and bottom-up approach. Top-down approach includes methods, such as milling and etching, where nanoscale dimensions are achieved by the disintegration of bulk matter. On the other hand, bottom-up approach consists of integration in the atomic scale forming clusters, followed by nucleation and growth processes to obtain nanocrystals. In this thesis a unique method, i.e., glass ceramics is used for obtaining nanostructures embedded in glass matrices. The fabrication process includes two steps – obtaining an amorphous system and inducing controlled crystallization of the desired phase(s), resulting in a composite structure of nanocrystals embedded in a continuous glass matrix. Apart from the ease and flexibility of synthesis, glass-nanocrystal composites possess uniformity and reproducibility in microstructure, with little or no porosity. The other method used to synthesize nanostructures was molten salt synthesis, which is categorized as one of the liquid phase syntheses, where a molten flux in the form of salts with a low melting point is used as a medium for the formation of the desired phase. The importance of molten-salt synthesis can be understood from the ease of synthesis and low time consumption; the technique is economical too.

The thesis focusses on obtaining nanostructures of lithium tantalite ($LiTaO_3$) and lithium niobite ($LiNbO_3$) in glass matrices. The versatility of these two compounds in the fields of electronics and optics is multi-fold. The intriguing properties exhibited by these compounds arise from their non-centrosymmetric rhombohedral crystal structure. Ferroelectricity, pyroelectricity, piezoelectricity, non-linear optic effect and electro-optic effect are some of the many incredible properties exhibited by these materials. More emphasis will be laid on the synthesis and characterization of $LiTaO_3$ in this thesis.

Fabrication of nanostructures of lithium tantalite embedded in a glass matrix is scarce in the literature owing to the tediousness involved in the glass preparation and requires high melting temperature (1600 oC). Therefore, it was worth attempting to find an appropriate glass matrix to crystallize $LiTaO_3$ and analyse their physical properties as a function of crystallite size and volume fraction of crystallization in order to be used in devices. Furthermore, the solid solutions of $LiTaO_3$ and $LiNbO_3$ crystallized in a glass matrix will be interesting from the perspective of tunability of microstructure and other properties. Whereas for nanoparticle synthesis using wet chemical methods, not many tantalum precursors are available. The commonly used tantalum precursor is tantalum ethoxide. Moreover, the synthesis of $LiTaO_3$ nanoparticles from this precursor involves rigorous methodology. This made it even more difficult to synthesize 1-D structures of $LiTaO_3$. Hence, employing molten-salt technique to yield $LiTaO_3$ nanorods proved very important that can be used in several miniaturized devices. The results obtained in the research work are categorized into five chapters apart from the chapters on introduction and experimental methods.

Chapter 1 constitutes a brief introduction to the phenomena associated with the piezoelectric, pyroelectric, ferroelectric and non-linear optical properties of materials with an added emphasis on the structures of lithium tantalite and lithium niobite. Principles behind the fabrication of glasses and glass–nanocrystal composites, and their structures and dielectric properties are also discussed.

Chapter 2 describes in detail the various experimental techniques employed to synthesize and characterize the materials under investigation.

Chapter 3 deals with the analysis of evolution of LiTaO3 nanocrystals in a borate-based glass matrix and, analyse their microstructural characteristics and pyro/ferroelectric properties as a function of heat treatment temperatures. The amorphous composites were obtained using conventional melt-quenching technique, which when heat-treated at temperatures in the range of 530–560 oC/3h yielded nanocrystals of LiTaO3 (of 18–32 nm size). In order to analyse the microstructural evolution during heat treatment, it is imperative to understand the crystallization process involved in the glass system. For that, isothermal crystallization kinetics were performed on the as-quenched glasses by invoking the Johnson–Mehul–Avrami–Kolmogorov equation. A three-dimensional growth with an Avrami exponent of 3.5 and effective activation energy for crystallization of 735 ± 65 kJ/mol was determined from the crystallization kinetics studies. The structural characteristics of the as quenched and heat-treated glasses were realized by employing ray diffraction and Raman spectra analyses. Coalesced nanocrystals forming dendritic spherulites on heat treatment of as-quenched glasses were observed using electron microscopy techniques. Byer and Roundy method was employed to determine the pyroelectric coefficient from the glass-nanocrystal composites and interestingly, the 550 oC/3h heat-treated glasses comprising ~30 nm-sized crystallites exhibit a pyroelectric coefficient as high as 15 nC/cm2K and a remnant polarization, Pr, in the order of 0.42 μC/cm2.

Chapter 4 presents the lithium ion conduction in LiTaO3-based glass–nanocrystal composites. Lithium tantalite in single-crystalline and coarse-grained configurations is a poor ionic conductor and does not qualify as a solid electrolyte for lithium-based batteries. In this chapter, ionic conductivity was sought to be enhanced by use of nanocrystals of LiTaO3 embedded in a borate-based glass matrix. Heat treatment of the as-quenched glasses of composition 3Li2O–4B2O3–Ta2O5 yielded coalesced LiTaO3 nanocrystals of 18–32 nm size, forming dendritic structures in the glass matrix. Impedance analyses of the as quenched and heat-treated glasses show a dramatic improvement in dc conductivity (σdc), with a maximum around 3×10–3 S/m at 200 Oc (σdcT = 1.5 S m–1 K) and activation energy of 0.54 eV for 530 oC/3h heat-treated glasses.

The values of σdc of the as-quenched glasses and of the 530 and 540 oC/3h heat-treated glasses are about seven orders of magnitude higher than that of single crystalline LiTaO3. Furthermore, the effect of heat treatment on lithium ion dynamics in the 40–200 oC temperature range was investigated by modulus formalism, invoking the stretched exponential Kohlrausch–Williams–Watts function. The stretched exponential function was found to be temperature dependent for all the samples under investigation. The activation energies determined from the modulus formalism matched that of impedance analysis.7Li magic angle spinning NMR was used to investigate lithium self-diffusion in the nanostructured glass-nanocrystal composites as a function of temperature between – 10 and 60 oC.

Chapter 5 comprises the synthesis of nanocrystals of LiNb*x*Ta1–*x*O3 (where *x* = 0.0, 0.25, 0.5, 0.75 and 1.0) embedded in a borate glass matrix, and their microstructure and nonlinear optical properties. The solid solution of LiTaO3 and LiNbO3 presents an opportunity to tune

various physical properties. The glasses of 1.5Li2O–2B2O3–*x*Nb2O5– (1–*x*) Ta2O5 system were fabricated by conventional melt-quenching technique where the precursors were melted in the 1200–1300 oC temperature region. Heat treatment of the as quenched glasses was performed in the 530–560 oC (with a dwelling period of 3h) temperature range to induce Nano crystallization. Rietveld refinement of XRD patterns and Raman spectral analysis of the glass–nanocrystal composites confirm the formation of solid solutions of LiTaO3 and LiNbO3. The sizes of the crystallites evolved during heat treatment were determined using Williamson-Hall plot and are in the range 19–37 nm (for *x* = 0–0.75) and 23–45 nm (for *x* = 1.00). Electron microscopic studies confirm a transformation of the morphology of the Nano-crystallites from dendritic star-shaped spherulites for x = 0 to rod-shaped structures for *x* = 1.00, brought about by a coalescence of crystallites. Broad Maker-fringe patterns (recorded at 532 nm) were obtained by subjecting heat-treated glass plates to 1064 nm fundamental radiation. An effective second order non-linear optical coefficient (deff) of 0.45 pm/V, which is nearly 1.2 times the d36 of KDP single crystal, is obtained from the heat-treated glasses of the composition *x* = 0.50 comprising 37 nm sized crystallites. The improved efficiency in *x* = 0.50 is correlated with the spherulitic microstructure obtained from the heat treatment.

Chapter 6 depicts the non-linear optical properties and photoluminescence exhibited by Pr-doped LiNb0.5Ta0.5O3 nanocrystals embedded in a borate-based glass. Glasses of composition 1.5Li2O–2B2O3–0.5Nb2O5–0. 5Ta2O5:xPr6O11 (*x* = 0.0025, 0.005 and 0.010) were synthesized by the conventional melt-quenching technique. Nanocrystal growth was induced by subjecting the as-quenched glasses to heat treatment between 530 and 560oC. Coalesced nanocrystals of sizes in the 20–38 nm range were obtained, which resulted in the formation of dendritic spherulites. Raman studies indicate that Pr3+ ions occupy Li+ vacancies or Nb/Ta andesites. A strong red emission at 620 nm, due to 1D2 → 3H4 electronic transition of Pr3+ ions, was observed upon excitation by a 450 nm radiation.

The maximum intensity of red emission was exhibited by the composition with a Pr doping level of 0.005. The second harmonic generation emanating from the glass nanocrystal composites were recorded as a function of crystallite size and composition. The non-linear optical coefficient as high as 0.77 pm/V (twice that of d36 of KDP single crystal) was obtained from the bulk glass–nanocrystal composites with *x* = 0.0025 comprising 33 nm sized crystallites.

Chapter 7 illustrates the synthesis of single-crystalline LiTaO3 nanorods (of average length 3 μm and width 300 nm) by a facile, yet rapid, molten-salt reaction. In addition to synthesis, the piezoelectric response and second harmonic generation from the nanorods are presented. Potassium chloride (KCl) was used as the flux and heat treatment of the mixture of precursors was performed at 850 oC over a period of 15 minutes. The X-ray diffraction and Raman spectral studies confirm the formation of LiTaO3 phase along with a minor impurity phase (K0.73Li0.27TaO3). The effect of heating rate and concentration of KCl on the yield of nanorods was also investigated. The piezoelectric coefficient of an individual nanorod was determined to be around 8 pm/V, using piezo-force microscopy. The second harmonic emission at 532 nm was recorded as a function of incident intensity (at 1064 nm) in a reflection mode. There was a significant enhancement in second harmonic intensity emanating from the nanorods as compared to the cubic-shaped crystallites of LiTaO3.