Synthesis and analysis of LiNbO$_3$ ceramic powders by co-precipitation method

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The present paper reports on the preparation and analysis of LiNbO$_3$ (LN) ceramic powder by a conventional chemical co-precipitation method. An aqueous mixture of ammonium carbonate along with ammonium hydroxide has been used. Lithium niobate ceramic powders have been sintered at 600, 700, 800, 900 and 1000°C, respectively. Structural analysis of this material has been carried out upon the measurement of XRD, SEM, EDAX Raman and FTIR spectral profiles systematically. Thermal, magnetic, dielectric ($\varepsilon'$ and $\varepsilon''$) and ac conductivity ($\sigma_{ac}$) studies have also been investigated. XRD features of LiNbO$_3$ ceramic powder reveal a hexagonal crystal structure (at an optimized temperature of 800°C) based on JCPDS card No: 20-631 and an average crystallite size of this powder has been calculated using the Scherrer’s formula. The morphology of the LiNbO$_3$ ceramic powder has been studied and the particles are in nano sizes from the HRSEM image. Thermal properties of the as synthesized chemicals mix of the sample have been investigated from the measurement of its TG-DTA features. The dielectric properties of the LiNbO$_3$ have been studied and also its ferromagnetic behaviour has been verified.

Keywords: LiNbO$_3$ ceramic powders, Co-precipitation method, Analysis

1 Introduction

Over the last few years, lithium niobate material has been identified as a significantly important ferroelectric material that possesses a wide range of physical properties which enable it to become technologically potential and relevant for their use in various applications$^{1-5}$. Earlier, solid state reaction method has been so popular in the development of lithium niobate ceramic powder$^{6-8}$. In recent times, special importance has been made towards the usage of co-precipitation method. The advantage of co-precipitation is, it is quite simple and fast, easy control of particle size and composition and various options in the modification of particle surface states and in obtaining the overall homogeneity$^{9}$. In the present work, chemical co-precipitation method has been employed to synthesize lithium niobate ferroelectric ceramic powders in nano-sized particles for understanding the material’s structure, morphology, thermal, electrical and magnetic properties more systematically.

2 Experimental Details

2.1 Preparation of LiNbO$_3$ ceramic powders

Stoichiometric amount of LiNbO$_3$ (99.9%) AR grade (SRL chemicals) was dissolved in a distilled water (100 mL) and also Nb$_2$O$_5$ (99.99%) AR grade (SRL chemicals) was dissolved in a minimum amount of HF after heating in a hot water bath for 20 h. Then, an equal amount of ethyl alcohol (C$_2$H$_5$OH) was added to the above mixed solution containing both lithium nitrate and niobium fluoride. The aqueous mixture of ammonium carbonate (NH$_4$CO$_3$) and ammonium hydroxide (NH$_4$OH) was added with a constant stirring of the above solution mixture to have the value of pH > 10 in order to ensure upon a complete precipitation of lithium carbonate and niobium hydroxide. After filtering, the precipitate was washed several times using distilled water and later it was dried in an oven at 100°C for 12 h. The powders thus obtained have been pressed into circular shaped pellets possessing 1 cm in diameter and having thickness of 1.5 mm by using the PVA as the binder. These pellets were slowly heated to 600°C to get rid of the binder. The pellets of LiNbO$_3$ were sintered at 600, 700, 800, 900 and 1000°C, respectively for 6 h.

2.2 Measurements

XRD pattern was recorded for the LiNbO$_3$ samples sintered at various temperatures using XRD 3003TT Seifert diffractometer with Cu K$_\alpha$ radiation (\(\lambda=1.5406\) Å) at 40 kV and 20 mA with a Si detector. The samples were scanned in the 20 range of 20°-60° at the rate of two degree per min. Peaks indexing were done by using an appropriate JCPDS card. The morphology of the LiNbO$_3$ powder was examined on
a FEI Quanta FEG 200-High resolution scanning electron microscope. The elemental analysis of the synthesized powders was carried out using the EDAX attachment to the SEM system. Raman spectrum was recorded with a He-Ne Laser with 633 nm in the range 100-1500 cm\(^{-1}\) with a spectral resolution of 5 cm\(^{-1}\). FTIR spectrum of LiNbO\(_3\) sample was recorded on a FTIR spectrophotometer with resolution (1.0 cm\(^{-1}\)) in the range 450-4000 cm\(^{-1}\) by using a KBR pellet.

For the synthesized precursor sample, differential thermal analysis (DTA) and thermo gravimetric analysis (TGA) were simultaneously measured in N\(_2\) atmosphere at a heating rate of 10\(^{°}\)C/min on a Netzsch STA 409 simultaneous thermal analyzer. M-H magnetic loop of the LiNbO\(_3\) powders was measured with vibrating sample magnetometer in the field range from \(-20000\) to \(+20000\) Oe. Dielectric properties were performed on an Agilent 4294A precision LCR meter. For measuring, the sample was pressed to form cylindrical pellets of LiNbO\(_3\), thereby forming parallel plate capacitor geometry and the dielectric constant (\(\varepsilon'\)) and also calculated the ac conductivity of the LiNbO\(_3\) ceramic powder.

3 Results and Discussion

X-ray diffraction profiles of the LiNbO\(_3\) powders sintered at 600, 700, 800, 900 and 1000\(^°\)C are shown in Fig.1. It is observed that at lower temperature (600\(^°\)C and 700\(^°\)C) few additional peaks are present and those are found disappearing at 800\(^°\)C during a phase change\(^16\) and the crystallinity of the synthesized LiNbO\(_3\) powders has clearly been found to be improved with an increase in temperature to 800\(^°\)C and also beyond up to 1000\(^°\)C. Since there exists no further betterment in crystallinity beyond 800\(^°\)C and this temperature has been considered to be an optimized sintering temperature. At 800\(^°\)C temperature, XRD pattern of the calcined powder indicating formation of pure LiNbO\(_3\) with hexagonal crystal structure according to JCPDS card No: 20-631 and lattice parameters\(^7\) are \(a = 5.146\)Å and \(c = 13.855\)Å and 800\(^°\)C is optimized temperature. The average crystallinity size is calculated from Scherrer’s formula \((t = K\lambda/(B\cos\theta))\), where \(t\) is the average size of the particles, assuming particles to be spherical, \(K = 0.9\), \(\lambda\) (=1.5406 \(\text{Å}\)) is the wavelength of X-ray radiation, \(B\) is the full width at half maximum of the diffracted peak and \(\theta\) is the angle of diffraction. The crystallite sizes of LiNbO\(_3\) ceramic powder sintered at 800\(^°\)C are at 68 nm.

Figure 2 shows the particles size and morphology of the LiNbO\(_3\) synthesized sample by using high resolution scanning electron microscopy that was sintered at 800\(^°\)C. The morphology of sintered powder is irregular in shape and the average particles are in nano size\(^17\). Systematic study of the microscopy reveals that porous and loosely packed grains of the synthesized sample of the LiNbO\(_3\). However, sintered LiNbO\(_3\) at 800\(^°\)C shows grain boundaries are overlapped to each other and densely packed microscopy is observed. Also, an increase in the grain size with increase in the sintering temperature is noticed\(^18\).

Figure 3 shows the EDAX elemental analysis of the LiNbO\(_3\) ceramic powders sintered at 800\(^°\)C. However, the EDAX of the matrices could not show the presence of lithium because of its atomic number being low\(^19-21\). EDAX of the matrices showing the presence of the niobium (Nb) and oxygen (O) whose
Weigh percentages are 69.88% (atomic percentage 28.55%) and 30.12% (atomic percentage 71.45%), respectively.

The exact composition $X_C = [\text{Li}]/(\text{Li} + [\text{Nb}])$ of the LiNbO$_3$ can be found from the linewidth of some Raman lines, as shown by Schlarb et al. The composition of our samples has been determined from linewidth for the lowest-frequency $E(\text{TO}_1)$ peak which is very intense and well separated from other lines.

The Raman spectrum of LiNbO$_3$ is shown in Fig. 4 exhibiting bands at 153, 172, 239, 258, 319, 368, 431, 471, 584, 621 and 876 cm$^{-1}$, respectively. It can be observed that only frequencies in the range 270-400 cm$^{-1}$ are influenced by Li cation displacements. According to previous results, the 670-550 cm$^{-1}$ range may be assigned to the Nb–O stretching modes involving essentially oxygen atom shifts. The O–Nb–O bending modes appear at and below 432 cm$^{-1}$ thus they are strongly coupled with the Li–O stretching and O–Li–O bending modes. The lowest frequencies at 238 cm$^{-1}$ and 152 cm$^{-1}$ are due to the deformation of the Nb–O framework.

For identifying the functional groups of LiNbO$_3$ ceramics powder, an FTIR spectrum has been recorded from 4000 to 400 cm$^{-1}$ and is shown in Fig. 5. The bands are at 721 cm$^{-1}$ and 624 cm$^{-1}$ are attributed due to the Nb–O vibrations. Peaks 1392 cm$^{-1}$ attributed to CO$_3^{2-}$ band are very weak when the precursor is calcined above 500°C. The bands at 1142 cm$^{-1}$ and 1104 cm$^{-1}$ could be due to anti-symmetric stretching vibration of Li–O. The band at 1629, 2916 and 3425 cm$^{-1}$ are attributed to the hydrogen bonds and is due to the stretching of OH$^-$. The infrared absorption band associated with the OH$^-$ stretching vibration in LiNbO$_3$ has earlier been reported by Smith et al.

The TG profile has been shown in Fig. 6 that the weight loss of the sample has been in a multi step process in the temperature range 30-700°C. The initial
weight loss of the sample takes place between 30°C and 258°C, the observed loss is 12.4% this corresponding to the evaporation of the residual solvent and combustion of organic species. The second weight loss has been noticed to be at 13% in the temperature range 258-550°C due to the evaporation of crystallization of oxide and loss of carbon and hydrogen, respectively. From the DTA curve, has peaks between 305°C to 385°C are believed to correspond to LiNbO$_3$ crystallization. The endothermic peak, lost chemically adsorbed water in the temperature range 180°C-200°C and began to decompose to oxides with the producing of CO, CO$_2$ and O$_2$ gases at 300°C and virtually complete at 420°C.

The $M$-$H$ curve of a material is simply a plot of magnetisation $M$ of the material versus the intensity of an applied magnetising field $H$. Analysis of a magnetic material’s $M$-$H$ curve offers useful insight into its properties and behaviour under an applied magnetic field. Magnetization dependence of the applied magnetic field for LiNbO$_3$ sample. Fig. 7 shows the room temperature magnetic hysteresis ($M$-$H$) loop of the pure LiNbO$_3$. The pure LiNbO$_3$ sample exhibits ferromagnetic behaviour at the room temperature at the applied magnetic field in the range (-20000 to +20000) Oe. From hysteresis loop, the magnetization saturation in forward direction is found to be 520.43×$10^{-6}$ emu and in reverse direction magnetization saturation is found to be-514.54×$10^{-6}$ emu, Coercitivity is 362.13 Oe and retentivity is 59.962×$10^{-6}$ emu.

The frequency dependent of dielectric constants (real part ($\varepsilon'$) and imaginary part ($\varepsilon''$)) of sintered (800°C) LiNbO$_3$ ceramic powder are shown in Fig. 8. Both the values of dielectric constants ($\varepsilon'$ and $\varepsilon''$) are found to be decreasing with an increase in frequency, this situation could be attributed to the relaxation behavior of the material. At lower frequencies, the dielectric constants ($\varepsilon'$ and $\varepsilon''$) are high because of polarization effects at the electrode electrolyte interface with the presence of Li$^+$ ion hopping conduction. The unchanged trends noticed at higher frequencies are because of the induced ionic and electronic dipole moments.

Variation of the ac conductivity ($\sigma_{ac}$) with frequency change for the LiNbO$_3$ ceramic powder sintered at 800°C is shown in Fig. 9. At lower frequency (1 Hz to 1 kHz), there is no significant changes in the ac conductivity. The ac conductivity of LiNbO$_3$ ceramics powder has been increasing with an increase in the frequency from 1 kHz to 1 MHz and the possible reason for this could be because of significant increase in Li$^+$ ion mobility which originates from the vacant sites created by the Nb$^{5+}$ ion of Nb$_2$O$_5$ matrix. The evaluated ac conductivity at
1 MHz is $2.52 \times 10^{-4}$ S cm$^{-1}$ of LiNbO$_3$ has been found to be satisfactorily compared with the literature reports on similar such materials$^{35}$. This material could be suggested as a potential and important electrolyte system for its application in the progress of power sources.

4 Conclusions

In summary, it could be concluded that we have successfully synthesized LiNbO$_3$ ceramic powders using a chemical co-precipitation method and thus obtained good quality samples for their analysis systematically. XRD analysis of the sample has shown that it possesses hexagonal structure and the optimized sintering temperature has been found to be at 800$^\circ$C. Both structural and morphological understanding of this material has been made based on the measurement of SEM, EDAX, Raman, FTIR features. For this technically potential ceramic powder, its dielectric, conductivity and magnetic properties have also been investigated. The hysteresis loop (Fig. 7) of LiNbO$_3$ ceramic powder clearly demonstrates the ferromagnetic nature of the material at the room temperature with an $ac$ conductivity value of $2.52 \times 10^{-4}$ S cm$^{-1}$ at 1MHz. Results of the present work thus provides all encouraging and supportive trends to suggest this material as a novel optical system for its further exploration technologically.

References