Synthesis and characterization of Mn\(^{2+}\): LiNbO\(_3\) nano-particles by co-precipitation method

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By employing a co-precipitation method, nano particles of LiNbO\(_3\) doped with Mn\(^{2+}\) ions have been synthesized from an appropriate stoichiometry of Li\(_{0.5}\)Mn\(_{0.25}\)NbO\(_3\) (which is labeled as LMN). These nano materials have been sintered at different temperatures of 700\(^°\), 800\(^°\), 900\(^°\) and 1000\(^°\)C, respectively in order to evaluate an optimized sintering temperature, based on the measurements of XRD profiles. Morphology of the LMN samples has been examined by HRSE images. Elemental analysis of the sample has been confirmed from EDAX analysis. Besides that, Raman and FTIR spectral profiles have been carried out. Thermal (TGA/DTA and also DSC), magnetic, dielectric (\(\varepsilon'\) & \(\varepsilon''\)), ac-conductivity (\(\sigma_{ac}\)) properties have also been studied for the LMN sample. To understand the structural details of the samples, we have synthesized LiNbO\(_3\) nano particles in addition to Li\(_{0.5}\)Mn\(_{0.25}\)NbO\(_3\) and made a comparison. These preliminary studies have been undertaken to identify their suitability for various applications.

Keywords: LMN-nano particles, Co-precipitation method, Characterization, Nanoparticles, Dielectric property, FTIR

1 Introduction
Lithium niobate, LiNbO\(_3\) (LN) powders have created a great deal of interest amongst the researchers because of their potential in many important applications specifically both in non linear optics and optoelectronics\(^1\). These materials have also been used in numerous other applications such as holographic storage devices, thermal detectors and filters in communication circuits\(^2-4\).

Photorefractive LiNbO\(_3\) crystals have been of intense interest for applications such as holographic data storage and narrow-band wavelength filters for optical telecommunications. Two of the most important properties of LiNbO\(_3\) crystals are dopant and doping level. Usually, LiNbO\(_3\) could be found to be more interesting photorefractive materials after doping it with suitable and appropriate quantities of transition-metal ions such as Fe, Cu, and Mn, to ensure upon photorefractive effects from them. The sensitivity of the LiNbO\(_3\) based holographic storage is to increase the doping of transition metal ions. It is interesting to mention that Fe ion containing LiNbO\(_3\) has extensively been investigated for holographic storage applications\(^5,6\). In the present work, we have undertaken Li\(_{0.5}\)Mn\(_{0.25}\)NbO\(_3\) composition to synthesize in nano particles form by a co-precipitation method and carried detailed studies on structural, thermal, magnetic and electrical properties in evaluating its suitability as a novel material of significant importance for its use in different applications.

2 Experimental Details
2.1 Preparation of Li\(_{0.5}\)Mn\(_{0.25}\)NbO\(_3\) nano powders
Stoichiometry amount of LiNO\(_3\) (99.9%) AR grade (SRL chemicals) was dissolved in distilled water (100 ml) and Nb\(_2\)O\(_5\) (99.99%) of AR grade (SRL chemicals) was dissolved in a required amount of HF after heating in a hot water bath for about 20 h. Then, LiNbO\(_3\) could be found to be more interesting photorefractive materials after doping it with suitable and appropriate quantities of transition-metal ions such as Fe, Cu, and Mn, to ensure upon photorefractive effects from them. The sensitivity of the LiNbO\(_3\) based holographic storage is to increase the doping of transition metal ions. It is interesting to mention that Fe ion containing LiNbO\(_3\) has extensively been investigated for holographic storage applications\(^5,6\). In the present work, we have undertaken Li\(_{0.5}\)Mn\(_{0.25}\)NbO\(_3\) composition to synthesize in nano particles form by a co-precipitation method and carried detailed studies on structural, thermal, magnetic and electrical properties in evaluating its suitability as a novel material of significant importance for its use in different applications.

Then to this, an equal amount of ethyl alcohol (C\(_2\)H\(_4\)OH) was added, hence the resultant solution contains lithium nitrate, manganese 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 pH > 10 in order to ensure upon a complete precipitation of lithium
carbonate, manganese carbonate and niobium hydroxide. After filtering process, the precipitate was washed many times using distilled water and later it was dried in an oven at 100°C for 12 h. The powders thus obtained were transformed into pellets in 1cm diameter and with a uniform thickness of 1.5mm with the PVA as the binder. These pellets were slowly heated to 600°C to evaporate the binder. The pellets of 

\[ \text{Li}_{0.5} \text{Mn}_{0.25} \text{NbO}_3 \] 

were sintered at 700°, 800°, 900° and 1000°C, respectively for 5 h. Further, LiNbO₃ nano particles were also synthesized by a co-precipitation method for making a comparison of its structure with 

\[ \text{Li}_{0.5}\text{Mn}_{0.25}\text{NbO}_3. \]

XRD patterns were recorded for 

\[ \text{Li}_{0.5} \text{Mn}_{0.25} \text{NbO}_3 \] 
samples sintered at various temperatures using XRD 3003TT Seifert diffractometer with CuKα radiation (\( \lambda =1.5406 \) Å) at 40 kV and 20 mA with a Si detector. The samples were scanned in the 2θ range 20°-60° at the rate of two degree per minute. The morphology of the LiNbO₃ 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 (633 nm) in the range 100-1500 cm\(^{-1}\). FTIR spectrum of 

\[ \text{Li}_{0.5} \text{Mn}_{0.25} \text{NbO}_3 \] 

sample was recorded on a FTIR spectrophotometer in the range 450-4000 cm\(^{-1}\) using a KBR pellet.

TGA-DTA was 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 was measured for 

\[ \text{Li}_{0.5} \text{Mn}_{0.25} \text{NbO}_3 \] 
powders using a vibrating sample magnetometer (VSM) in the field range-20000 to +20000G. Dielectric properties were investigated on an Agilent 4294A precision LCR meter and from those, \( ac \) and \( dc \) conductivities of the sample were carried out.

### 3 Results and Discussion

Simultaneous measurement of TGA-DTA allows both heat flow and weight changes in 

\[ \text{Li}_{0.5} \text{Mn}_{0.25} \text{NbO}_3 \] 
sample as a function of temperature in a controlled nitrogen (N\(_2\)) atmosphere as is shown in Fig. 1. The TG profile shows the weight loss of the sample in a multi step process in the temperature range 30°-700°C. The sample initial mass is estimated as 11.02 mg and there exists a major weight loss of the sample between 30°C and 250°C and the observed weight loss is 2.75 mg (25%), this weight loss is due to the evaporation of water, residual solvent and combustion of organic species and decomposition of oxalate group, respectively. DTA analysis shows two exothermic peaks and one endothermic peak at 88°, 218° and 153°C, respectively within the temperature range 30°-250°C. The first endothermic peak at 153°C is assigned to the loss of moisture from the washed precursor powders. The sharp exothermic peak at 218°C corresponds to formation of the crystalline nature of the sample. The second weight loss has been noticed in the range 250°-700°C and is equal to 1.27 mg (11.5%) due to the decomposing oxides in terms of CO and CO\(_2\) which begins at 300°C and gets completed at 420°C. In the temperature range 250°-700°C, DTA curve shows an endothermic and an exothermic peak at 250°C and 368°C, respectively. The endothermic peak at 250°C corresponds to the combustion of organic species and exothermic peak at 368°C which might be attributed to a phase change occurrence in crystallization. The DSC profile of the precursor of 

\[ \text{Li}_{0.5} \text{Mn}_{0.25} \text{NbO}_3 \] 
nano particles is shown in Fig. 2. In DSC measurement, sample undergoes a physical transformation such as a phase transition due to the heat flow. Nature of heat flow in the sample depends on whether the process is exothermic or endothermic.

X-ray diffraction profiles of the 

\[ \text{Li}_{0.5}\text{Mn}_{0.25}\text{NbO}_3 \] 
powders sintered at 700°, 800°, 900° and 1000°C as compared with XRD patterns of LiNbO\(_3\) nano powder are shown in Fig. 3. XRD patterns of LiNbO\(_3\) indicate a hexagonal crystal structure based on the JCPDS card No: 20-631 and lattice parameters are \( a = 5.146 \) Å and \( c = 13.855 \) Å and comparing the XRD result of LiNbO\(_3\) with 

\[ \text{Li}_{0.5}\text{Mn}_{0.25}\text{NbO}_3 \] 
these XRD patterns are found to be shifted towards high diffracting angle and
crystallinity of the Li$_{0.5}$Mn$_{0.25}$NbO$_3$ has been improved with the change in sintering temperature. Sintering temperature of 800°C is found to be optimal sintering 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 Å) is the wavelength of X-ray radiation, $B$ is the full width at half maximum of the diffracted peak in radians and $\theta$ is the angle of diffraction. The average crystallite size is decreased (30 nm) in the case of the Li$_{0.5}$Mn$_{0.25}$NbO$_3$ as compared to LiNbO$_3$ nano powders that are in average crystallite size (68 nm). The crystallite sizes of the Mn: LiNbO$_3$ at different temperatures are found to be at 26, 30, 38, 45 nm for sintering at 700º, 800º, 900º and 1000ºC, respectively.

Figure 4 shows HR SEM images of the morphology of the Li$_{0.5}$Mn$_{0.25}$NbO$_3$ samples that were sintered at different temperatures: 700º, 800º, 900º and 1000ºC. A careful examination of these images indicates that the sample sintered at 700ºC shows porous and loosely packed grains that are in nano sizes whereas the sample sintered at 800ºC shows porous nature of the sample, is found to be decreased and hence, densely packed grains are in existence. However, the sample sintered at 900ºC shows grain boundaries overlap on each other and finally, the sample sintered at 1000ºC shows grain boundaries which are found to be completely overlapped on each other and hence, densely packed situation prevails and similar such trends are earlier reported on a related material in literature 14.

Figure 5 shows the EDAX elemental analysis of the Li$_{0.5}$Mn$_{0.25}$NbO$_3$ nano particles sintered at 800ºC. However, the EDAX of the matrices could not show the presence of lithium because of its atomic number being low as has been observed earlier 15-17. EDAX profile reveals the presence of the niobium (Nb), manganese (Mn) and oxygen (O) whose weight percentages are 69.59% (in terms of atomic percentage 34.45%), 10.74% (atomic percentage 8.99%) and 19.67% (atomic percentage 56.56%), respectively.

The Raman spectrum of Li$_{0.5}$Mn$_{0.25}$NbO$_3$ is shown in Fig. 6 exhibiting bands at 84, 134, 243, 401, 482, 532, 614 and 881 cm$^{-1}$, respectively. It can be observed that only frequencies in the 270-400 cm$^{-1}$ range are influenced by Li cation displacements. Following the earlier reports 18,19, 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 432 cm$^{-1}$ and Li-O stretching mode appears at 395 cm$^{-1}$. The lower frequency based bands at 84, 134 and 243 cm$^{-1}$ are due to the deformation of the Nb–O and Mn–O framework 20.

For identifying the functional groups of Li$_{0.5}$Mn$_{0.25}$NbO$_3$ nano particles, an FTIR spectrum has been recorded from 4000 cm$^{-1}$ to 400 cm$^{-1}$ as shown in Fig. 7. The bands are at 712 cm$^{-1}$ which are attributed to Mn-O stretching vibrations 21 and 504 cm$^{-1}$ are attributed to the Nb-O vibrations. The band at 2925 cm$^{-1}$ is assigned to the C-H stretching. The band at 1065 cm$^{-1}$ could be due to anti-symmetric stretching vibration of Li-O, the bands at 1632 cm$^{-1}$...
Hysteresis loop of magnetization ($M$) versus the intensity of an applied magnetizing field ($H$) of the Li$_{0.5}$Mn$_{0.25}$NbO$_3$ is shown in Fig. 8. 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 Li$_{0.5}$Mn$_{0.25}$NbO$_3$ sample.
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shows paramagnetic behaviour at the room temperature at the applied magnetic field of (−20000 to +20000) G.

The frequency dependence of dielectric constants [real part (\(\varepsilon'\)) and imaginary part (\(\varepsilon''\))] of sintered (800°C) Li\textsubscript{0.5}Mn\textsubscript{0.25}NbO\textsubscript{3} nano particles at room temperature is shown in Fig. 9. Both the values of dielectric constants (\(\varepsilon'\) and \(\varepsilon''\)) are found to be decreasing with an increase in frequency because of a relaxation behaviour of the sample investigated. 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\textsuperscript{+} ion hopping conduction\textsuperscript{23,24}. At higher frequencies, the polarization decreases with an increase in the frequency and then reaches to a constant value. Beyond a certain frequency, external field ions diffusion could not be affected by the alternating field. Hence, the dielectric constant (\(\varepsilon'\)) decreases with an increase in the frequency\textsuperscript{25,26}.

Variation of the ac conductivity (\(\sigma_{ac}\)) with frequency change for the Li\textsubscript{0.5}Mn\textsubscript{0.25}NbO\textsubscript{3} nano powders sintered at 800°C is shown in Fig.10. At lower frequency (1Hz to 1 kHz), there is no significant change in the ac conductivity. Ac conductivity of Li\textsubscript{0.5}Mn\textsubscript{0.25}NbO\textsubscript{3} nano particles increases with an increase in the frequency from 1 kHz to 1MHz and the possible reason for this could be the of significant increase in Li\textsuperscript{+} ion mobility which originates from the vacant sites created by the Nb\textsuperscript{5+} ion of Nb\textsubscript{2}O\textsubscript{5} matrix\textsuperscript{27}. The evaluated ac conductivity at 1 M Hz is \(1.22 \times 10^{-4}\) S cm\textsuperscript{-1}.

The room temperature complex impedance plots (\(Z'\) versus \(Z''\)) of Li\textsubscript{0.5}Mn\textsubscript{0.25}NbO\textsubscript{3} nano particles are
shown in Fig. 11. Plot shape depends on electrode polarization and nature of the current carriers i.e. whether these are electrons or ions. The impedance plot exhibits one semicircle with non zero intercept on Z’-axis at higher frequency. The semicircle is understood to be originating from grain boundary response and high frequency non-zero intercept. The diameter of the semicircle and high frequency intercept on Z’-axis can approximately be considered as grain boundary resistance (\( R_g \)) and grain resistance (\( R_e \)), respectively. From Fig. 11, the single semicircle is attributed to the grain property, which occurs due to a parallel combination of grain resistance \( R_g \) and grain capacitance \( C_g \) of the sample. To evaluate dc conductivity of the sample, \( \sigma_{dc} \), the resistance, \( R_{gb} \) is obtained from the impedance graph with an extrapolation of the impedance at zero frequency. The dc conductivity is calculated from the equation \( \sigma_{dc} = \frac{d}{R_{gb} A} \) (where \( d \) and \( A \) are thickness and area of the of the pellet,respectively) and value of \( \sigma_{dc} \) is \( 1.39 \times 10^{-4} \) S cm\(^{-1}\).

4 Conclusions

Hence, Li\(_{0.5}\)Mn\(_{0.25}\)Nb\(_3\)O\(_7\) nano powders using a chemical co-precipitation method for their analysis systematically, has been successfully synthesized. XRD profiles analysis of the Li\(_{0.5}\)Mn\(_{0.25}\)Nb\(_3\)O\(_7\) sample has enabled us to evaluate the optimized sintering temperature as 800°C. Both structural and morphological understanding of this material has been made based on the measurement of SEM, EDAX, Raman, FTIR features. Form the TG-DTA, and also from DSC features, its thermal stability has been analyzed. For this potential nano sized powder, its dielectric, conductivity and magnetic properties have also been investigated. The hysteresis loop (Fig. 8) of Li\(_{0.5}\)Mn\(_{0.25}\)Nb\(_3\)O\(_7\) nano powder clearly demonstrates the paramagnetic nature of the material at the room temperature with an ac conductivity value of \( 1.22 \times 10^{-2} \) S cm\(^{-1}\) at 1 MHz. and its dc conductivity is at 1.39x10\(^{-4}\) S cm\(^{-1}\). Based on the interesting results, we could therefore suggest this material as a novel material for its use in different applications.

References