Structural characterization of Pr-doped NdMnO$_3$

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ABSTRACT

NdMnO$_3$ is an antiferromagnetic insulator which shows potential applications in spintronics. The microstructural and structural parameters of this compound plays significant role on its properties. The basic building block of the NdMnO$_3$ perovskite structure is MnO$_6$ octahedra. Doping at Nd site of NdMnO$_3$ can significantly change the structural parameters of the compound. In the present work, we have synthesized Nd$_{0.85}$Pr$_{0.15}$MnO$_3$ using sol-gel technique and its structural properties have been studied. Synthesized sample was characterized using TG-DTA, FTIR and XRD analysis. TG-DTA plot shows stability of Nd$_{0.85}$Pr$_{0.15}$MnO$_3$ sample above 700°C. FTIR spectrum shows intrinsic nature of the synthesized sample. Rietveld analysis was performed for the structural analysis of the synthesized sample which shows orthorhombic crystal structure with space group Pnma. Crystallite size was found ~89 nm through Scherer’s formula.

KEYWORDS: X-ray; TGA; DTA; FTIR

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INTRODUCTION

The discovery of magneto-resistance (MR) in doped perovskite manganites such as \( R_{1-x}A_xMnO_3 \), (\( R = \) rare earth cation, La, Nd, Pr, Sm, and \( A = \) alkali or alkaline earth cation, Ca, Sr, Ba, Pb etc.) have attracted considerable attention for their interesting physics and potential for device applications[1-2]. The unique magneto-resistance (MR) behavior has opened up potential applications of these oxide materials such as magnetic sensors and magnetic memories. In addition, understanding the novel transport and magneto-transport properties of these materials is a substantial challenge. NdMnO\(_3\) is an antiferromagnetic insulator which shows potential applications in spintronics. The microstructural and structural parameters of this compounds plays significant role on its properties. The basic building block of the NdMnO\(_3\) perovskite structure is MnO\(_6\) octahedra[3 – 6]. Doping at Nd site of NdMnO\(_3\) can significantly changes the structural parameters of the compound. Many researchers have studied structural and magnetic properties of pure and doped NdMnO\(_3\) compounds but structural investigation after Pr doping at Nd site have not been studied in detail till date. In the present work, we have synthesized \( \text{Nd}_{0.85}\text{Pr}_{0.15}\text{MnO}_3 \) using sol-gel technique and its structural properties have been investigated.

EXPERIMENTAL SECTION

Synthesis of the sample was carried out as shown in figure 1. High purity (>99 %) chemicals were used to synthesize \( \text{Nd}_{0.85}\text{Pr}_{0.15}\text{MnO}_3 \) sample. Initially acetate powders of neodymium, praseodymium and manganese were weighed in the stoichiometric ratio. After weighing, powder acetates were individually dissolved into the mixture of water and acetic acid. Prepared solutions were mixed together then ethylene glycol was added as a fuel and prepared mixture was heated on a hot plate with constant stirring until gel was formed. Gel was then decomposed to obtain precursor. After obtaining dried precursor of \( \text{Nd}_{0.85}\text{Pr}_{0.15}\text{MnO}_3 \), small amount of powder was collected for TG-DTA analysis. After drying, precursor powder was ground using pestle and mortar and then calcined at 400 °C for 12 hours. Calcined powder of the sample was ground again using pestle and mortar. Pallets of ground powder were prepared using hydraulic press and all the prepared pellets were sintered at 1000 °C for 24 hours. The polycrystalline \( \text{Nd}_{0.85}\text{Pr}_{0.15}\text{MnO}_3 \) manganite hereafter will be referred as NPMO.

After sintering, pellets were ground using pestle and mortar and achieved homogeneous powder. Homogeneous powder of sintered pellets was used for FTIR and XRD analysis. Thermo gravimetric and differential thermal analysis (TG-DTA) of the precursor was done using Linseis, STA PT-1600 thermal analyzer. TG-DTA measurement of the sample was performed in the
temperature range of 25 to 800 °C with heating rate of 15 °C/min in an air environment. FTIR measurement of the sample was performed in the range of 400 to 4000 cm\(^{-1}\) using Thermo Scientific, Nilcolet 6700 FTIR spectrometer. Room temperature x-ray diffraction (XRD) measurement of the sample was carried out using Philips X’pert PRO x-ray diffractometer. Software packages like FULLPROF and DIAMOND were used for structural and phase analysis and software packages like OriginLAB and MATLAB were used for graphical analysis.

**Figure 1**: Flow chart of synthesis process.

**RESULTS AND DISCUSSION**

*Thermogravimetric and differential thermal analysis (TG-DTA)*:

TG-DTA measurements of the precursor obtained after drying of gel were carried out using Linseis make STA PT-1600 thermal analyzer to determine the sintering temperature and structural stability. The analysis of the reaction was performed by TGA measurements, in static air atmosphere with heating rate of 15 °C/min in the temperature range of 25 to 800 °C. Figure 2 shows TG and DTA curves of NPMO precursor powder. Plotted TG curve of the sample suggests that reaction was occurred in three stages. Approximately 7% weight loss was observed up to 100°C which is likely due to the evaporation of surface absorbed moisture. Due to release of large amount of gases on combustion of fueland other organic byproducts, almost 2% weight loss was observed in the temperature range of 100-300 °C which was simultaneously confirmed by exothermic peaks in DTA plot. These released energies are useful for oxides formation. Another weight loss was observed up
to 800°C due to the crystallization of NPMO[7]. Therefore, for the required phase formation the sintering temperature and sintering time were adjusted above 800 °C and 24 h respectively for the synthesis of the sample.

**FTIR analysis:**

![Figure 2: TG-DTA curves of NPMO precursor.](image)

![Figure 3: FTIR spectrum of NPMO.](image)
FTIR analysis was carried out using Thermo Scientific make Nilcolet 6700 FTIR spectrometer. Figure 3 shows the room temperature FTIR spectrum of NPMO. Transmittance peak observed in the range 400-600 cm$^{-1}$ normally corresponds to the typical metal oxide bonds. Transmittance observed in the wavelength range of 420-450 cm$^{-1}$ is one of the fundamental absorption which can be assigned to MnO$_6$ Octahedral bending vibration$^8$. Peak present in the region from 580 to 600 cm$^{-1}$ suggests presence of stretching mode of Mn-O bond. No absorption peaks were observed above 600 cm$^{-1}$ which confirms absence of organic impurities in the synthesized compound.

**XRD analysis:**

![Figure 4: Rietveld refined XRD spectrum of NPMO.](image)

X-ray diffraction (XRD) measurement of NPMO powder was carried using Philips X’pert PRO x-ray diffractometer. Rietveld refinement program Full Prof suite was used to refine the crystalline structure of the sintered sample from the obtained XRD measurement. The Rietveld method was used to refine a theoretical profile until it matches the measured profile based on least squares approach. The phase analysis was performed by fitting parameters of the orthorhombic unit cell. Space group “Pnma” was used for the Rietveld refinement of XRD patterns of all the samples. Figure 4 shows Rietveld refined XRD spectrum of NPMO compound. The refined pattern is represented as black continuous lines over the red circled experimental data points. At the bottom of the pattern the residue between the observed data and calculated (I_o-I_c) pattern is shown.
Table 1: Profile factor and crystal structure parameters derived through the Rietveld refinement program.

<table>
<thead>
<tr>
<th>Bragg R-factor</th>
<th>R_{p}^- factor</th>
<th>$\chi^2$</th>
<th>Space Group</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>$\alpha=\beta=\gamma$</th>
<th>Unit cell Volume (Å$^3$)</th>
<th>Crystallite size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12.6</td>
<td>6.45</td>
<td>1.1</td>
<td>Pnma</td>
<td>5.634</td>
<td>7.620</td>
<td>5.413</td>
<td>90</td>
<td>232.41</td>
<td>89</td>
</tr>
</tbody>
</table>

Table 1 represents obtained values of crystal structure parameters, profile factors and cell volume for the NPMO sample derived from the Rietveld analysis. Small R-values of refinement and goodness of fitting ($\chi^2$) indicate that the finest fits have been observed amongst the simulated and measured values of XRD pattern. The measured data for the sample agreed well with the simulated values. The fitted XRD peaks clearly indicate the formation of the NPMO. No unwanted peaks are present in XRD pattern which confirms the absence of other impurity phase in the synthesized NPMO compound.

Average crystallite size was calculated from XRD peaks using Debye-Scherrer’s formula,

$$D = \frac{K\lambda}{\beta_{hkl} \cos \theta}$$

where, D is crystallite size, K is shape factor (0.9) and $\lambda$ is wavelength of x-ray radiation$^1$. Calculated values of crystallite size is 89 nm which confirms nano sized crystallites in the synthesized NPMO compound.

CONCLUSIONS

Pr-doped NdMnO$_3$ compound was successfully synthesized using sol-gel technique. TGA analysis shows stability of sample after 800 $^\circ$C. FTIR analysis confirms the intrinsic nature of the compound. FTIR analysis clearly indicates presence of characteristic MnO$_6$ octahedron in the synthesized sample. XRD results indicate formation of Nd$_{0.85}$Pr$_{0.15}$MnO$_3$ with appropriate amount of Pr doping at Nd site in the sample. Crystallite size calculated using Scherrer’s formula indicates presence of nano sized crystallites in the synthesized compound.

ACKNOWLEDGEMENTS
Authors from Department of Physics, Saurashtra University, Rajkot are thankful to the departmental UGC DRS-SAP & DST-FIST programmes for providing basic facilities.

REFERENCES


[5] Saravanan C. ThiyagarajanR. et al. Effect of Cd doping on magnetocaloric effect and critical behavior analysis on perovskite Nd_{1-x}Cd_xMnO_3 (x = 0, 0.1, 0.2, 0.3, and 0.4) manganite polycrystals. Jou. of Appl. Phy. 2017;122 (24): 245109.

