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Physics

EVIDENCE OF ELECTRICAL CONDUCTIVITY IN $Li_{(4-2x)}NixTi_2O_6$ DOUBLE PEROVSKITE

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ABSTRACT The polycrystalline nature of $Li_{(4-2x)}Ni_xTi_2O_6$ (where X = 0, 0.25, 0.50, 0.75) (LNT) were synthesized by sol-gel method and microwave processing method. The powder X-ray diffraction technique confirms the monoclinic crystal structure and C2/c space group. The high resolution scanning electron microscope studies revealed particle size 30 [1]. The temperature scan of conductivity demonstrated the existence of thermally generated charge carriers. The conduction mechanism in LNT compositions is discussed and found to be band type conduction.

KEYWORDS : lithium nickel titanate; double perovskite; conduction mechanism; activation energy; tolerance factor.

1 INTRODUCTION

Lithium based compounds are important materials in the charge storage device[2]. Lithium based ceramics also find their applications as test blanket. In lithium based compounds, lithium releases its outer electron easily and ceramics are mostly dielectric in nature and titanates are known for their very high dielectric constant[2][3]. The present article gives an insight on the electrical behavior of lithium in double perovskite structure. Partial replacement of lithium with Ni^{2+} resulted in no significant behavioral change.

2 SYNTHESIS PROCEDURE

The starting materials are lithium monohydrate (Sigma- Aldrich, 97%, $LiOH.H_2O$), and nickel nitrate (Sigma-Aldrich, 97.0%, $Ni(NO_3)_2.6H_2O$) and titanium butoxide (Sigma-Aldrich, 97.0%, $Ti(OC_4H_9)_4$). The details of sol-gel synthesis are published in our previous article [1]. The obtained gel from the sol-gel technique is dried. Further obtained powder is calcinated at 900 °C and sintered at 1100 °C for 45 min using microwave furnace[4]. The conductivity measurements are carried on a pelletized sample using LCR bridge (HIOKI-HI Tester 50-3532).

3 RESULTS AND DISCUSSION

The single phase formation of double perovskite LNT is confirmed using the powder X-ray diffraction. The details of the structure and microstructural properties are discussed elsewhere [1]. The perovskite formation is confirmed by the Goldschimit tolerance factor (t) given in relation (1) [5].

$$t = \frac{R_A + R_o}{\sqrt{2}\,(R_B + R_o)} \qquad (1)$$

Where, R_A, R_B is the ionic radii of the A-site and B-site cations and R_o are the ionic radii of O^{2-} ions. Perovskite structure is said to be stable if 't' is between 0.8 and 1.1. On increasing the nickel concentration the perovskite formation t-value decreases. The calculated 't' value for LNT is plotted in Fig 1. As the concentration of nickel increases 't' is found to decrease linearly setting a limit on the nickel concentration in the series[6].

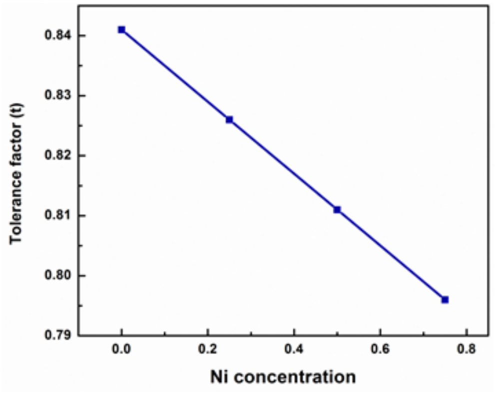


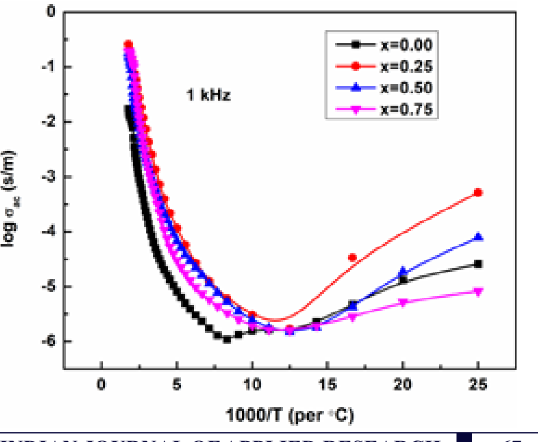
Fig 1: Tolerance factor at different N_i^{2+} composition

3.1 AC CONDUCTIVITY OF LNT

Ac electrical conductivity as a function of 1000/T with different nickel concentration is shown in Fig 2 at 1 kHz and Fig 3 at 10 kHz. The temperature dependent conductivity will explain the intrinsic and extrinsic behavior of the material. It is observed that there are three different regions of conductivity of LNT. The decrease in conductivity with temperature is the low temperature region III (<80°C) suggest metallic behavior is this region. However on further increase of temperature (region II) the conductivity increases linearly then at very high temperatures (region I) a rapid steep rise is observed. This is semiconducting type of behavior with temperature. At this temperature the material can be used as a thermal switch. This change of conduction behavior at around 80°C can act as an instrument safety and health measure to control the electrical supply through the system/device. The sudden change is conduction mechanism might be due to thermally generated charge carriers. Further at high temperature the conductivity due to different nickel concentrations are merging with each other at both the frequencies. This suggests that at high temperatures the thermally generated charge carriers reach saturation. These plots clearly show the multiple conduction and different activation energies. The activation energies are evaluated from Fig 1 and Fig 2 the values are tabulated in Table 1. Activation energy is calculated from the linear variation of ac conduction with 1000/T using Arrhenius relation (2)

$$\sigma_{ac} = \sigma_o \exp(-E_a/kT) \qquad (2)$$

Where, σ_o is the ac conductivity pre-exponential factor and E_a is the ac conductivity activation energy and k is the Boltzmann constant [7]. The donar or acceptor ionization energies are usually 0.1eV as observed in region I. The activation energies ≤0.1 eV suggests band type of conduction in temperature range of region I and II. Very low values of E_a in the low temperature regions III and II once again confirms metallic and semiconducting band nature as observed from the plots [8]. However in the high temperature region I, the steep rise and activation energy ≥0.1 eV suggests electron hopping between multivalent cations. Thus at very high temperatures the conduction is purely due to electron hopping and the mechanism shifts from band type to hopping.



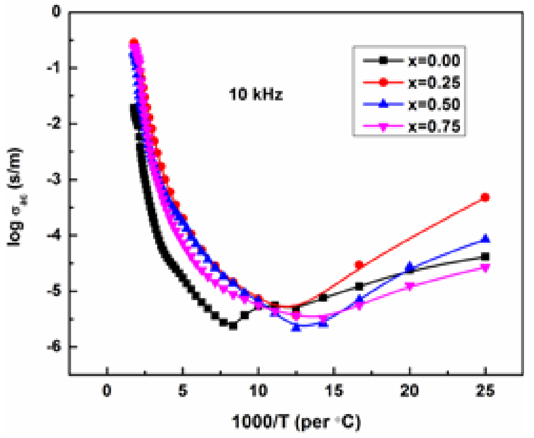


Fig 2: AC conductivity with 1000/T at 1 kHz and 10 kHz

Table 1: Activation Energy at 1 kHz and 10 kHz frequency

Ni concentration	1 kHz			10 kHz		
	E_1	E_2	E_3	E_1	E_2	E_3
0.00	0.137	0.029	0.007	0.131	0.026	0.005
0.25	0.106	0.029	0.014	0.102	0.026	0.014
0.50	0.104	0.023	0.012	0.081	0.019	0.011
0.75	0.126	0.189	0.048	0.115	0.011	0.007

CONCLUSION

The LNT is successfully synthesized by sol-gel method and microwave sintering process. The perovskite structure formation and stability is established the Goldschimit tolerance factor. The thermal spectra of ac conductivity exhibited metallic nature in the low temperature region and semiconducting behavior in the high temperature region. This behavior can be explored in conditional semiconducting devices.

REFERENCES

1. C. Pavithra, W. Madhuri.: Chemical composition of $Li_{(4-2x)}NixTi_2O_6$ by sol–gel method and microwave processing. J. Mat Sci. Mat Ele. (2018) 29:2259–2266.
2. Th. Fehr, E. Schmidbauer.: Electrical conductivity of Li_2TiO_3 ceramics. Solid State Ionics 178 (2007) 35–41.
3. Jun Liang, Wen-Zhong Lu, Jia-Min Wu, Jian-Guo Guan.: Microwave dielectric properties of Li_2TiO_3 ceramics sintered at low temperatures. Materials Science and Engineering B 176 (2011) 99–102.
4. C. Pavithra1, W. Madhuri.: Conductivity and Modulus Study of Lithium Nickel Titanate. Mechanics, Materials Science & Engineering, December 2017 – ISSN 2412-5954. DOI: 10.2412/mmse.86.65.206.
5. S Shanmuga Sundari1, Binay Kumar , R Dhanasekaran.: Structural, Dielectric, Piezoelectric and Ferroelectric Characterization of NBT-BT Lead-Free Piezoelectric Ceramics. *IOP Conf. Ser.: Mater. Sci. Eng.* 43 012010.
6. Chonghe Li, Kitty Chi Kwan Soh, Ping Wu.: Formability of ABO3 perovskites. Journal of Alloys and Compounds 372 (2004) 40–48.
7. M. Krimi, K. Karoui, A. Ben Rhaiem.: Electrical and dielectric properties of the Li 1.5Na0.5WO4 compound. Journal of Alloys and Compounds 698 (2017) 510e517.
8. W. Madhuri, M. Penchal Reddy, Il Gon Kim, N. Rama Manohar Reddy, K.V. Siva Kumar, V.R.K Murthy.: Transport Properties of microwave sintered pure and glass added MgCuZn ferrites. Materials Science and Engineering B 178 (2013) 843-850.