Research Article *ISSN: 2319-507X*
Romakanta Padhy, IJPRET, 2013; Volume 1(8):210-219 *IJPRET*

INTERNATIONAL JOURNAL OF PURE AND APPLIED RESEARCH IN ENGINEERING AND TECHNOLOGY

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NEGATIVE TEMPERATURE COEFFICIENT OF RESISTANCE (NTCR) EFFECT OF NANO LI_2TIO_3

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Accepted Date: 27/02/2013

Publish Date: 01/04/2013

Keywords

Nano ceramic,
NTCR,
Activation energy,
AC conductivity,
Impedance spectroscopy

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Abstract

The electrical properties of nano Lithium titanate (Li_2TiO_3) have been determined with AC impedance spectroscopy was prepared by high energy ball milling (HEBM) technique. The temperature dependence of AC conductivity variations clearly indicates the negative temperature coefficient of resistance (NTCR) behavior. The microstructure of the LT ceramic (sintered at 1000 ^{0}C) were determined by SEM, good crystalline nature was observed with an average of granular size 1 µm. The frequency dependent NTCR behavior with temperature has been determined with AC conductivity. Without doping of Nano LT ceramic has low activation energy (0.238 eV at 10 kHz) and high conductivity in the range of (10^{-3} to 10^{-5} S/cm). The material has semiconducting properties with temperature coefficient in the range of 600 – 800 (K) and following the non-Debye's relaxation process.

INTRODUCTION

Negative temperature coefficients are desirable from the safety point of view, because they help to avoid reactor excursions i.e. to decrease the reactivity growth. The compound formulation is not only for the reactivity growth but also for the development of tritium breeding blankets for fusion reactor. For this many researchers provide different lithium based Ceramics such as lithium orthosilicate (Li_4SiO_4), lithium titanate (Li_2TiO_3), lithium zirconate (Li_2ZrO_3), and lithium oxide (Li_2O). Among them Lithium titanate (Li_2TiO_3) is one of the most promising tritium breeding materials due to their reasonable lithium atom density, low activation, good compatibility with structural materials, excellent tritium release performance and chemical stability [1-3].

Electrical properties may reflect some characteristic features, hence analysis of electrical charge transport in small grained Li_2TiO_3 ceramics, as envisaged for tritium breeding, may contribute to gain information of certain high energy ball-milling process. The NTCR and electrical conductivity is the objective of this study.

In the last decade, reports of conductivity, activation energies of lithium titanate have no one reached minimum activation energy and higher AC conductivity of LT. The AC conductivity increases with increase temperature nothing but a NTCR behavior, due to the contribution of grain and grain boundary resistance. The vanadium doped LLTO, $Li_{0.5-x}La_{0.5}Ti_{1-x}V_xO_3$ (x = 0, 0.05, 0.1 and 0.15) have activation energies and AC conductivities at room temperature (0.2570, 0.2954, 0.2939, 0.2741) and (1.21 x 10^{-6}, 4.438 x 10-5, 8.546 x 10-5, 9.066 x 10-5) compound was prepared by solid state reaction method at 1300 °C [4]. At high temperatures the AC conductivity of LLTO are in the range of 1.4 x 10^{-5} S/cm. These all results clearly indicate the requirement of high AC conductivity and low activation energy of lithium titanate for ceramic breeder blanket applications and solid state electrolyte [1-4].

In the following, we present the microstructure analysis, high AC Conductivity, and low activation energy using SEM and impedance spectroscopy. The frequency dependent NTCR behavior and temperature coefficient (β) explained with the help of AC conductivity, grain and grain boundary resistance. Here we are achieved without doping of LT, low activation energy and high AC conductivity, by following the high energy ball mill (HEBM) technique.

2. EXPERIMENTAL PROCEDURE

2.1. Sample preparation

Polycrystalline Li_2TiO_3 ceramic were synthesized by the high energy ball mill technique (HEBM).The mixture of Li_2CO_3 (Merck 99 %) and TiO_2 (Merck 99 %) powders were used with atomic ratio and ball milled for 10h. For every 1h mill, 15minutes given for cool the samples to decrease the generated heat during the mill period. The temperature of the powders during mill can be high due to two different reasons: firstly, due to the kinetic energy of the grinding medium and secondly, exothermic processes occurring during the mill [5]. Li_2TiO_3 ceramic was obtained by calcining the dried precursors at 700 ^{0}C for 2h. The calcinied powder was pressed uniaxially with 3wt. % PVA (poly vinyl alcohol) solution added as binder. The circular disc sample of 13.5 mm diameter and 2.2 mm thickness. The pellets were sintered at 1000 ^{0}C for 2h. Silver contacts were made on the opposite disc faces and heated at 700 ^{0}C for 15 minutes for electrical measurement.

Compound formation and the microstructure of the sintered pellets were observed by scanning electron microscopy (SEM). The electrical properties of sintered samples were characterized by a HIOKI 3532-50 Hi-Tester LCR at 100 Hz to 1MHz, as a function of temperature.

3. RESULT AND DISCUSSION

3.1. Microstructure analysis

Fig 1 shows the 5 µm scale of SEM morphology of the Li_2TiO_3 ceramic which are sintered at 1000 ^{0}C for 2h. It was found that sintered ceramic has good crystalline and well defined granular nature. The ceramic has average granular size nearly about 1 µm and it can be seen that a few pores were found in the interior of the ceramic. The sizes of the pores were small with distribution in the range of 1-2 µm. However, SEM micrographs show the polycrystalline nature of microstructures with good density.

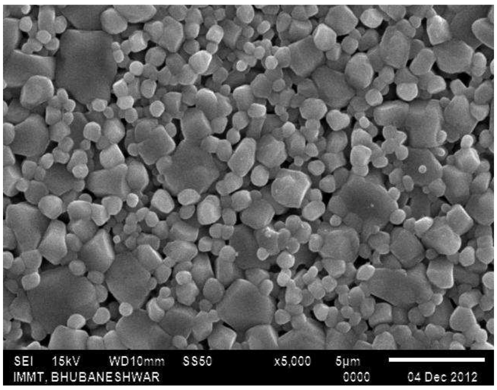

Fig. 1. SEM micrograph of Li_2TiO_3 ceramic sintered at 1000 ^{0}C for 2h.

3.2. Impedance analysis

Impedance analysis is one of the most interesting phenomena, to identify the physical process and characterization of different electrical parameters for the appropriate system. It is useful to understand the dielectric behavior of polycrystalline materials. The most commonly used model is equivalent electric circuits consisting of resistors, capacitors, inductors and specialized distributed elements, when represented in the Nyquist plot. In polycrystalline materials show both grain and grain boundary effects with different time constants, in high frequency semicircle corresponds to the bulk property, and the low frequency corresponds to the grain boundary property [6, 7]. The real and imaginary part of impedance with frequency as a function of temperature is shown in fig. 2(a, b).

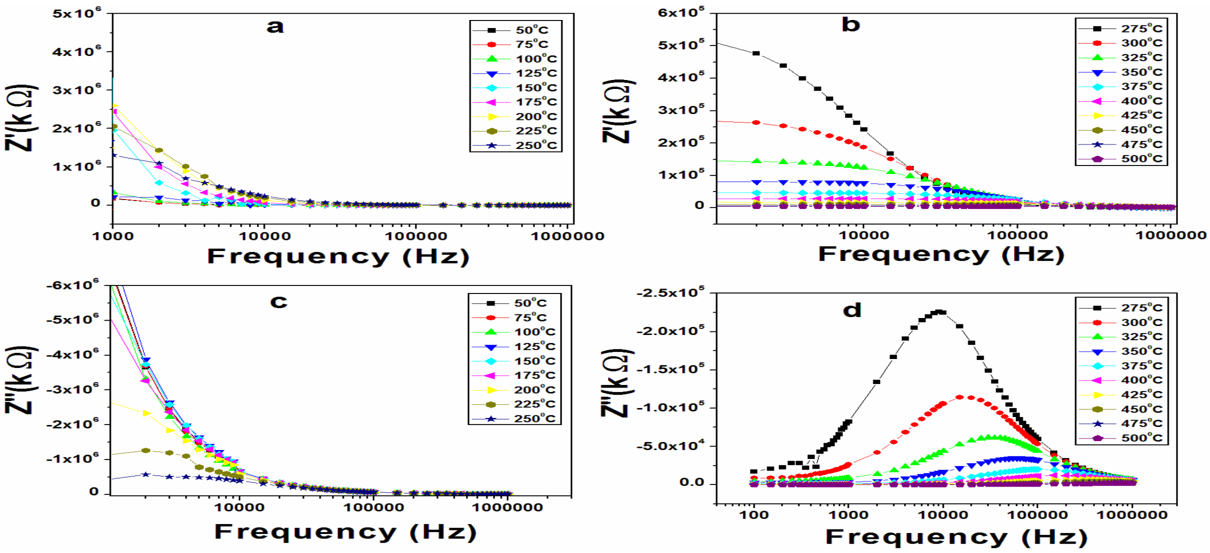

Fig.2. Re (Z) and Im (Z) with frequency as a function of temperature: (a-b) f vs Z' and (c, d) f vs Z"

The magnitude value of peak at resonance frequency decreases and shifting towards high frequency side with change in temperature is shown in fig.2 (c, d). This will indicates the temperature dependence of electrical relaxation phenomena of the materials. The peak point in $Z^{"}$ vs. frequency indicates the relaxation frequency or resonance frequency according to the relation $\omega_{\max}\tau = 1$, where $\omega_{\max}$ is the angular frequency at the $Z^{"}_{\max}$.

The complex impedance spectra (Nyquist-plots) of sintered ceramic measured at different temperatures are shown in fig 3 (a, b). The complex impedance spectrum (CIS) comprised of high frequency semicircle and a low frequency spike in the temperature. The semicircle arcs are gradually decreases with the increase of temperature.

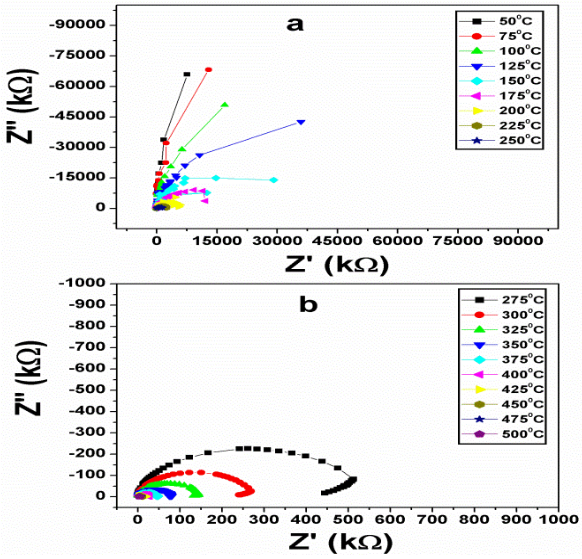

Fig. 3. CIS of Li_2TiO_3 samples at 1000^{0}C: (a) 50 ^{0}C -250 ^{0}C; (b) 275 ^{0}C-500 ^{0}C

At low temperatures the CIS has no identification of semicircular arcs. The semicircular arcs are starts at 175 ^{0}C onwards and well-formed up to 500 ^{0}C, due to the contribution of bulk and grain boundary effect. From this, the material is temperature and frequency dependent. The change in bulk and grain boundary resistance with temperature leads to change in capacitance parameters, bulk capacitance (C_b),and grain boundary capacitance (C_{gb}) with relation frequency (f_r) by the following relation [8]: $2\pi f_r R_b C_b = 1$ and $2\pi f_r R_{gb} C_{gb} = 1$. Debye-type relaxation, has semicircular Argand (Cole-Cole or Nyquist) plots with the center located on the z'-axis. On the other hand for a non-Debye-type relaxation, these Argand complex plane plots are close to semicircular arcs with endpoint on the real axis and the center lying below the abscissa [9, 10]. The proposed system has semicircular Argand plots with center located bellow the real axis, clearly indicates the non-Debye's relaxation.

3.3. Electrical conductivity

Conductivity analysis provides significant information related to transport of charge carriers, i.e. electron/hole or cations/anions that predominate the conduction process and their response as a function of temperature and frequency [11].

A better way of displaying the log-log plot of AC electrical conductivity (σ_{ac}) versus frequency at different temperatures shown in fig. 4 (a, b). The transition from the DC plateau to AC conductivity dispersion region shifts towards higher frequency range. The high frequency dispersion is due to the high probability for the correlated forward and backward hopping at high frequency together of the dynamic cage potential. Therefore we can say that AC Conductivity is dominant in high frequency region [12].

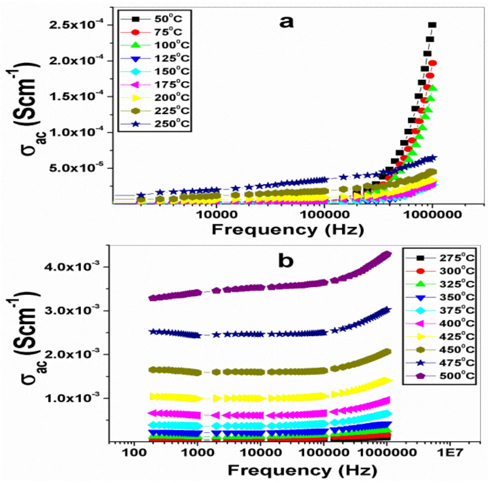

Fig. 4. Variation of AC conductivity with frequency as a function of temperature: (a) 50 ^{0}C-250 ^{0}C (b) 275 ^{0}C-500 ^{0}C

The overall trend of AC conductivity characteristics with frequency represents ''universal'' power law, which is based on rigorous many-body dielectric interaction. Result of ac measurement have been to all Manner of materials and the type of frequency dependence given by universal power law virtually became the hallmark of hopping conduction [14]. The AC conductivity σ can be derived from the universal power law [9, 13] directly related to the imaginary part of dielectric constant (ε'') as:

$$\sigma = \varepsilon_0 \omega \varepsilon''$$

Where, ε_0 and ω is the permittivity of free space and angular frequency respectively. The tangential loss of dielectric material (ε'') was calculated with the real (Z') and imaginary part (Z'') of the impedance parameters. The electrical conductivity (σ_{ac}) of the material is thermally activated and obyes the Arrhenius equation [15]:

$$\sigma_{ac} = \sigma_0 \exp\left(-E_a / K_B T\right)$$

Where E_a activation energy, K_B the Boltzmann constant and σ_0 is the pre exponential factor. AC electrical conductivity of the Li_2TiO_3 evaluated from complex impedance spectrum data was observed as a function of temperature. Fig. 4 (a-b) patterns indicate an increase in conductivity with rise in temperature; it clearly shows the negative temperature coefficient of resistance (NTCR) behavior [16]. The activation energy was calculated with the help of inverse temperature vs. ln(σ_{ac})at 10 kHz, 100 kHz within the temperature range 275 ^{0}C – 500 ^{0}C are 0.238 eV and 0.21 eV. The Ea value decreases with increase in frequency, due to the increase in ionic conductivity. The ionic conductivity is a combination of both macroscopic and microscopic conduction, which is indirectly depend on the bulk R_b and grain boundary R_{gb} resistance. At high temperature only single semicircle could be found, using high frequency data, indicate dominant behavior of grain. The value of activation energy (0.238eV) and conductivity range (10^{-3} to 10^{-4} S/cm) says that material is a semiconductor. Fig. 5 (a, b) shows the variation of resistance with temperature as a function of frequency of Li_2TiO_3 ceramic, has negative temperature coefficient (NTCR) effect which is a contribution of grain boundary effect.The peak point in temperature vs resistivity shifting towards high temperature side with increase the frequency is shown in fig.5. At very high frequencies nearly 1 MHz may be the ceramic will exhibit both NTCR-PTCR effects. The resistance can be calculated by $R = (\frac{1}{\sigma_{ac}}) * (\frac{l}{A})$, where electrical conductivity(σ_{ac}), sample thickness (l) and area of sample (A).

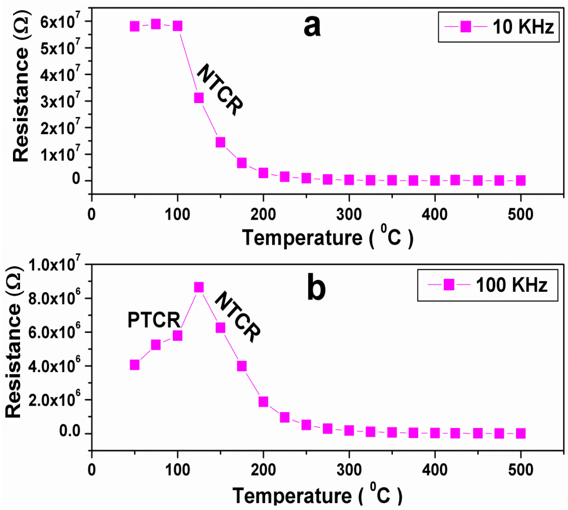

Fig. 5. Temperature dependence of resistance of Li_2TiO_3 sintered at 1000 ^{0}C for 2h: (a) 10 kHz (b) 100 kHz

The resistance variations lie in the range of 10^3 to 10^7i.e in semiconductor range. The nature of NTCR can be explained based on the following equation [17]:

$$R_T = R_O e^{\beta(\frac{1}{T}-\frac{1}{T_O})}$$

Where R_T the resistance at is measured temperature, R_o is the resistance at reference temperature, T is measured temperature, and T_o is reference temperature, and β is negative temperature coefficient of the material. The temperature coefficient value is obtained by above equation, which is in the range of 600 – 800(K). Which means the resistance value will change per degree centigrade is very less. The coefficient is negative when a temperature increases reduces the reactivity. Negative temperature coefficients are desirable from the safety point of view, because they help to avoid reactor excursions. The electrical properties of ceramic have semiconducting properties, which is more suitable for other applications like temperature sensor, self-regulating heaters and current limiting applications.

4. CONCLUSION

The electrical properties of nano Li_2TiO_3 has semiconducting nature and following the non-Debye's relaxation process. The average granular size of 1 µmnano LT were successfully prepared by high energy ball milling sintered at 1000 ^{0}C for 2h. The electrical studies of ceramic have shown that high AC conductivity (10^{-3}S/cm) and low activation energy of lithium titanate for ceramic breeder blanket application and solid state electrolyte. The activation energy decreases (i.e. 0.238eV at 10 kHz to 0.21eV at 100 kHz) with the increase of frequency. The temperature dependence of

AC conductivity variations clearly indicates the negative temperature coefficient of resistance (NTCR) behavior, due to the contribution of grain and grain boundary resistance. The enhancement of the ionic conductivity will also depend on the size of the particle and improvement of the ceramic sample with temperature. At high frequency (1 MHz) and low temperature (below 125 ^{0}C), ceramic has both PTCR-NTCR effect, due to ionic conductivity variations. The knowledge of NTCR behavior of LT ceramic is helpful to avoid reactor excursions.

ACKNOWLEDGMENTS

The authors are thankful to the Board of Research in Fusion Science and Technology (BRFST), for the financially support of "Project No. NFP-MAT-F10-01"

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