Electrical properties of bulk and nano Li_2TiO_3 ceramics: A comparative study

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Abstract: Nanocrystalline and bulk Li_2TiO_3 having monoclinic structure were prepared by mechanical alloying as well as conventional ceramic route. Complex impedance analysis in the frequency range of 100 Hz–1 MHz over a wide range of temperature (50–500 °C) indicates the presence of grain boundary effect along with the bulk contribution. The frequency-dependent conductivity plots exhibit power law dependence, suggesting three types of conduction in the material: low-frequency (100 Hz–1 kHz) conductivity showing long-range translational motion of electrons (frequency independent), mid-frequency (1–10 kHz) conductivity showing short-range hopping of charge carriers and high-frequency (10 kHz–1 MHz) conductivity showing conduction due to localized orientation of hopping mechanism. The electrical conductivity measurement of nanocrystalline and bulk Li_2TiO_3 with temperature shows the negative temperature coefficient of resistance (NTCR) behavior. The activation energy (0.77 eV for nano sample and 0.88 eV for bulk sample) study shows the conduction mechanism in both samples. The low activation energies of the samples suggest the presence of singly ionized oxygen vacancies in the conduction process.

Keywords: nanocrystalline; complex impedance spectroscopy (CIS); AC conductivity; X-ray diffraction (XRD)

1 Introduction

Lithium-based ceramics such as (Li_2TiO_3 , Li_2SiO_4 , Li_2ZrO_3 and LiAlO_3) have been considered as candidates for tritium breeding material in D–T fusion reactors. Li_2TiO_3 has attracted many researchers due to

its strong tritium releasing capacity, high chemical stability, low activation energy and good lithium density. This material shows acceptable mechanical strength when used in a fusion blanket. Much effort has been given to study the properties of Li_2TiO_3 in order to establish it as a blanket material [1–5]. As we know, ^6Li is used as a fuel in the fusion reaction for the generation of tritium. The reaction is as follows:

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Lithium density in the blanket is an important parameter for the economy of fusion reactor. To date, much work has already been done on the fabrication of both pellets and pebbles of Li_2TiO_3 , characterizing tritium releasing behavior and developing the database. Different techniques are routinely utilized to produce Li_2TiO_3 nanoceramic materials, such as sol–gel [6–10], extrusion spherodization [11,12], wet chemical method [13], solution combustion [14], polymer solution [15] and many more. All these chemical and metallo–organic methods have drawbacks with respect to large-scale production, reproducibility, maintenance of stoichiometry and homogeneity in composition, and furthermore require extra high-temperature calcinations. In contrast to the above mentioned techniques, high-energy ball milling (HEBM) provides an environmentally friendly way to prepare Li_2TiO_3 nanoparticles with exceptionally high conductivity, sinterability and good lithium density.

A few works have been reported for the synthesis of Li_2TiO_3 . The feasibility of preparing Li_2TiO_3 that can be compacted and sintered to high density with relatively low sintering temperature and short sintering time in order to have an ideal microstructure and reduce the overall production costs, has been studied by HEBM technique. In this contribution, we discuss the electrical conductivity and complex modulus spectroscopy of both nanocrystalline and bulk Li_2TiO_3 .

2 Experimental procedure

2.1 Conventional solid state technique

Lithium carbonate and titanium dioxide powder was taken in a stoichiometric ratio for the preparation of lithium titanate. The mixture was grinded in a motor pestle with the addition of acetone. The mixture was dried and calcined at different temperatures. Phase analysis of the powder was done by using $\text{Cu K}\alpha$ X-ray diffractometry (XRD). Single-phase monoclinic structure was observed at 1000 °C.

2.2 Mechanical alloying route

Lithium carbonate and titanium dioxide powder was taken in BPR (ball to powder ratio) of 40:1. The mixture was milled in a high-energy planetary ball mill for 10 h. The mixture was allowed to cool every hour. The milled powder was subjected to calcination at different temperatures. Calcined powder was

characterized with respect to phase identification and lattice parameter measurement using $\text{Cu K}\alpha$ XRD. The calcined powder was pressed uniaxially at 41 MPa with 3 wt% PVA solution as binder. The green pellets were sintered at 1000 °C for 2 h. The microstructure of the sintered pellets was studied by scanning electron microscope (SEM, JEOL). The complex impedance spectroscopy (CIS) measurement was done by using LCR meter (Hioki 3532, Japan) in the frequency range of 100 Hz–1 MHz.

3 Results and discussion

Figure 1 shows the X-ray analysis of bulk and nanocrystalline of lithium titanate calcined at 1000 °C and 700 °C respectively. It is observed that the single-phase monoclinic structure is observed at 1000 °C in the case of bulk sample and 700 °C for nano sample. In the case of nano sample, it is observed from the XRD pattern that the formation of lithium titanate starts at 500 °C and the single phase of lithium titanate is formed at 700 °C. The powder calcined at 700 °C demonstrates the monoclinic phase with space group $C2/c$ and is found to be well matched with JCPDS No. 33-0831 with $a = 5.069$ Å, $b = 8.799$ Å and $c = 9.759$ Å. The crystallite size is calculated by using Scherer's equation, which results in an average crystallite size of 88 nm in the case of ball-milled sample after removing crystal strain and instrumental broadening.

Figure 2 shows the differential scanning calorimetry (DSC) curve for the mixture of Li_2CO_3 and TiO_2 with the stoichiometric ratio. The broad endothermic range

Fig. 1 XRD patterns of Li_2TiO_3 : (a) bulk and (b) nanocrystalline.

Fig. 2 DSC and TGA curves of the 10-h milled sample.

of 300–700 °C is present which is associated with the reaction of Li_2CO_3 and TiO_2 as follows:

This reaction is completed at 700 °C. The three broad endothermic peaks at 125 °C, 270 °C and 450 °C are indicated as the removal of bonded water and the decomposition of lithium carbonate and titanium dioxide, respectively. However, it exhibits a highly exothermic event with a major weight loss (about 85%) starting at 292 °C, and there is no further thermal event up to 400 °C. The endotherm from 80 °C to 292 °C is less than 5%, and mass loss occurs up to 660 °C as shown by thermogravimetric analysis (TGA). The most important evidence from the thermal studies is the absence of enthalpy changes at high temperatures, which implies that the reaction is complete and no organic matter or un-reacted phase is present in the sample, and there is no evidence of a phase transition taking place in the sample up to the temperature of 700 °C.

Figure 3 shows the microstructure of bulk and nanocrystalline Li_2TiO_3 . The micrographs reveal well defined grains with limited porosity. It is also clear from the micrographs that there is a variation in grain morphology from the bulk sample to the nano sample. In the bulk sample, neck formation occurs and interparticle distance decreases. Grain boundary distance decreases and bulk transport occurs. Bulk transport mechanism includes volume diffusion, grain boundary diffusion, plastic flow and viscous flow. Plastic flow, which is the most important, occurs during the heating period where the initial dislocation of density is large. It is usually best verified by compacted powder samples.

Fig. 3 SEM micrographs of Li_2TiO_3 : (a) bulk and (b) nanocrystalline.

Complex impedance spectroscopy (CIS) is a useful technique for measurement of electrical response in material. This analysis enables us to resolve the contribution of various processes, such as bulk, grain boundary and electrode effects in the frequency domain [16–18]. Electrical AC data can be represented in any one of the four interrelated formulas:

$$\text{Relative permittivity: } \epsilon^* = \epsilon' - j\epsilon'' \quad (3)$$

$$\text{Impedance: } Z^* = Z' - jZ'' = 1 / (j\omega C_0 \epsilon^*) \quad (4)$$

$$\text{Electric modulus: } M^* = M' + jM'' = 1 / \epsilon^* \quad (5)$$

$$\text{Admittance: } Y^* = Y' + jY'' = j\omega C_0 \epsilon^* \quad (6)$$

$$\tan \delta = \epsilon'' / \epsilon' = M'' / M' = Z' / Z'' = Y' / Y'' \quad (7)$$

where $\omega = 2\pi f$ is the angular frequency; $C_0 = \epsilon_0 A d^{-1}$ is the geometrical capacitance; ϵ_0 is the permittivity of free space; and d and A are the thickness and area of the pellet, respectively.

Figure 4 shows the complex plots of the lithium metatitanate sample. The electrical behavior of the system has been studied over a wide range of temperature starting from 50 °C to 500 °C and

frequency from 100 Hz to 1 MHz. The CIS technique helps us to find various microscopic elements such as intragrain, intergrain, electrode effect and relaxation process. The figures show the Cole–Cole plots of nanocrystalline and bulk Li_2TiO_3 at different temperatures. At low temperature, we have noticed that there is only one semicircle present in the plot which shows only bulk property of the material. After increasing the temperature, the curve bends which forms a depression in the real axis, confirming relaxation in the material. This non-ideal behavior could be attributed to several factors such as grain orientation, grain boundary stress strain phenomena and atomic defect distribution. The semicircular arc of the CIS can be expressed as an equivalent circuit consisting of RC circuits. The presence of two semicircular arcs in the impedance spectrum indicates the presence of both bulk and grain boundary effects in the material. The high-frequency curves are attributed to the bulk property, whereas the low-frequency curves are attributed to grain boundary effect. It has been seen that the sample resistance decreases with increase in

measuring temperature which is an effect analogous to the negative temperature coefficient of resistance (NTCR) of the material. The two equivalent circuits containing RC elements are frequently encountered to describe the grain and grain boundary phenomena in the material. In the circuit model, both grain and grain boundary behaviors are assumed to follow a Debye-like behavior. By considering well-known Brick layer model where the conduction through the grain and grain boundary dominates, the equivalent electrical equation can be written as

$$Z^* = Z' - jZ'' = \frac{1}{R_g^{-1} + j\omega C_g} + \frac{1}{R_{gb}^{-1} + j\omega C_{gb}} \quad (8)$$

$$Z' = \frac{R_g}{1 + (\omega R_g C_g)^2} + \frac{R_{gb}}{1 + (\omega R_{gb} C_{gb})^2} \quad (9)$$

$$Z'' = R_g \left[\frac{\omega R_g C_g}{1 + (\omega R_g C_g)^2} \right] + R_{gb} \left[\frac{\omega R_{gb} C_{gb}}{1 + (\omega R_{gb} C_{gb})^2} \right] \quad (10)$$

At high temperature, the grain boundary plays an important role. The value of Z'' can be written as

$$Z'' = R_{gb} \left[\frac{\omega R_{gb} C_{gb}}{1 + (\omega R_{gb} C_{gb})^2} \right] \quad (11)$$

Figure 5 shows the variations of real part of the impedance with frequency at different temperatures. It is observed from the figures that magnitude of Z' decreases with both frequency and temperature, indicating an increase in AC conductivity with rise in temperature and frequency. The Z' values for all temperatures merge at high frequency. This is due to the release of space charges as a result of reduction in barrier properties of the material with rise in temperature [19,20]. Further at low frequency, the values of Z' decrease with rise in temperature showing NTCR-type behavior similar to that of semiconductors. It is noticed that before merging into a single line, real part of impedance gives a dip which is associated with the paraelectric phase of the material. This dip may be due to charge carrier hopping associated with the material.

Figure 6 shows the variations of imaginary part of the impedance with frequency at different temperatures. The spectrum is characterized by a few important features, such as (1) appearance of peaks in the spectrum, (2) peak broadening with increase in temperature and (3) asymmetric peak broadening. The curves show that the value of Z'' reaches a maximum peak ($Z''_{\max}$) at certain frequencies and falls down with

Fig. 4 Variations of real (Z') and imaginary (Z'') parts of complex impedance of Li_2TiO_3 at different temperatures: (a) bulk and (b) nanocrystalline .

Fig. 5 Variations of real part (Z') of complex impedance of Li_2TiO_3 with $\log f$ at different temperatures: (a) bulk and (b) nanocrystalline.

Fig. 6 Variations of imaginary part (Z'') of complex impedance of Li_2TiO_3 with $\log f$ at different temperatures: (a) bulk and (b) nanocrystalline.

the value of the peak shifts towards higher frequency, which indicates active conduction through the grain boundary. The magnitude of grain boundary also decreases with increase in temperature, which shows loss in resistivity property in the material. With increase in temperature, the value of Z'' merges in the high-frequency region. This may be the temperature-dependent relaxation phenomenon in which the hopping of charge carriers and polarons is dominating in the polycrystalline material [21,22]. From the graphs, it shows that with the increase in temperature, peak broadening occurs which shows the temperature-dependent relaxation phenomenon in the material. The asymmetric broadening of peaks suggests the spread of relaxation time in the material.

Figure 7 shows variations of AC conductivity with frequency at different temperatures. The conductivity has increased monotonically with frequency in the measured frequency range from 100 Hz to 1 MHz. The slope of the conductivity gives the amount of charge carriers present in the material. The value of AC conductivity can be easily understood from the power law given by Ref. [23]:

$$\sigma(\omega) = A(T)\omega^n + \sigma(T) \quad (12)$$

where $A(T)$ is a pre-exponential function dependent on temperature; $\sigma(T)$ corresponds to the DC conductivity; and n is a universal factor. It is a function of both temperature and frequency and corresponds to short-range hopping of charge carriers through trap sites separated by energy barriers of different heights. Figure 8 shows variations of AC conductivity with temperature at different frequencies. The bulk electrical conductivity can be written as

$$\sigma_b = \frac{1}{R_b} \times \frac{l}{A} \quad (13)$$

where l is the thickness; A is the area of the electrode deposited in the sample. The values of bulk resistance R_b and grain boundary resistance R_{gb} are obtained from the high-frequency and low-frequency intercepts of the semicircle on the real axis in the CIS plot, respectively. Figure 9 shows the variations of DC conductivity of both bulk and nanocrystalline Li_2TiO_3 .

When the starting reactants are used to prepare Li_2TiO_3 , there is a distinct possibility that the resulting compound will be oxygen rich and cations will act as acceptor sources causing conduction in the material. In ceramic samples, some conduction mechanisms associated with material properties are as follows:

Fig. 7 Variations of AC conductivity of Li_2TiO_3 with $\log f$ at different temperatures: (a) bulk and (b) nanocrystalline.

Fig. 8 Arrhenius plots of AC conductivity of Li_2TiO_3 : (a) bulk and (b) nanocrystalline.

Fig. 9 Variations of DC conductivity of bulk and nanocrystalline Li_2TiO_3 with inverse of temperature.

(1) The conduction mechanism due to the small polarons associated with lattice strain accompanied by free charges.

(2) Ionic conductivity, which is an intrinsic conduction mechanism in dielectric materials at high temperatures.

Each one of the above mentioned mechanisms contributes to the total electrical conductivity of the compound and is thermally activated. In order to explain the conductivity as a function of temperature and frequency, we have to investigate lithium incorporation and microstructure of the compound [23]. In ceramic samples, oxygen vacancies are usually considered as one of the mobile charge carriers. The ionization of oxygen vacancies creates conducting electrons, which are easily thermally activated. From the results of conduction and the value of the activation energy for conduction, it clearly suggests a possibility that the conduction of charge carriers in the high-temperature range may be oxygen vacancies [24]. The conductivity variation indicates an increase of conductivity with rise in temperature with a typical Arrhenius-type behavior having linear dependence on logarithm of frequency. The type of temperature dependence of DC conductivity indicates that the electrical conduction in the material is a thermally activated process [25]. The activation energy is calculated from the linear portion of the plot of DC conductivity versus $10^3/T$. The activation energy calculated from bulk and grain boundary effects is higher as compared to bulk sample. Bulk resistance (R_b), bulk capacitance (C_b) and relaxation frequency (f_0) of Li_2TiO_3 sample are shown in Table 1.

Table 1 Bulk resistance (R_b), bulk capacitance (C_b) and relaxation frequency (f_0) of Li_2TiO_3 nanoceramic sample and $\omega R_b C_b$ as product

Parameter	System	Temperature ($^{\circ}\text{C}$)								
		300	325	350	375	400	425	450	475	500
R_b ($10^4\Omega$)	Bulk	55	27	13.5	7.25	4.1	2.4	1.4	0.85	0.52
	Nano	28	14	8.1	4.8	2.9	1.8	1.1	0.7	0.52
C_b (10^{-11}F)	Bulk	72.3568	1.17914	1.68449	87.8261	86.2791	1.20594	1.51604	2.08084	3.06124
	Nano	1.13703	1.17914	1.96524	73.6967	1.09782	1.36055	1.80892	2.39375	3.06124
f_0 (10^4Hz)	Bulk	4	5	7	25	45	55	75	90	100
	Nano	5	6.5	10	45	50	65	80	95	100
$\omega R_b C_b$	Bulk	0.9999	0.9999	0.9999	0.9999	0.9999	0.9999	0.9999	0.9999	0.9999
	Nano	0.9999	0.9999	0.9999	0.9999	0.9999	0.9999	0.9999	0.9999	0.9999

Electric modulus formula is proposed to understand the electrical conduction phenomena occurred in the material. The complex electric modulus M^* is defined in terms of complex dielectric constant ε^* and represented as

$$M^* = M' + iM'' = 1/\varepsilon^* \quad (14)$$

$$M^* = M' + iM'' = \frac{\varepsilon'_r}{(\varepsilon'_r)^2 + (\varepsilon''_r)^2} + i \frac{\varepsilon''_r}{(\varepsilon'_r)^2 + (\varepsilon''_r)^2} \quad (15)$$

where $M' = \omega C_0 Z''$ and $M'' = \omega C_0 Z'$; C_0 is the geometrical capacitance.

Figure 10 shows the variation of real part of complex modulus with frequency at different temperatures. M' approaches to zero at all temperatures suggesting the suppression of electrode polarization. M' reaches a maximum value corresponding to $M_{\infty} = (\varepsilon_{\infty})^{-1}$ due to the relaxation process. It is also observed that the value of M_{∞} decreases with increase in temperature. Figure 11 shows the variation of imaginary part of complex modulus with frequency at different temperatures. The modulus peak shifts towards higher frequencies with increase in temperature. This evidently suggests the involvement of temperature-dependent relaxation phenomenon occurs in the material. The frequency region below the M'' peak indicates the long range drift of Li^+ ions, whereas above the peak the ions are spatially confined to potential wells and are free to move within the wells. The frequency range where the imaginary peak occurs shows the long range to short range mobility of charge carriers. The electric modulus (M^*) could be expressed in terms of Fourier transform of a relaxation function $\varphi(t)$:

$$M^* = M_{\infty} \left[1 - \int_0^{\infty} \exp(-\omega t) \left(-\frac{d\varphi}{dt} \right) dt \right] \quad (16)$$

where the function $\varphi(t)$ is the time evolution of the

Fig. 10 Variation of real part of modulus of Li_2TiO_3 with $\log f$ at different temperatures: (a) bulk and (b) nanocrystalline.

electric field within the material and is usually taken as the Kohlrausch–Williams–Watts (KWW) function:

$$\varphi(t) = \exp \left[- \left(\frac{t}{\tau_m} \right)^{\beta} \right] \quad (17)$$

where τ_m is the conductivity relaxation time; the exponent β ($0 < \beta < 1$) indicates the deviation from Debye-type relaxation. The imaginary part of electric modulus (M'') is defined as

Fig. 11 Variation of imaginary part of modulus of Li_2TiO_3 with $\log f$ at different temperatures: (a) bulk and (b) nanocrystalline.

$$M'' = \frac{M''_{\max}}{(1-\beta) + \frac{\beta}{1+\beta} \left[\beta \left(\frac{\omega_{\max}}{\omega} \right) + \left(\frac{\omega}{\omega_{\max}} \right)^\beta \right]} \quad (18)$$

where $M''_{\max}$ is the peak value of M'' ; $\omega_{\max}$ is the corresponding frequency.

Figure 12 shows the variation of M'' with M' at different temperatures from 300 °C to 500 °C. It shows a complete semicircle overlapping each other. The overlapping in the case of M'/M'' shows a strong evidence of long range of conductivity. It also shows that all dynamic processes occurring at different frequencies exhibit the same thermal activation energy.

4 Conclusions

In summary, we have performed a comparative investigation of bulk and nanocrystalline Li_2TiO_3 ceramics. We find that (1) single-phase monoclinic structure is exhibited at 700 °C (nano sample) as compared to bulk sample (1000 °C); (2) charge carriers

Fig. 12 Complex modulus plot of Li_2TiO_3 at different temperatures: (a) bulk and (b) nanocrystalline.

are more prominent in the nano sample for which it gives more conduction; (3) activation energy, AC conductivity, DC conductivity are greatly improved in the case of nano sample which in turn improves conductivity; (4) bulk resistance and grain boundary resistance of nano sample are found to be lower than those of bulk sample. From the electrical properties, it shows that charge carriers are confined in their respective potential well. It also shows that due to oxide ions conduction process occurs in the material. Two semicircles reflect both bulk and grain boundary conduction in the material.

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