Solid State Sciences 12 (2010) 350–354

Contents lists available at ScienceDirect

Solid State Sciences

journal homepage: www.elsevier.com/locate/ssscie

# Synthesis and electrical properties of $(LiCo_{3/5}Fe_{1/5}Mn_{1/5})VO_4$ ceramics

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ARTICLE INFO

*Article history:*
Received 21 August 2009
Received in revised form
25 October 2009
Accepted 23 November 2009
Available online 26 November 2009

*Keywords:*
Ceramic oxides
Solution-based chemical method
Electrical impedance
Electrical conductivity

ABSTRACT

$(LiCo_{3/5}Fe_{1/5}Mn_{1/5})VO_4$ ceramic was synthesized via solution-based chemical method. X-ray diffraction analysis was carried out on the synthesized powder sample at room temperature, which confirms the orthorhombic structure with the lattice parameters of $a = 10.3646$ (20) Å, $b = 3.7926$ (20) Å, $c = 9.2131$ (20) Å. Field emission scanning electron microscopic analysis was carried out on the sintered pellet sample that indicates grains of unequal sizes (~0.1 to 2 μm) presents average grains size with polydisperse distribution on the surface of the ceramic. Complex impedance spectroscopy (CIS) technique is used for the study of electrical properties. CIS analysis identifies: (i) grain interior, grain boundary and electrode–material interface contributions to electrical response (ii) the presence of temperature dependent electrical relaxation phenomena in the ceramics. Detailed conductivity study indicates that electrical conduction in the material is a thermally activated process. The variation of A.C. conductivity with frequency at different temperatures obeys Jonscher's universal law.



## 1. Introduction

Recently, the study of the properties of lithium-based ceramic oxides has considerable interest due to its importance in the fundamental understanding of the physical processes as well as its proposed applications for many technological purposes [1–4]. A number of such oxides such as $LiMnO_4$ [2,3], $LiCoVO_4$ [4], $LiNiVO_4$ [4], $LiCoO_2$ [5,6], $LiMnO_2$ [7], etc have been prepared via various routes and are very useful for applications in lithium batteries. One such lithium-based ceramic oxide is $(LiCo_{3/5}Fe_{1/5}Mn_{1/5})VO_4$ ceramic which is mechanically strong. One physical property of this oxide can be (electrical impedance, electrical conductivity, etc) studied using complex impedance spectroscopy technique [8]. Many researchers have studied the electrical properties of different lithium-based ceramic oxides using this technique [1,9–10]. The complex impedance spectroscopy measurement of electrical properties is based on the measurement of cell impedance/admittance over a range of temperatures and frequencies and analyzing/plotting them in complex impedance plane (Nyquist diagrams) [8,11]. Semicircles in Nyquist diagrams represent electrical phenomena due to the bulk material, grain boundary effect and interfacial polarization [8,11,12]. Therefore, in this paper, I report the structural, microstructural and electrical properties of $(LiCo_{3/5}Fe_{1/5}Mn_{1/5})VO_4$ compound. Electrical properties are examined by A.C. technique of complex impedance spectroscopy (CIS).

## 2. Experimental details

### 2.1. Materials preparation

Solution-based chemical method was used to prepare the $(LiCo_{3/5}Fe_{1/5}Mn_{1/5})VO_4$ fine powder. The stoichiometric amount of highly pure $LiNO_3$ (98%, M/s Loba Chemie Pvt. Ltd., India), $Co(NO_3)_2 \cdot 6H_2O$ (97%, E. Merck (India) Ltd.), $FeCO_3$ (97%, M/s CDH, India), $MnCO_3$ (98%, M/s Loba Chemie Pvt. Ltd., India) and $NH_4VO_3$ (99%, M/s s.d. fine-chem Pvt. Ltd., India) were dissolved in distilled water and mixed together. $FeCO_3$ and $MnCO_3$ were dissolved in warm distilled water in the presence of oxalic acid. After some time triethanolamine (TEA) (>97%, E. Merck (India) Ltd.) was added maintaining a ratio of 3:1 with metal ions. $HNO_3$ (68–72%, E. Merck (India) Ltd.) and oxalic acid (>99%, E. Merck (India) Ltd.) were added to dissolve the precipitation and then the clear solution was evaporated at ~200 °C temperature with continuous stirring. A fluffy, mesoporous and carbon-rich precursor mass was formed by complete evaporation of the solution. After grinding, the voluminous, fluffy and black carbonaceous mass was calcined at 550 °C for 3 h to produce the desired phase, which is confirmed by X-ray diffraction analysis. The calcined powder was cold pressed into circular disc shaped pellet of diameter of 12–13 mm and various thicknesses with polyvinyl alcohol as the binder using hydraulic press at a load of ~3 to 4 tonnes. These pellets were then sintered

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doi:10.1016/j.solidstatesciences.2009.11.012

at 575 °C for 2 h followed by slow cooling process. Subsequently, the pellets were polished by fine emery paper to make their faces smooth and parallel. The pellets were finally coated with conductive silver paint and dried at 150 °C for 3 h before carrying out electrical measurements.

### 2.2. Materials characterization

X-ray diffraction analysis of the calcined powder was studied at room temperature using a diffractometer (PANalytical PW 3040/60 X'Pert PRO) in the angle range $20^\circ \leq 2\theta \leq 80^\circ$ on being irradiated by Cu K$\alpha$ radiation of wavelength equal to 1.5419 Å. The surface morphology of the gold-sputtered sample has been recorded with different magnifications at room temperature using a ZEISS (Model: SUPRA™ 40) field emission scanning electron microscope. Electrical impedance ($Z$), phase angle ($\theta$), tangent loss ($\tan\delta$) and capacitance ($C_p$) were measured by applying a voltage of ~0.701 V using a computer-controlled frequency response analyzer (HIOKI LCR Hi TESTER, Model: 3532-50) with varying temperature over the frequency range of $10^2$–$10^6$ Hz.

## 3. Results and discussion

### 3.1. Structure/microstructure

X-ray diffraction study has been carried out to confirm the formation and phase formation of the prepared compound. Fig. 1 represents the X-ray diffraction pattern of the sample at room temperature. X-ray diffraction data have been analyzed using standard computer software (POWD MULT) [13], which identifies orthorhombic structure of the compound with lattice parameters of $a = 10.3646\ (20)$ Å, $b = 3.7926\ (20)$ Å, $c = 9.2131\ (20)$ Å. The lattice parameters were refined by a least squares refinement method. The microdensity, i.e. theoretical density ($\rho_{theoretical}$) of the compound was found out to be 3.2891 g/cm$^3$ which are calculated using the given formula:

$$\rho_{theoretical} = \frac{\sum A/N}{V} = \frac{1.66\sum A}{V}. \quad (1)$$

where $A$ is the sum of the atomic weights of all the atoms in the unit cell, $N$ is the Avogadro number and $V$ is the volume of the unit cell (cm$^3$). Corresponding bulk (measured) density ($\rho_{measured}$) of the compound is worked out to be 3.2321 g/cm$^3$ which are calculated using the formula:

$$\rho_{measured} = \frac{\text{mass of the sample pellet}}{\text{volume of the sample pellet}}. \quad (2)$$

The percentage (%) of porosity is evaluated using the defined relation:

$$\%\text{porosity} = \frac{(\rho_{theoretical} \sim \rho_{measured}) \times 100}{\rho_{theoretical}}. \quad (3)$$

and works out to be 1.73.

Field emission scanning electron microscopy was used to study the microstructure of the compound. Fig. 1 (inset) shows the field emission scanning electron micrograph of material's sintered pellet at room temperature. It identifies a polycrystalline texture of the material. Also, it indicates grains of unequal sizes (~0.1 to 2 μm) presents average grains size with polydisperse distribution on the surface of the ceramic. These morphological characteristics are governed by the matter transport mechanism between the grains

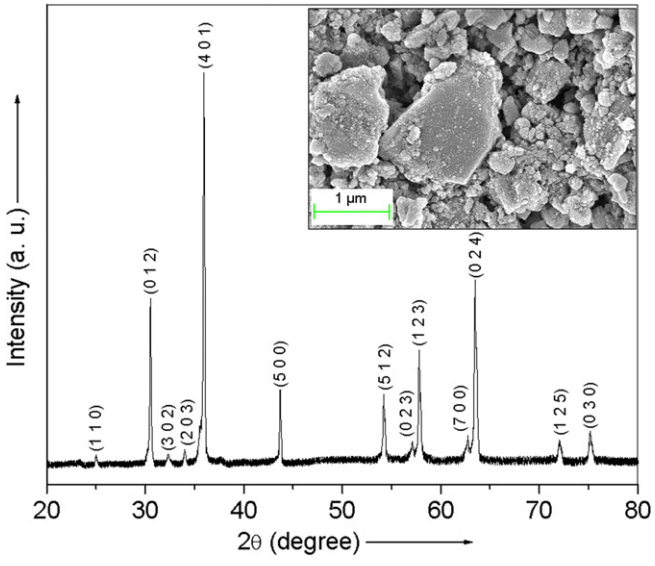


**Fig. 1.** X-ray diffraction pattern and field emission scanning electron micrograph (inset) of $(LiCo_{3/5}Fe_{1/5}Mn_{1/5})VO_4$ at room temperature.

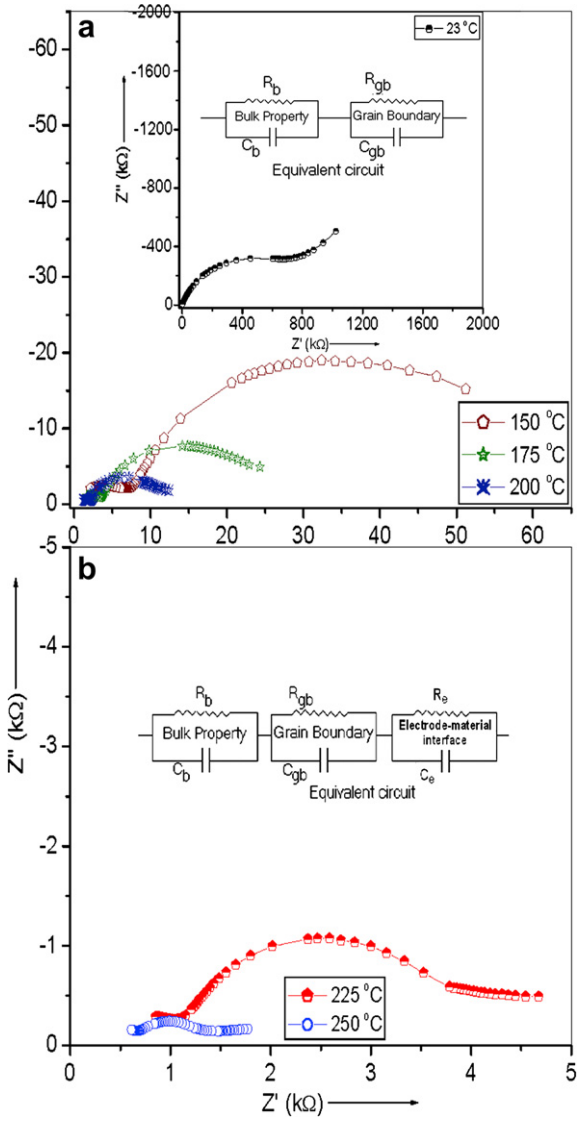


**Fig. 2.** Nyquist plots at different temperatures with electrical equivalent circuit (inset).