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# Investigations on Structural and Electrical Properties of Li<sub>2</sub>NiSiO<sub>4</sub>

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**Abstract:** A nanocrystalline Li<sub>2</sub>NiSiO<sub>4</sub> has been prepared by sol-gel synthesis technique. The annealed samples were characterized using TG-DTA, XRD and SEM-EDX. XRD pattern show the crystalline nature of the samples well appreciating the thermal behaviour of the materials, at temperature between 800°C-1000°C given stable phase. Morphology of the materials was investigated through the Scanning Electron Microscope (SEM) and the particles were found to be ofspherical shapes. The chemical composition was identified by the techniques of Energy Dispersive X-ray spectroscopy (EDX) along with X-ray mapping that is integrated with SEM. The electrical relaxation studies were explored using the conductivity spectrum comprises of super-linear power law (SPL) dependence. The activation energies were calculated from straight line fit to beE $\sigma$ = (0.25±0.03) eV, Ec<sub>1</sub> = (0.21±0.03) and Ec<sub>2</sub>= (0.13±0.02) eV. The temperature dependence of dc conductivity and hopping frequency is evident from Arrhenius plots.

Keywords: Silicates; cathode materials; stable phase; super-linear power law (SPL).

#### **Introduction and Experimental:**

Many experimental and theoretical studies have proved that  $\text{Li}_2\text{MSiO}_4$  are promising candidates that can replace for LiFePO<sub>4</sub> [1]. The reason for the alternative is the possibility of extracting two lithium ions for a two electron redox process while only one lithium ion can be extracted in LiFePO<sub>4</sub>. Among them, Fe and Mn systems have been studied well and proven to exhibit a very high capacity as well as chemical stability properties [2]. With the same structure,  $\text{Li}_2\text{NiSiO}_4$  is also expected to possess such high capacity and stability and a higher voltage, and needed a systematic investigation of its electrochemical and transport properties. In this work, to determine the energy barrier of the Li diffusion, we calculated the activation energy profile of the elementary processes.By using the super-linear power law (SPL) method[3]. High purity Nickel (II) Nitrate (Ni(NO<sub>3</sub>)<sub>2</sub>),Tetraethyl Orthosilicate (Si(OC H  $_2$   $_5$   $_4$ ) are used as the starting materials and Citric acid (C H  $_6$   $_8$   $_7$  as the fuel for this method .In order to avoid moisture the experiment was done in the nitrogen atmosphere. The as prepared sample was annealed at 800 °C, 900 °C and 1000 °C respectively in air for 4 hrs.

#### **Results and Discussion:**

All the observed diffraction lines are indexed to most frequently observe in the  $Pmn2_1$  space group [4] with the orthorhombic structure [5, 6]. The average crystallites size calculated for each sample using Scherer's

formula (D=K $\lambda/\beta$ cos $\theta$ ) are found to be 14.96 nm, 23.28 nm, 29.92 nm and 41.86 nm for as prepared, 800°C, 900 °C and 1000 °C annealed samples respectively. It increased directly with the increase in annealed temperature.TG curve presents four steps of weight loss along with one endothermic and two exothermic peaks on DTA curve. The removal of complexed metal acetates and citric acid which is obvious from the large exothermic peak at around 600 °C in the DTA curve. A slow and continuous decrease in weight above 700 °C is observed, which may be attributed to the process of crystallization of Li<sub>2</sub>NiSiO<sub>4</sub>.

Morphology of the materials was investigated through the Scanning Electron Microscope (SEM) and the particles werefound to be of the spherical shapes. The particle sizes calculated were approximately 146 nm at 800 °C and 164 nm at 900 °C. EDX spectrum confirmed that the prepared sample consists of only the desired elements as there are no extra peaks found from the graph. From the EDX table data the weight percentages of individual elements of the sample is being obtained. X-ray mapping or compositional imaging of elemental distributions is the tool to identify the density of the elements present in the specified area. X-ray mapping of  $Li_2NiSiO_4$  shows the spatial distribution of specific elements oxygen, silicon and nickel throughout the grains uniformly.



Figure 1: XRD pattern of all annealed samples



Figure 2: TG/DTA curves for Li<sub>2</sub>NiSiO<sub>4</sub>



Figure 3:SEM, EDX and X-ray mapping of ASP and 800 °C sintered samples.

We report the ac conductivity measurements of the Li<sub>2</sub>NiSiO<sub>4</sub> over the temperature range RT to 453K and the frequency range 1 to 10 MHz The conductivity spectrum comprises of super-linear power law (SPL) dependence [3]. These results clearly demonstrate the existence of the SPL at the lowest temperatures. It is interesting to point out that the SPL (m >1) seems to exist in the same frequency (or time)-temperature domain as the NCL and, moreover, exhibits similar characteristics, apart from the numerical value of the frequency exponent. Thus, it appears reasonable to suggest that the total  $\sigma^{*}(\omega)$  spectrum may be described by a modified Jonscher's equation,

$$\sigma'(\omega) = \sigma_{dc}(T) + A(T)\omega^{n} + B(T)\omega^{m}$$
(1)

Where n < 1 accounts for JPL and m  $\geq$ 1 for SPL/NCL. The first term in Eq. (1),  $\sigma_{dc}(T)$ , is the well-known dc conductivity arising from uninhibited random hopping of the ions, the second is the JPL arising due to restricted ion hopping and the third (SPL) may be due to two-level systems or low-energy excitation modes of vibration. The temperature dependence of  $\sigma_{dc}$ , and  $\omega_c$  shows Arrhenius behaviour as:

$$\sigma_{dc}(T) = \sigma \sigma_{exp(-E\sigma/K_{B}T)}$$
(2)  
$$\omega_{c} = \omega_{0} \exp(-E_{c}/K_{B}T)$$
(3)

where **GO** is the pre-exponential factor, T is temperature in Kelvin,  $E_{\sigma}$  and  $E_c$  are activation energies for dc conduction and hopping,  $K_B$  is Boltzmann's constant, and  $\omega_o$  is the attempt frequency. The activation energies are calculated from straight line fit to Eqns. (2) and (3) which are found to be  $E_{\sigma} = (0.25 \pm 0.03) \text{ eV}$ ,  $Ec_1 = (0.21 \pm 0.03) \text{ and} Ec_2 = (0.13 \pm 0.02) \text{eV}$  respectively.

In conclusion, nano-crystalline material  $Li_2NiSiO_4$  were successfully prepared by sol-gel synthesis. The XRD data confirms the phase formation The TG-DTA data shows stable phase after 800 °C The activation energies of dc conduction calculated successfully. The temperature dependence of dc conductivity and hopping frequency is evident from Arrhenius plots. As for the suitable values of conductivity this material can be used for cathode for the lithium ion batteries.



Figure 4: Log–log plot of frequency dependence of ac conductivity fitted with Almond–West formalism.

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