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Structural and Electrical Conductivity Studies of Nanocrystalline Olivine Type $LiNiPO_4$ Material

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Abstract: A dense core spherical shaped nanocrystalline $LiNiPO_4$ material was synthesized by template free sucrose assisted hydrothermal synthesis. The material possesses orthorhombic crystal structure with Pnma, space group having four formula units. TEM analysis revealed that material was formed as nano-crystallites. The structural characterization was accomplished through X-ray diffraction, thermo gravimetry/differential thermal analysis. Morphology was identified by the SEM, VSM was used to verify the magnetic behavior of the material and electrical characterization was done through impedance spectroscopy.

Keywords- Hydrothermal synthesis; nano-crystallites; electrical conductivity.

Introduction and Experimental:

Olivine family is widely used as cathodes in Li ion batteries because of their high energy density and high voltage [1]. Out of these materials, $LiNiPO_4$ is interested because $LiNiPO_4$ has high redox potential, good thermal stability and high specific capacity but suffers from a low electronic conductivity [2]. Research works are progressing by focusing to improve it electrical conductivity by carbon nano-coating or by inter-grain precipitation of conductive metallic particles or by different shapes of materials. In the present study, $LiNiPO_4$ is synthesized by template free hydrothermal method. This material exhibits considerable conductivity and is a possible candidate for electrode material in solid state batteries.

In hydrothermal method, sucrose dissolved in water is mixed with metal nitrates and ammonium di-hydrogen phosphate by maintaining the stoichiometry. The mixture is thoroughly stirred using the magnetic stirrer and is heated in oven in an autoclave at 120°C for 12hrs for complete the reaction. The product was washed off and dried in an oven. After synthesis, the metal oxide-carbon composites are calcined at 550°C for 4hrs to remove the carbon and further, hightemperature calcination yields crystallized phase. The X-ray diffraction, thermal analysis, SEM, TEM and VSM studies are performed to characterize and to study the magnetic properties. AC electrical measurements of 800°C sintered samples were carried out using broadband dielectric spectrometer (1Hz-10^7Hz) in the temperature range from 473K to 573K.

Results and Discussion

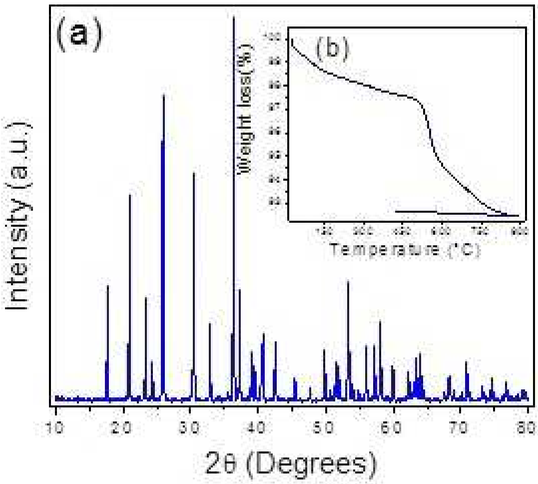

Figure1.(a) X-ray diffraction pattern of $LiNiPO_4$calcined at 800 °C and **(b)** TG-plot of as prepared $LiNiPO_4$.

Figure 1(a) shows powder XRD pattern $LiNiPO_4$calcined at 800°C. The phase pure crystallites are formed in a stable orthorhombic structure (2) of space group Pnma. The average crystallite size is calculated using Scherrer's formula and it is found in nanometer range. Figure 1(b) shows TG plot of as-prepared $LiNiPO_4$ material. The weight loss is maximum in temperature region 250°C to 400°C is due to oxidation of decomposed citric-nitrate gel and phase formation of material after the 400°C. While cooling there is no phase transition in the material as it is reflected in the TG plot.

The behavior of magnetic field is linear with the appearance of small hysteresis loop for $LiNiPO_4$. Its overall behavior is of antiferromagnetic character as shown in Figure 2(a). The lack of ferromagnetic interaction indicates the absence of different valence states, implying the negligible contribution from the electronic part and it indicates the ion conducting nature of the material. Figure 2(b) shows the SEM image having uniform morphology and it confirms the material formed spherical shaped particles. The selected area electron diffraction pattern from different (hkl) planes of $LiNiPO_4$ is shown in Figure 2(c).

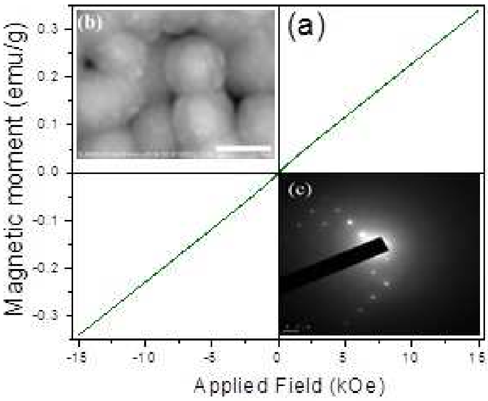

Figure 2. (a) VSM data at RT **(b)** SEM image of $LiNiPO_4$ **(c)**The selected area electron diffraction pattern of 800 °C calcined $LiNiPO_4$.

The sublinear frequency dispersive ac conductivity has been observed at high frequencies and the real part of ac conductivity, $\sigma'(\omega)$, can be expressed as [3-6]:

$$\sigma'(\omega)= \sigma_{dc}+A\omega^{n} \qquad (1)$$

where, σ_{dc} is the dc conductivity, Ais temperature dependent parameter and nis fractional exponent between 0 and 1. Figure 3(a) shows the log-log plot of frequency dependence of ac conductivity.Almond and West [3-6] proposed the following power-law expression to describe the real part of ac conductivity:

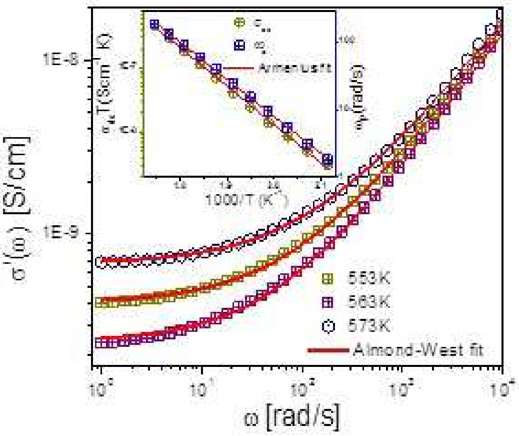

Figure 3.A log-log plot of frequency dependence of ac conductivity fitted with Almond West formalism and inset showsthe Arrhenius behavior of dc conductivity and cross-over frequency for 800 °C calcined $LiNiPO_4$.

$$\sigma'(\omega)= \sigma_{dc}[1+(\omega/ \omega_P)^n] \quad (2)$$

where, σ_{dc} is dc conductivity and ω_P is cross-over frequency from dc to dispersive part. In Figure 3 solid line represents best fit to Eq. (2) at different temperatures. The reciprocal temperature dependence of σ_{dc} and $\omega_P$shows Arrhenius behaviour. The activation energies calculated from straight-line fit as (1.04±0.02)eV for σ_{dc} and (1.03±0.02)eV for ω_p. The temperature dependence of dc conductivity and hopping frequency is evident from Arrhenius plots as shown in inset of Figure 3.

$LiNiPO_4$ material in spherical shape particles are prepared for the first time using hydrothermal method. The synthesized crystallites are of nanometer range and are crystallized in a stable orthorhombic structure of space group Pnma. TG confirmed that there is no secondary phase present in the material while cooling. TEM results authenticated that the material crystallized in the nanocrystalline form. VSM result confirmed that the absence of different valence states, implying the negligible contribution from the electronic part and it indicates the ion conducting nature of the material. This material exhibits considerable conductivity and is a possible candidate for electrode material in solid state batteries.

Acknowledgments

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