Ionic conductivity and electrical relaxation study of polycrystalline LiNaSO₄

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Abstract. The temperature dependence of ion conduction and electrical relaxation mechanism of LiNaSO₄ has been carried out. DSC curve shows phase transition peak at 520.2 °C. The temperature dependence relaxation time and dc conductivity follows the Arrhenius relation. We have obtained same activation energy for the hoping and the conduction within the error limit. The activation energy is 1.30±0.04eV in the temperature range between 493 K and 733 K. The dc conductivity varied from 7.30x10⁻¹⁰ S/cm at 493K to 3.96x10⁻⁴ S/cm at 793K. The sample becomes fast ionic conductor at high temperature phase.

1. Introduction
In search for good solid electrolyte materials for applications in high temperature solid state batteries, solid oxide fuel cells and sensors, sulfate based alkali cation systems are vital for achieving a good ionic conductivity during solid-solid phase transition [1]. LiNaSO₄ is well known as a high temperature rotator phase and super ionic conductor. The electrical properties were studied by many researchers and the mechanism of conduction has been a subject of discussion [2]. In this paper, we reported the ionic conductivity and electrical relaxation mechanism in β-phase. At high temperature phase, a dramatic increase of conductivity is found. This was due to the combination of “percolation” and “paddle-wheel” mechanism. ‘Paddle wheel’ model describes the transport of cations is strongly correlated to the rotation of the SO₄ tetrahedra. ‘Percolation’ model, suggests that there is no direct correlation between the ionic conduction and SO₄ rotations, but that the rotations and vibrations indirectly produce conduction pathways [3].

2. Experimental
LiNaSO₄ is synthesized by solid state reaction technique by heating the equimolar amount of Li₂SO₄.H₂O and Na₂SO₄ at 500 °C. Powder XRD pattern was recorded with 2θ in the range 10° -80° with a 0.01° step size and step scan of 0.5 s at room temperature. Thermal analysis was performed in the temperature range of 40 °C to 1000 °C with a heating rate of 10 °C/min. The mass of the used sample is 17.18 mg. A pellet with diameter 11.40 mm and 1.35 mm thickness was used for impedance measurement. The impedance measurements were carried out using Novacontrol broadband dielectric spectrometer (BDS) in the frequency range 100Hz to 20MHz, with an applied potential of 1 V, between the temperatures ranges 493 K to 593 K under 1 atmospheric pressure.
3. Results and discussion

3.1. Thermal analysis

Thermo-gravimetric curve Figure 1, shows there is no weight loss occurs over the temperature range 30 °C to 1000 °C. The endothermic peak at 793.2K of DSC curve belongs to structural phase transition. The calculated enthalpy change was 89.87J/g (12.26KJ/mol) and the corresponding entropy change was 15.40J/K mol. The value of entropy change is almost equal to Rln6 (=15.40 J/Kmol). Hence it is reasonable to say that the disorder was increased by 6 times at the high temperature phase transition. The second peak at 612 °C belongs to melting of the sample.

3.2 X-ray powder diffraction analysis

The XRD spectrum of LiNaSO₄ material sintered at 400 °C as shown in Figure 2. The spectra match well with JCPDS data reference number 01-071-2172. The unit cell volume and lattice parameters are calculated by Rietveld profile fit using FULLPROF software. XRD spectrum is fitted with hexagonal crystal system with P6/mmm space group and the lattice parameter a=7.6249±0.0011 Å, c=9.8545±0.0024 Å and the volume v=496.17x10⁶ pm³. The reliable factors χ² is 4.17 and Bragg R-factor is 0.15.

3.3. Impedance spectroscopy study

Figure 3 (a)-(d) shows the complex impedance plane plot of the material from temperature 513 K to 733 K. A depressed semicircle was found for each temperature at higher frequency range and a tail is observed at lower frequency end from 633 K to 713 K. Cole-Cole function form of complex impedance is used to describe the depressed semicircle in complex impedance plane and it is given by:

\[ Z'(\omega) = R_b/(1+(i\omega\tau)^{\alpha}) \]

where \( R_b \) is the bulk resistance, \( \tau \) is the mean relaxation time and the parameter \( \alpha \) is 0≤α<1. The bulk resistance, relaxation time and \( \alpha \) were extracted by fitting the above equation in the complex plane using non-linear least square fit software Winfit. At high frequencies ion migration process connected to the sample and at low frequencies the electrode polarization occurs due to space charge accumulation between the electrode and sample. This happens due to the multiple point contacts result to spreading the resistance and the air gap capacitance at electrodes [4]. The bulk resistance is decreases with increasing the temperature. The temperature dependence of relaxation time follows the Arrhenius equation as:

\[ \tau = \tau_0 \exp(E_a/k_B T) \]

where \( \tau_0 \) is the pre-exponential factor, \( E_a \) is the activation energy from impedance, \( k_B \) is Boltzmann’s constant and \( T \) is the absolute temperature. The activation energy was calculated from the slope of the straight line plot of log(1/\( \tau \)) versus reciprocal temperature 1000/T as shown in Figure 4. The activation energy obtained for β-LiNaSO₄ is 1.30±0.04 eV.
3.4. Conductivity

The conductivity study gives the information of dynamic behaviour of ion conducting materials. Almond and West proposed the following power law to describe the total conductivity:

$$\sigma(f) = \sigma_{dc}(1 + (f/f_H)^n)$$  \hspace{1cm} (3)

where $\sigma_{dc}$ is the dc conductivity, $f_H$ is hoping frequency for conduction and $n$ is the frequency exponent. These parameters are extracted by fitting the conductivity spectra to Equation (3). The frequency dependence of real part of conductivity at temperature range 493 K to 793 K as shown in the Figure 5. From the conductivity spectra we observe, $\sigma''(o)$ is independent of frequency at lower frequencies and this gives the dc conductivity. At high frequencies, the conductivity becomes strongly frequency dependent, varying approximately as a fractional power of frequency. The transition point between the frequency independent to frequency dependent region is the signature of onset of conductivity relaxation, which shifts towards high frequency as the temperature increases [4]. The dc conductivity is found to be increases with increasing temperature. This is due to the increase in the thermally activated drift mobility of the ions according to hopping conduction mechanism. The temperature dependence of dc conductivity is well described by Arrhenius law:

$$\sigma_{dc}T = \sigma_0 \exp(-E_{z}/k_B T)$$  \hspace{1cm} (4)

Figure 3 (a)-(d). Cole-Cole fit complex impedance spectra at different temperatures

Figure 4. Arrhenius plot of relaxation time
reflecting the activated nature of ionic hopping processes, where \( \sigma_0 \) is the pre-exponential factor, \( T \) is the temperature in K, \( E_\sigma \) is the activation energy and \( k_B \) is the Boltzmann’s constant. Figure 6 shows the Arrhenius plot of the sample. The activation energy for the conduction process was calculated from the slope of the straight line plot of \( \log(\sigma_{dc}T) \) versus reciprocal of temperature. The activation energy obtained for \( \beta \)-LiNaSO\(_4\) is 1.32±0.04 eV. At the phase transition region there is a large increase of dc conductivity was found. The dc conductivity obtained at temperature 793 K is 3.96x10\(^{-4}\) S/cm.

4. Conclusions
The impedance plots shows non-Debye behaviour and is asymmetric with respect to the peak maximum which indicates the distribution of relaxation time in the conduction process. The activation energy for hoping is obtained from Arrhenius plot and it is found to be 1.30 ± 0.04 eV for the \( \beta \)-LiNaSO\(_4\). This is less than the value reported for the LiNaSO\(_4\) crystals by Mellander et al. (2.15 eV) [5], Kanashiro et al. (1.59 eV) [6], Chen et al., (1.63 eV) [2] and comparable to the value obtained Wilmer et al. (1.34 eV) [7].

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