Materials Letters 223 (2018) 29–32

Contents lists available at ScienceDirect

Materials Letters

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

Featured Letter

$LiNaSO_4$ dispersed $NaNO_3$ composite – A new solid electrolyte?

Zdravka Slavkova [a], Paweł Ławniczak [b], Łukasz Lindner [b], Ofeliya Kostadinova [a], Tamara Petkova [a], Maria Zdanowska-Frączek [b,*]

[a] Institute of Electrochemistry and Energy Systems Acad. Evgeni Budevsky, Bulgarian Academy of Sciences, Acad. G. Bonchev Str., Bl 10, 1113 Sofia, Bulgaria
[b] Institute of Molecular Physics, Polish Academy of Sciences, Smoluchowskiego 17, 60-179 Poznań, Poland

ARTICLE INFO

Article history:
Received 14 February 2018
Received in revised form 28 March 2018
Accepted 29 March 2018
Available online 30 March 2018

Keywords:
Composite materials
Electrical properties
Phase transformation
Mechanochemical synthesis
Ionic conduction

ABSTRACT

DC ionic conductivity of the composite formed between $LiNaSO_4$ and dispersed Na ion conductor ($NaNO_3$) was studied. The material was prepared by the ball milled technique. X-ray diffraction and differential scanning calorimetry studies confirmed the formation of composite between the host material and the dispersoid. The experimental data indicate that addition of $NaNO_3$ significantly improves electrical conductivity of pure $LiNaSO_4$ in the low temperature phase. A possible mechanism of conductivity enhancement in dispersed system is interpreted in terms of the formation of space charge layer between the host material and the dispersoid in which defect concentration increases.

1. Introduction

Lithium sodium sulfate, $LiNaSO_4$ (LNS), belongs to the family of double sulfate compounds of the general formula $LiMSO_4$, where M stands for Na^{+1}, K^{+1}, Rb^{+1}, Cs^{+1} or NH_4^{+1}. At room temperature (β-phase), the crystalline lattice of LNS is trigonal with space group symmetry P31c and six formula units per unit cell [1,2]. It undergoes a structural phase transition to the α-modification (cubic phase) at 788 K [2]. In the cubic phase, LNS has a superionic conductivity of about 1 S/cm [3] and can be used as a solid electrolyte and as a supplement to a functional layer in medium temperature fuel cells [4]. What makes this material very attractive as a subject for basic research, is the mechanism of conduction which could involve both Li^+ and Na^+ [5,6]. The hitherto efforts to understand the mechanism of the superionic conductivity in the double sulfate materials have led to the following models. The first is the "paddle-wheel" mechanism based on strong coupling between the rotational motions of SO_4 anions and the respective cations, while the size of the cation has a negligible impact [5]. The rotating sulfate anions are likely to lower the potential barrier and make it easier for the cation to jump to an empty nearby position. In the second theory, assuming the percolation mechanism [6], the cation transport is caused by the lattice expansion and structural transition. According to this model the rotating SO_4 anions affect the conductivity indirectly by lowering the potential barrier and supporting the cation jumping to an empty position. Unfortunately, although LNS shows high ionic conductivity, it has been ineffective and unstable as an electrolyte in a fuel cell because of high temperatures of the superionic phase. The ionic conductivity of solid electrolytes has been found to increase significantly in low temperature phases with dispersion of insulating second phase particles [7–10]. In general, it is believed that no chemical reaction occurs between the host matrix and the dispersoid in the composite solid electrolyte systems. The materials behave as quasi-homogeneous solids with their own characteristic properties. The degree of the conduction enhancement depends largely on concentration, size and type of dispersed particles, which allows control of the electrical properties of the material through varying of the dopant type and concentration. It makes the composites very attractive for various electrochemical devices, such as solid state batteries, sensors, intermediate temperature fuel cells, etc. The aim of our work was to obtain the composite containing $LiNaSO_4$ as the host matrix with dispersed $NaNO_3$, using the mechanical ball milling technique. We have chosen sodium nitrate because of its high ionic conductivity (10^{-4} S/cm above 548 K) which involves Na^+ ions.

This paper is concerned essentially with the relationships between the electrical properties of $LiNaSO_4$/$NaNO_3$ composite and the properties of the separate phases $LiNaSO_4$ and $NaNO_3$. The DC ionic conductivity of the composite was compared to that reported for pure $LiNaSO_4$. The material was characterized by differential scanning calorimetry (DSC), X-ray diffractometry (XRD) in a wide temperature range and scanning electron microscopy

---

* Corresponding author.
E-mail address: mzf@ifmpan.poznan.pl (M. Zdanowska-Frączek).

https://doi.org/10.1016/j.matlet.2018.03.192

(SEM). An attempt was made to identify a possible mechanism of enhancement of conduction in this system with the help of existing theoretical models.

2. Material and methods

2.1. Sample preparation

$LiNaSO_4/NaNO_3$ composite was prepared by mechanical ball milling using a Retsch planetary mill. The masses of initial materials: sodium sulfate anhydrous, Na_2SO_4, (Alfa Aeasar), lithium sulfate monohydrate Li_2SO_4 (Sigma-Aldrich) and lithium nitrates, LiNO3, (Sigma-Aldrich) were calculated in molar percent to be at the ratio 40:40:20. The powders were milled for 72 h (at the speed of 580 rpm) in isopropyl alcohol at room temperature and dried afterwards in a vacuum oven for 2 h at 473 K.

2.2. Sample morphology

SEM images were recorded using an EM-200CX scanning electron microscope, JEOL. The samples were coated with thin films of carbon and gold to improve the surface conductivity. The sample images were recorded in the SE (secondary electrons) mode at accelerating voltage of 80 KeV.

2.3. X-ray analyses

Detailed X-ray investigation versus temperature was carried out using a Panalytical multifunction X-ray diffractometer, provided with an Anton Paar accessory for high temperatures (APHTK-16N) and a 3D PIXcel detector. Measurements were performed in the temperature range from room temperature (RT) up to 853 K at the heating rate of 20 K/min.

2.4. Differential scanning calorimetric measurements (DSC)

DSC measurements were accomplished in a Netzsch DSC 404 cell under argon in Al_2O_3 crucible. The temperature range of the experiment was from 323 K to 1023 K, while the heating rate was 10 K/min.

2.5. The electric conductivity

Complex impedance spectra were collected using a Novocontrol Alpha-A frequency analyzer in the frequency range from 1 Hz to 10 MHz and in the temperature range from 330 K up to 850 K for powder samples. A tablet was sintered at 523 K between ferrous plates with a load of 70 kp/cm. Both sides of the tablet were covered with a platinum thin film.

3. Results and discussion

The XRD patterns of the synthesized material (after 72 h milling) recorded at different temperatures are shown in Fig. 1. Data Rietveld refinement confirmed that the composite obtained consists of β-LNS (90%) and 10% of $NaNO_3$. The characteristic peaks of the low temperature β- phase $LiNaSO_4$ are clearly visible until about 793 K. The formation of α-phase of $LiNaSO_4$ is detected at 813 K. At 853 K the transformation is complete and only the peaks related to pure cubic LNS are visible in the XRD pattern [2]. Below 548 K, the peaks related to $NaNO_3$ are also visible; their intensity progressively decreases with increasing temperature. The peaks disappear in the spectra recorded at 544 K at which $NaNO_3$ undergoes a second order-like transition to a structure in which nitrate ions are in rotational disorder [11,12]. No additional peaks were observed in the patterns that would indicate a chemical reaction or formation of solid solution between the $LiNaSO_4$ and $NaNO_3$.

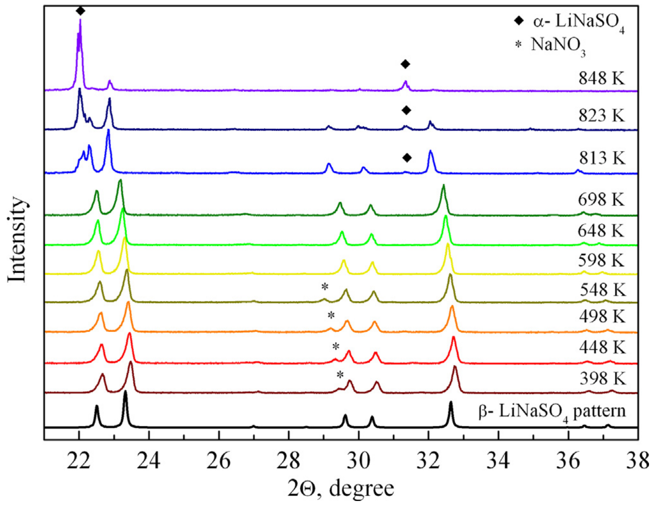

Fig. 1. X-ray diffractogramms recorded at various temperatures.

The SEM micrograph of the LNS/$NaNO_3$ (presented in Fig. 2) shows that the samples are homogenous and are made of particles with different sizes and shapes clustered into groups. The particle size histogram (inset in Fig. 2) was determined over a total number of 120 particles. The particle size distribution can be well fitted using a single log-normal function [13].

Impedance analyses indicate that both grains and grain boundaries contribute to the electric conductivity of the $LiNaSO_4/NaNO_3$ composite. The material resistance was evaluated by the fitting procedure using a parallel RC equivalent circuit model taking into account the sub-circuits representing intragrain and grain boundary properties [14]. The variation of DC conductivity of the composite with reciprocal temperature, in the temperature range between 550 K and 1000 K, is presented in Fig. 3. For comparison, the data for pure $LiNaSO_4$ powder taken from [15] (red dots) and the single crystal data taken from [16] (green dots) are included in the same figure.

The DSC thermogram of the composite, shown in the inset of Fig. 3, clearly evidences the existence of the LNS phase transformation from β to α phase (788 K) and the order-disorder phase transition of $NaNO_3$ (544 K). The rapid conductivity enhancement when heating the sample up to 548 K can be interpreted in terms of the space-charge model proposed by Maier [17]. According to the model, the enhancement of conductivity in the composites is mainly attributed to the increased concentration of point defects (vacancies and interstitials) in the space-charge layer formed between the host material and the dispersoid.

Additionally, the larger size of the sodium ion in comparison to that of lithium (+25% to +55% for the ion, depending on the coordination) leads to volume changes in the material and an enhanced mobility of Na^+ which, together with diffusion of Li ions, is probably the reason for the rapid nonlinear increase in the conductivity.

At about 544 K the conductivity reaches the value of 10^{-2} S/cm and remains unaltered within the range of next 200 K. It could be a consequence of successive processes that occur in $NaNO_3$, i.e. premelting state (phenomenon associated with the order–disorder transition of nitrate orientations in the crystal lattice), melting which takes place at 580 K, and decomposition which starts from 653 K [11,18]. After that, close to 788 K and above this temperature, the further rise in conductivity is associated with β-α transition of $LiNaSO_4$ and the sulfate ion reorientational jumps, which lead to an enhanced diffusion of the cationic species. The