Materials Research Bulletin 47 (2012) 2498–2505

Contents lists available at SciVerse ScienceDirect

Materials Research Bulletin

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

Effects of the intercalation time on the dielectric properties of $Na_{2x}Mn_{1-x}PS_3$

L. Silipigni [a,b,*], L. Schirò [a], L. Monsù Scolaro [c], G. De Luca [d], G. Salvato [e]

[a] Dipartimento di Fisica della Materia e Ingegneria Elettronica-Università di Messina – V.le F.Stagno d'Alcontres 31, I-98166 Messina, Italy
[b] CNISM-Messina – Salita Sperone 31, I-98166 Messina, Italy
[c] Dipartimento di Chimica Inorganica, Chimica Analitica e Chimica Fisica-Università di Messina – Salita Sperone 31, I-98166 Messina, Italy
[d] Istituto per i Materiali Compositi e Biomedici del C.N.R – sede di Napoli – P.le Tecchio 80, I-80125 Napoli, Italy
[e] CNR-IPCF Istituto per i Processi Chimico-Fisici – V.le F. Stagno d'Alcontres 37, I-98158 Messina, Italy

ARTICLE INFO

Article history:
Received 14 September 2011
Received in revised form 12 April 2012
Accepted 8 May 2012
Available online 15 May 2012

Keywords:
A. Layered compounds
B. Intercalation reactions
C. Impedance spectroscopy
D. Dielectric properties

ABSTRACT

Manganese thiophosphate powders have been intercalated with sodium ions at two different intercalation times (150 min and 180 min) in order to evaluate the influence of this parameter on the dielectric properties of the obtained compounds labeled like $Na_{2x}Mn_{1-x}PS_3$. In particular, dielectric permittivity measures have been carried out as a function of temperature (80 K–350 K) and frequency (20 Hz to 1 MHz) and compared with each other and with those of the pure matrix and of the $Na_{2x}Mn_{1-x}PS_3$ compound corresponding to a 120 min intercalation time. Both investigated compounds show a dielectric response characterized by a loss peak at low temperatures, by a strong dispersion at low frequency and at not very high temperatures and by a crossover frequency showing an Arrhenius temperature dependence in agreement with what already observed in $Na_{2x}Mn_{1-x}PS_3$ (120 min). The results have been also discussed in terms of *ac* conductivity, Maxwell–Wagner–Sillar (MWS) polarization, electrode polarization and *dc* conductivity and all the above cited features have been attributed to the Na^+ ions which are, by their nature, hopping charge carriers that behave like jumping dipoles in their alternate motions and simultaneously show conducting characteristics resulting from their extended hopping over many sites. This attribution allows us to classify the analyzed sodium compounds like hopping charge carrier systems in which a greater Na intercalation time translates into a decrease in the loss peak intensity and an increase in the activation energy associated to the crossover frequency.

© 2012 Elsevier Ltd. All rights reserved.

1. Introduction

The engineering of compounds on nanoscale is an intense area of research for the production of new multifunctional materials with energetic, optical, conductive and catalytic applications. In this context the insertion of a given guest species into layered inorganic hosts by the intercalation process is a simple method to modify the physical properties of the host.

Among the lamellar hosts, the thiophosphate $MnPS_3$ is well-known for its ability to form intercalation compounds, called also nanocomposites, with a large variety of atoms like alkali-metals, rare-earth, organic molecules or even cationic binuclear macrocyclic complexes [1–3]. This occurs by means of a unique non-redox reaction based on the cation exchange between host and guest: in particular a fraction of the Mn^{2+} intralayer cations leaves their sites while the guest species enter the van der Waals gaps. The so-obtained compounds are labeled like $A_{2x}Mn_{1-x}PS_3$ where A is the guest species cation or molecule which is inserted between the $MnPS_3$ basic sandwiches. These last ones, indicated like $S[Mn_{2/3}(P_2)_{1/3}]S$, consist of double layers of sulfur atoms within which there are octahedral sites that are alternately filled, one third by the P–P couples and two thirds by the Mn^{2+} ions. Since these basic building blocks are weakly bonded each other by type van der Waals forces their stacking along the crystallographic *c* axis gives rise to the $MnPS_3$ two-dimensional structure.

During the intercalation process the $S[Mn_{2/3}(P_2)_{1/3}]S$ minimal sandwiches remain largely intact while the guest species fit into the van der Waals gaps existing between the $MnPS_3$ basic sandwiches where there are empty and accessible sites. In this way the intercalation by substitution expands the van der Waals gaps and this increase in the spacing between the basic sandwiches is the first and main effect of this type of intercalation that can be detected by X-ray diffraction.

When the guest species is great in size the intercalation by substitution can occur in two steps. In the first step some alkali metal ions, like K^+ or Na^+, are inserted to pre-expand the $MnPS_3$

---

[*] Corresponding author. Tel.: +39 0906765143; fax: +39 090391382.
E-mail addresses: lsilipigni@unime.it (L. Silipigni), lschiro@unime.it (L. Schirò), lmonsu@unime.it (L.M. Scolaro), giovanna.deluca@cnr.it (G. De Luca), salvato@me.cnr.it (G. Salvato).

0025-5408/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.materresbull.2012.05.007

interlamellar space and in the second step they can be exchanged with other, larger size, guest species [1]. This further exchange is possible owing to the weak bond with which the K^+ or Na^+ ions are linked to the negatively charged $Mn_{1-x}PS_3$ sheets as showed by XPS measurements [4,5]. Moreover previously reported dielectric data on $Na_{2x}Mn_{1-x}PS_3$ (120 min) [6] indicate that this material, obtained with an intercalation time of 120 min, is a hopping charge carrier system in the (20–10^6) Hz range over the (78–350) K temperature interval. What happens to its dielectric response when the intercalation time is greater than 120 min? To answer this question is the aim of this paper in which we report the results of the dielectric measurements on two $Na_{2x}Mn_{1-x}PS_3$ compounds prepared at two different intercalation times, 150 min and 180 min. The so-obtained dielectric data are also compared with those relative to $Na_{2x}Mn_{1-x}PS_3$ (120 min) and $MnPS_3$.

2. Experimental

Powders of $MnPS_3$, $K_{2x}Mn_{1-x}PS_3$ and $Na_{2x}Mn_{1-x}PS_3$ have been synthesized as reported in the literature [4,5] with the only difference that the $Na_{2x}Mn_{1-x}PS_3$ powders have been obtained by stirring powders of $K_{2x}Mn_{1-x}PS_3$ with 20 ml of a 2 M NaCl aqueous solution for a longer time than 120 min and precisely for about 150 min and 180 min. X-ray powder diffraction has been used to confirm the formation of these nanocomposites. The diffractograms, obtained by using the Cu Kα radiation (1.54 Å) in the $5^\circ < 2\theta < 60^\circ$, are shown in Fig. 1 together with the XRD pattern of $Na_{2x}Mn_{1-x}PS_3$ compound corresponding to a 120 min intercalation time. Approximate values of 0.31, 0.44 and 0.52 have been deduced for the intercalation rate x in $Na_{2x}Mn_{1-x}PS_3$ (120 min), $Na_{2x}Mn_{1-x}PS_3$ (150 min) and $Na_{2x}Mn_{1-x}PS_3$ (180 min) respectively by X-ray photoelectron spectroscopy measurements [5,7]. The dielectric measurements have been made on pelletized samples using indium electrodes in a cryostat over a wide range in temperature (80 K–350 K) employing liquid nitrogen: a RLC bridge Agilent model HP4284A, interfaced to a personal computer, has been used to carry out dielectric measurements from 20 Hz to 1 MHz. All measurements have been performed at about 10^{-6} Torr. Not to allow the free-surface adsorbate formation, each sample has been heated at 375 K under vacuum before each run.

3. Results and discussion

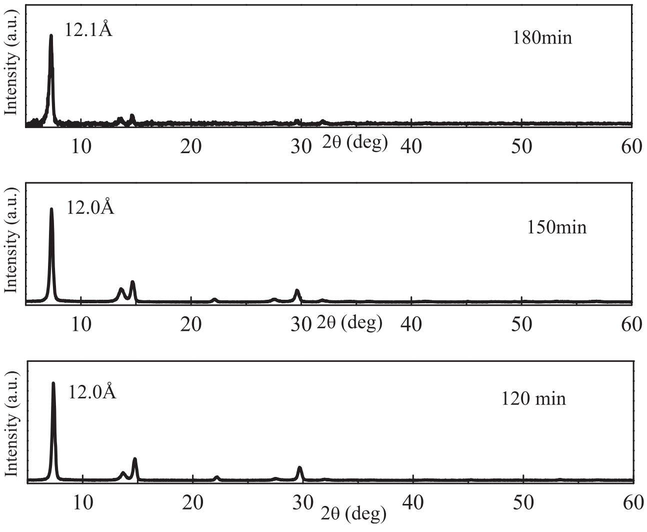

Fig. 1. Powder XRD patterns of $Na_{2x}Mn_{1-x}PS_3$ compounds at 120, 150 and 180 min respectively.

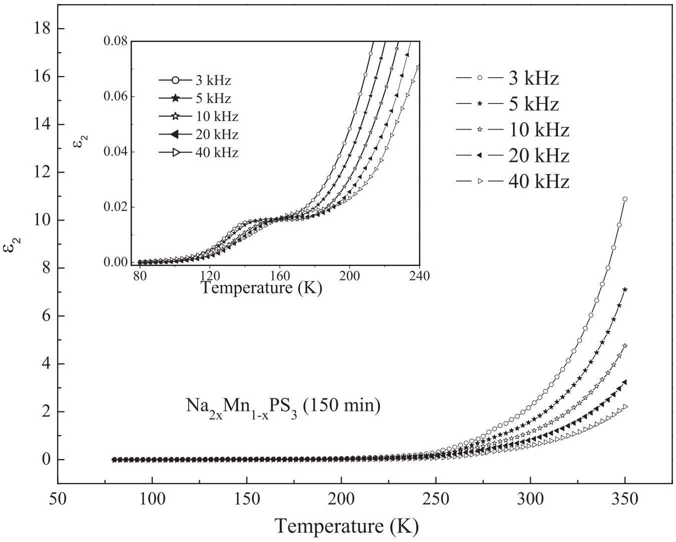

Fig. 2. Temperature dependence of the $Na_{2x}Mn_{1-x}PS_3$ (150 min) dielectric constant imaginary part ε_2 at some investigated frequencies; in the inset the region at low temperatures is zoomed.

Fig. 1 illustrates the powder XRD patterns of the $Na_{2x}Mn_{1-x}PS_3$ samples at the different investigated intercalation times. In each pattern sharp *00l* reflections are visible from which a value between 12.0 and 12.1 Å is calculated for the interlamelllar (basal) spacing *d*. This result is in agreement with the literature [5,8,9] and suggests that the intercalated sodium ions are highly solvated by water molecules which they loss either on evacuation or on heating as indicated from thermogravimetric analysis [10] and from the analogy to cadmium thiophosphate $CdPS_3$ [11]. Moreover, a careful glance at the same figure emphasizes as a prolonged Na intercalation time leads no remarkable change in both the basal *d*-spacing value and the nature of these intercalation compounds which are well ordered even at the longest intercalation time.

Figs. 2 and 3 show respectively the temperature dependence of the dielectric constant imaginary part, ε_2, for $Na_{2x}Mn_{1-x}PS_3$ (150 min) and $Na_{2x}Mn_{1-x}PS_3$ (180 min) at some of the analyzed frequencies.

By zooming the low temperature region (see the insets) it is possible to observe a loss peak that moves to higher temperatures with increasing frequency in both compounds in analogy to what reported for $Na_{2x}Mn_{1-x}PS_3$ (120 min) [6]. However the main effect of a greater intercalation time can be noted in Fig. 4 in which the

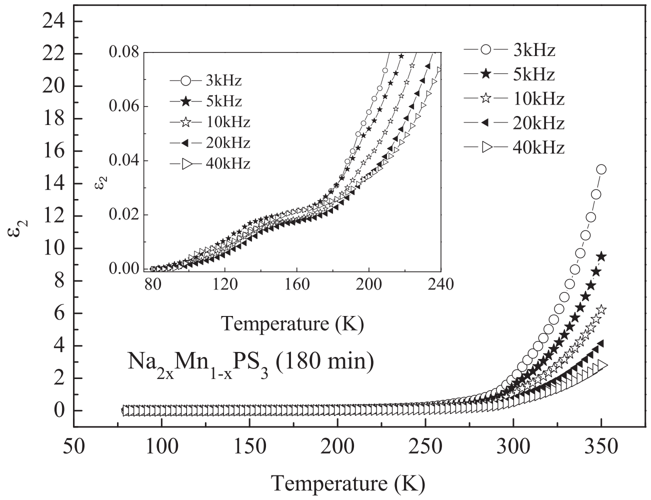

Fig. 3. Temperature dependence of the $Na_{2x}Mn_{1-x}PS_3$ (180 min) dielectric constant imaginary part ε_2 at some investigated frequencies; in the inset the region at low temperatures is zoomed.

Download English Version:

https://daneshyari.com/en/article/1490400

Download Persian Version:

https://daneshyari.com/article/1490400

Daneshyari.com