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Electrical conductivity and dielectric behavior in sodium zinc divanadates

F. Sallemi *, B. Louati, K. Guidara

Condensed Matter Laboratory, Faculty of Sciences, University of Sfax, B. P. 1171, 3000 Sfax, Tunisia

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ABSTRACT

The $Na_2ZnV_2O_7$ compound was obtained by the conventional solid-state reaction. The sample was characterized by X-ray powder diffraction, Raman and impedance spectroscopy. The ac electrical conductivity and dielectric properties have been investigated in the frequency and temperature range of 200 Hz–1 MHz and 513 K–729 K, respectively. The direct current conductivity process is thermally activated. The frequency dependence of the conductivity is interpreted using the power law. The close values of activation energies obtained from the analysis of hopping frequency and dc conductivity implies that the transport is due to Na^+ cation displacement parallel to (0 0 1) plane located between ZnO_4 and VO_4 tetrahedra. The evolution of the complex permittivity as a function of angular frequency was investigated. Several important parameters such as charge carrier concentration, ionic mobility and diffusion coefficient were determined. Thermodynamic parameters such as the free energy of activation ΔF, the enthalpy ΔH, and the change in entropy ΔS have been calculated.

1. Introduction

Nowadays, much attention has been paid to the preparation and characterization of vanadates with special morphology due to their abnormal behavior and subsequent desirable properties which mainly deal with electrics and magnetic [1,2]. Vanadium oxides and vanadates have activated a new interest as a promising electrode material [3–5]. This may be ascribed to their high-specific capacity and layered crystal structure [6].

The akermanite type structure, $A_2^+B^{2+}V_2O_7$ formula (A=Na, K, B=Zn, Mg, Co, Cu) have a structure that is a derivative of the mineral. It consists of $[B^{2+}V_2O_7]^{2-}$ and A_2^+ layers stacked alternately along the *c* axis. In $[B^{2+}V_2O_7]^{2-}$ layers, $B^{2+}O_4$ tetrahedra share corners with V_2O_7 pyrovanadates units. $Na_2ZnV_2O_7$ compound crystallizes in the tetragonal system with $P\text{-}42_1m$ ($Z=2$). The structure consists of ZnV_2O_7 layers parallel to (0 0 1) made corner-sharing VO_4 and ZnO_4 tetrahedra (Fig. 1). The cations Na^+ are lying between these layers in distorted square antiprisms of oxygen atoms [7].

The interest for $Na_2ZnV_2O_7$ compound is essentially associated to their wide applications [5] as luminescent materials, chemical sensor, catalysis cathode materials in batteries, electrochromic devices and minerals.

In this study we report the electrical and dielectrical properties of $Na_2ZnV_2O_7$ by means of impedance spectroscopy and discuss the conduction mechanism in this material.

2. Experimental procedure

The sodium zinc divanadate was synthesized using a classic ceramic method. Analytical grade reagents with 99% purity of Na_2CO_3, ZnO and V_2O_5 were well ground, mixed and progressively heated to 573 K for 10 h in order to eliminate CO_2. The obtained product is again ground manually pressed in a pellet, and heated at 843 K for 5 h.

An X-ray powder diffraction pattern was recorded using a Philips PW 1710 diffractometer operating with copper radiation $K\alpha=1.5418$ Å. Unit cell parameters of the synthesized compound have been refined by Rietveld method from the powder data. Back scattering Raman spectrum was obtained at room temperature using as excitation the 647.1 nm radiation and a T-64000 Raman Spectrometer (Yvon-Jobin) equipped with nitrogen cooled CCD.

The electrical measurements were performed using a two gold electrodes configuration. The sample was pressed into pellets of 8 mm diameter and 1.1 mm thickness using 3 t/cm^2 uniaxial pressure. Electrical impedances were recorded in the frequency ranging from 200 Hz to 1 MHz with the TEGAM 3550 ALF automatic bridge monitored by a microcomputer and a temperature controller. Measurements were carried out at temperatures from 513 K to 729 K.

* Corresponding author. Tel./fax: +216 22585989.
E-mail address: foufa1280@yahoo.fr (F. Sallemi).

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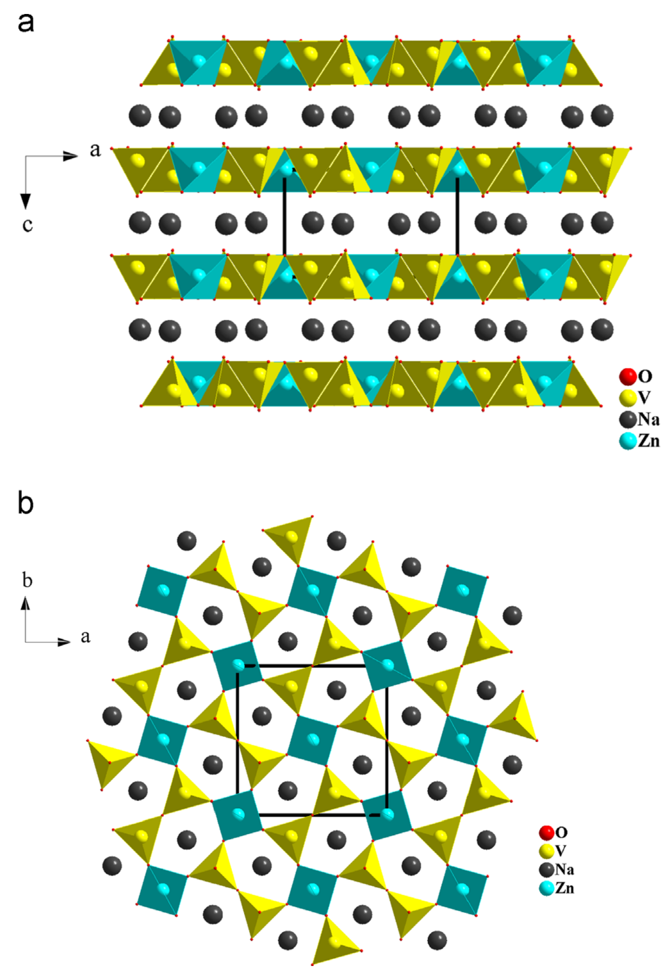

Fig. 1. Structure of $Na_2ZnV_2O_7$ compound (a and b).

3. Results and discussions

3.1. X-ray powder analysis

At room temperature, the X- ray diffractogram (XRD) pattern of $Na_2ZnV_2O_7$ is shown in Fig. 2. The peaks have been successfully indexed using fullprof suite programs [8] in the tetragonal system with P-42$_1$m. The refined lattice parameters were $a=b=8.277$ Å, $c=5.115$ Å and $V=350.236$ Å^3 with a reliability factor of $X^2=2.06$ which are in agreement with the literature [7].

3.2. Raman scattering

Fig. 3 shows the Raman spectrum of the prepared pyrovanadate $Na_2ZnV_2O_7$. The tentative assignments given were made on the basis of the published results [9–11]. Three low-frequency Raman peaks at 185, 224 and 244 cm^{-1} are assigned to the deformation mode of (OVO_3). The bands located at 345 and 376 cm^{-1} are associated to the deformation stretching vibration (VO_3). In addition, the mode detected at 509 cm^{-1} is due to the symmetric stretching mode of (VOV). The frequencies observed at 874 and 916 cm^{-1} are related to the symmetric stretching vibration (VO_3). The peak at 956 cm^{-1} corresponds to the stretching vibration (VO_3).

3.3. Electrical properties

The Nyquist plots for $Na_2ZnV_2O_7$ for some temperature are displayed in Fig. 4. The plots, drawn between imaginary (Z'') and real parts of impedance (Z') show semicircular arcs with a tail at low frequency. Therefore, the equivalent circuit of this sample could be regarded as a parallel combination (R_b, C, CPE_1), CPE_1

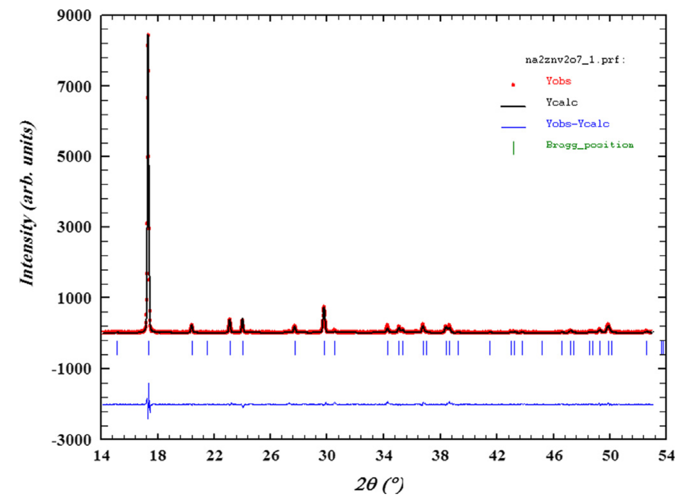

Fig. 2. Plot of the Rietveld refinement given the comparison of the experimental (.) with the calculated (-) XRD patterns of $Na_2ZnV_2O_7$ compound at room temperature. Vertical lines refer to the calculated Bragg positions.

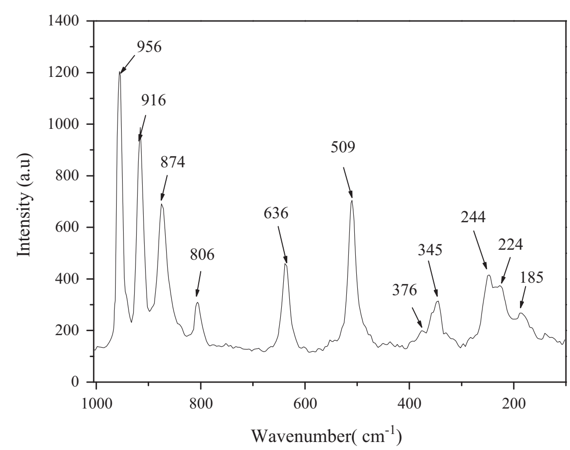

Fig. 3. Raman spectrum of $Na_2ZnV_2O_7$ at room temperature.

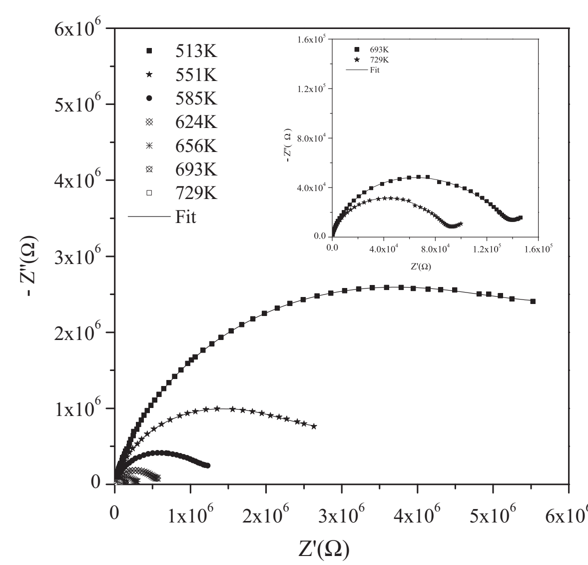

Fig. 4. Experimental and calculated semicircle plots at different temperatures.