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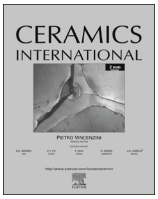

AC conductivity, electric modulus analysis and electrical conduction mechanism of $RbFeP_2O_7$ ceramic compound

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ABSTRACT

In this work, the diphosphate compound, $RbFeP_2O_7$, was prepared by the conventional solid-state reaction. The X-ray diffraction pattern revealed that the sample presents a single phase, that crystallizes in the monoclinic structure with a $P2_1/C$ space group. Impedance analysis was performed using the equivalent circuit model, and, it indicated the presence of intra- and inter-granular contribution. Furthermore, the electrical conductivity, the dielectric properties and the relaxation behavior of this material were studied in detail using the impedance spectroscopy technique, in a frequency ranging from 200 Hz to 5 MHz at several temperatures. The temperature dependency of frequency exponent 's' shows that the correlated barrier-hopping model (CBH) is the most responsible mechanism for AC conduction in the investigated compound. In terms of CBH model, the values of maximum barrier s height, the hopping distance and the density of localized states are determined and discussed. A correlation between electrical and structural properties was also discussed.

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1. Introduction

Diphosphates are one of the most widely investigated families of condensed phosphates, notably because of their synthetic variability, compositional flexibility and fascinating physical properties [1–5]. In recent years, double pyrophosphate with chemical formula $A^IM^{III}P_2O_7$ (A^I= Li, Na, Ag, Rb, Cs and K; M^{III}=Al, Ga, Cr, Fe, In, Y) have been the subject of investigation, due to the potential applications for example some of them may have some unforeseeable magnetic [6] and useful catalytic [7] properties. Besides, recently some of them have been proposed as cathode materials for lithium ion batteries [8] as well as nanoparticles, for decontamination and disinfection of water [9,10].

During the last decade, investigations about structural and electrical properties of these diphosphates have been tremendously interesting for research. In fact, the diphosphates generally formed by the decomposition of phosphates that exhibits interconnected interstitial spaces, which may potentially be fast ionic conductors. Also, the presence of transition metal in the framework helps to pioneer the mixed valence responsible for the electronic conductivity. And more importantly, recent studies showed that frameworks built up from PO_4 or P_2O_7 groups offer good candidates to be used as membrane in advanced batteries that address the growing needs of portable electronics, for example, laptops, cell phones, medical devices, and other modern e-commodities [11,12].

Among the most interesting diphosphates, the $\mathbf{RbFeP_2O_7}$ to which this paper is devoted. As a matter of fact, $\mathbf{RbFeP_2O_7}$ material belongs to the $NaFeP_2O_7$-I family is isostructural with $\mathbf{KFeP_2O_7}$ and $\mathbf{CsFeP_2O_7}$ [13]. Its framework is built up from corner-sharing FeO_6 octahedra and P_2O_7 moieties. Each FeO_6 octahedron is linked with five different P_2O_7 groups, and each P_2O_7 group shares its six corners with five different FeO_6 octahedra and is also bonded to one of the FeO_6 through a bidentale bonding. The two PO_4 tetrahedra of the P_2O_7 group are in a staggered configuration. More generally, the structure consists of intersecting tunnels running along [001] and [110] directions Fig. 1. Note that, these tunnels and the associated cavities are at the origin of possible Rb^+ cation migration within the structure and further intercalation of extra alkali cations.

Here, our synthesis and investigation of $\mathbf{RbFeP_2O_7}$ aimed to analyze a comprehensive overview of the electrical and dielectrical properties. Thus, we were investigated for the first time the impedance spectroscopy properties of $RbFeP_2O_7$ ceramic materials using an impedance analyzer as a function of frequency and temperature. In fact, impedance spectroscopy parameters were determined and discussed. Ac conductivity and its related conduction mechanism were analyzed and defined on the scope of Ac theories. To our know- ledge, there are no reports available on the ac and dielectrical properties of $\mathbf{RbFeP_2O_7}$.

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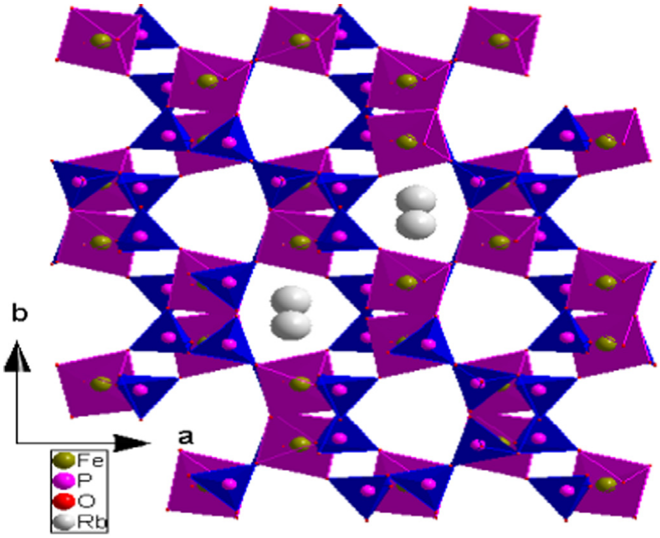

Fig. 1. Plot of XRD data for **$RbFeP_2O_7$** at room temperature.

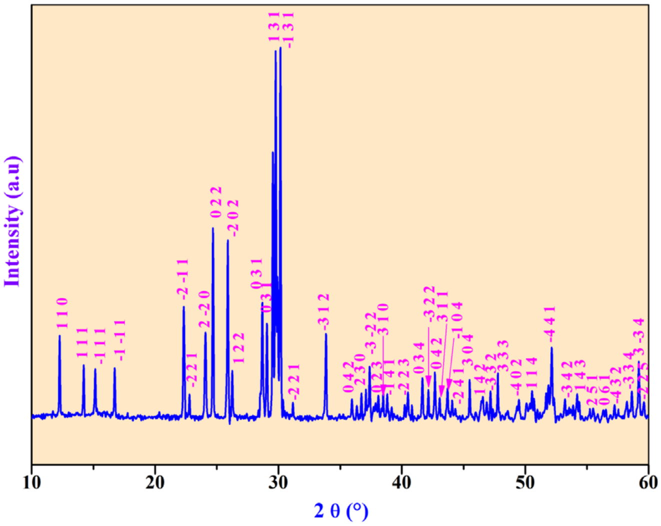

Fig. 2. Projection view of RbFeP2O7 along c axis showing tunnels where Rb+ cations are located.

2. Synthesis procedure

The **$RbFeP_2O_7$** ceramic sample was prepared using the solid state reaction method. Commercially available AR grade chemicals were used to prepare the **$RbFeP_2O_7$** compound. Rb_2CO_3 (Sigma-Aldrich, 99%), Fe_2O_3 (Sigma-Aldrich, 99%) and $NH_4H_2PO_4$ (Sigma-Aldrich, 99%) were used as starting materials.

The reagents were mixed with their stoichiometric ratios and ground thoroughly in an agate mortar. The homogenized powder was calcined at 573 K for 8 h to eliminate NH_3, CO_2 and H_2O. The resulting product was reground, pelletized into circular disc, again, and heated from the room temperature to 1200 K during 8 h.

The phase analysis phase was examined at room temperature by using a Phillips powder diffractmeter PW 1710 with CuK_α radiation ($\lambda = 1.5405$ Å) at glancing angles between 10° and 60°. IR spectroscopic analyses were carried out with a FTIR-100 Perkin Elmer spectrophotometer in the wave number range 1600–400 cm^{-1}. Raman scattering investigation was performed on powder, using a spectrometer type Horiba Jobin-Yvon T64000. Raman spectra were recorded at room temperature from 400 to 1300 cm^{-1}.

The electrical measurements were performed using a two platinum electrode configuration. The sample was pressed into pellets of 8 mm diameter and 1.3 mm thickness using 3 t/cm^2 uniaxial pressure. The study was carried out at various temperatures from 613 to 723 K with a frequency range 209 Hz–1 MHz using a Tegam 3550 ALF impedance analyzer.

3. Results and discussions

3.1. Crystalline parameters

Fig. 2 shows the (XRD) pattern of the prepared sample. All the observed peaks diffraction of $RbFeP_2O_7$ show some sharp and possess high intensity peaks which clearly indicate the high crystalline nature of material. In addition, no additional peaks belonging to other phases can be observed, which confirms the formation of pure single phase. The patterns are indexed as monoclinic crystal structure with $P2_1/C$ space group. The calculated lattice parameters using.

CELLREF software are, a = 7.454(2) Å, b = 10.031(3) Å, c = 8.313 (4) Å, $\beta = 107.52$ (8)°. These results are in well agreement with the literature [14].

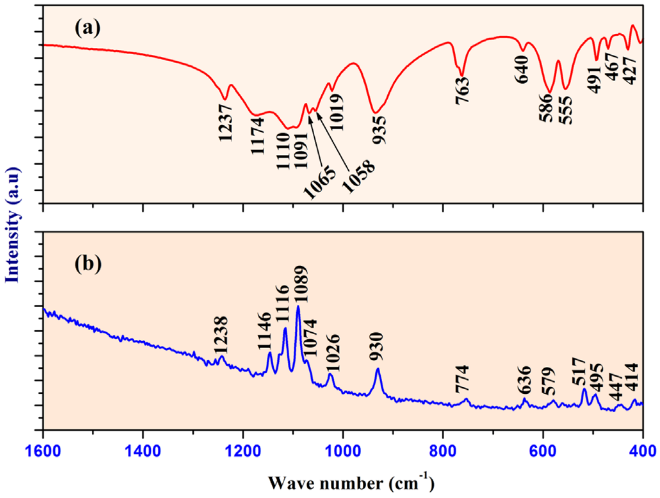

Fig. 3. IR and Raman spectrum of **$RbFeP_2O_7$** diphosphate.

3.2. Infrared and Raman spectroscopy

The infrared and Raman spectra of the investigated compound are respectively shown in Fig. 3(a) and (b). The assignment of the observed spectral features is based on a comparison using structurally related materials [15].

In this case, the band assignments for the fundamental modes of $[P_2O_7]^{4-}$ anions are given in Table 1. Due to the symmetric and antisymmetric stretching frequencies of PO_3 in $[P_2O_7]^{4-}$ the bands are generally observed in the regions 1233–1020 cm^{-1} [13]. Besides, the antisymmetric and symmetric P–O–P stretching modes are observed in the regions 927 cm^{-1} and 757–766 cm^{-1} [13]. Also due to PO_3 deformations, the bands are identified in 635–548 cm^{-1} region [13]. This situation has also been observed in other diphosphates [16] as well as in diarsenates [17] and divanadates [18].

3.3. Impedance analysis

Fig. 4 shows the Nyquist plots of complex impedance data (Z″ vs Z′) with frequency at different temperatures. The figure shows that the feature of impedance spectra is almost the same at different temperatures, only for a decrease in the radius of

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