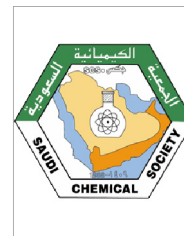




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REVIEW

Conductivity studies of some diphosphates with the general formula $A^I_2B^{II}P_2O_7$ by impedance spectroscopy

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Abstract The conductivity mechanism of three crystalline diphosphates of $(A^I_2B^{II}P_2O_7)$ type, $Na_2CaP_2O_7$, $Na_2CuP_2O_7$ and $K_2MnP_2O_7$ has been investigated using combined complex impedance and modulus formalisms. Their conductivity measurements showed that $Na_2CaP_2O_7$ and $Na_2CuP_2O_7$ can be considered pure ionic conductors, while $K_2MnP_2O_7$ is a mixed ionic-electronic conductor with relatively an electronic nature. In the case of $K_2MnP_2O_7$, the electron transport, originated from the electronic hopping, is due to the presence of various oxidation states of the manganese ion. The conductivity measurements of the diphosphate compounds have been carried out using the frequency range between 10^{-1} and 10^6 Hz over a temperature interval from 300 to 700 K. The equivalent circuit, which provides the most realistic model of the electrical properties

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of each compound under investigation, was studied using the least squares immittance fitting program (LEVEM). A correlation between electrical and structural properties of the diphosphates has been conducted.

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1. Introduction

Existence of transition metal ions in phosphate glasses is of great interest due to their potential applications in electro-chemical, electronic and electro-optical devices (Minami et al., 1980; Selveraj and Roa, 1985; Satyanarayana et al., 1991; Jamnicky et al., 1995). The investigation of the electrical properties, for instance, of phosphate glasses containing molybdenum transition metal showed two types of conductivities: ionic and electronic (Bih et al., 2000, 2001). The correlation between electrical and structural properties seems to be very complicated if all parameters are taken into account because of the disorder in glassy compounds.

In order to understand the electrical properties of phosphates and to define their physical and chemical parameters, which enable the high electrical performance of the compounds, various crystalline phosphates with well-known structures have been investigated.

Very little is known about electrical properties of crystalline diphosphate materials with mixed monovalent and divalent cations. Investigations on the electrical properties of $\text{Na}_2\text{PbP}_2\text{O}_7$ (Dridi et al., 2000), $\text{Na}_2\text{CoP}_2\text{O}_7$ (Sanz et al., 1999), $\text{Ag}_2\text{PbP}_2\text{O}_7$ (Dridi et al., 2001) and $(\text{Na}_{0.8}\text{Ag}_{0.2})\text{PbP}_2\text{O}_7$ (Loutati et al., 2009) using impedance spectroscopy showed that these crystalline materials were purely ionic conductors of Na^+ or Ag^+ . Other study on diphosphates of $\text{ARu}_2(\text{P}_2\text{O}_7)_2$ type with $\text{A} = \text{Li}; \text{Na}$ and Ag (Fukuoka et al., 2003) revealed that the total conductivity is a contribution of both electronic and ionic components. However, their phases exhibit low electronic conductivity.

The purpose of the present paper is to investigate the electrical properties of various $\text{A}^{\text{I}}_2\text{B}^{\text{II}}\text{P}_2\text{O}_7$ crystalline diphosphates and to establish correlations between their structure and electrical properties. For that purpose, three diphos-

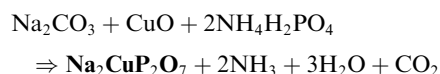
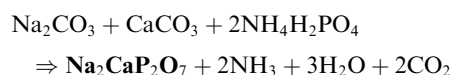
phates $\text{Na}_2\text{CaP}_2\text{O}_7$, $\text{Na}_2\text{CuP}_2\text{O}_7$ and $\text{K}_2\text{MnP}_2\text{O}_7$ have been selected.

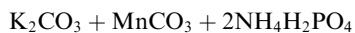
Despite the fact that $\text{Na}_2\text{CaP}_2\text{O}_7$ and $\text{K}_2\text{MnP}_2\text{O}_7$ crystallize in different symmetries ($P\bar{1}$ and $P2_1/c$ respectively) (Ben-nazha et al., 1999; Elmaadi et al., 1994) (Fig. 1 a and b), their respective structures, however, are very similar. The P_2O_7 groups and MO_6 ($\text{M} = \text{Ca}, \text{Mn}$) octahedra are connected to each other forming tunnels, while the alkali cations are located between these tunnels. P_2O_7 groups are parallel to each other. In contrast, the structure of $\text{Na}_2\text{CuP}_2\text{O}_7$ (H.T) Erragh et al., 1995 (Fig. 1c) exhibit layer structures formed by P_2O_7 and CuO_4 groups. The alkali cations are located between the layers. The figures of the three diphosphates related to crystal structures were drawn from crystallographic data using atoms for windows software (Dowty, 1995) for better visualization of the location of alkaline cations responsible for the conductivity.

2. Materials and methods

2.1. Synthesis

The crystalline diphosphates $\text{Na}_2\text{CaP}_2\text{O}_7$, $\text{Na}_2\text{CuP}_2\text{O}_7$ and $\text{K}_2\text{MnP}_2\text{O}_7$ were obtained in a powder state from starting materials with high purity grade ($>99\%$) and using a solid state technique. Reactions occurred according to the following equations:





For each diphosphate, starting materials were mixed and ground together in an agate mortar and heated progressively in porcelain crucible with intermittent cooling and regrinding. The synthesis temperatures were 950 K for $\text{Na}_2\text{CaP}_2\text{O}_7$ and 873 K for $\text{Na}_2\text{CuP}_2\text{O}_7$ and $\text{K}_2\text{MnP}_2\text{O}_7$.

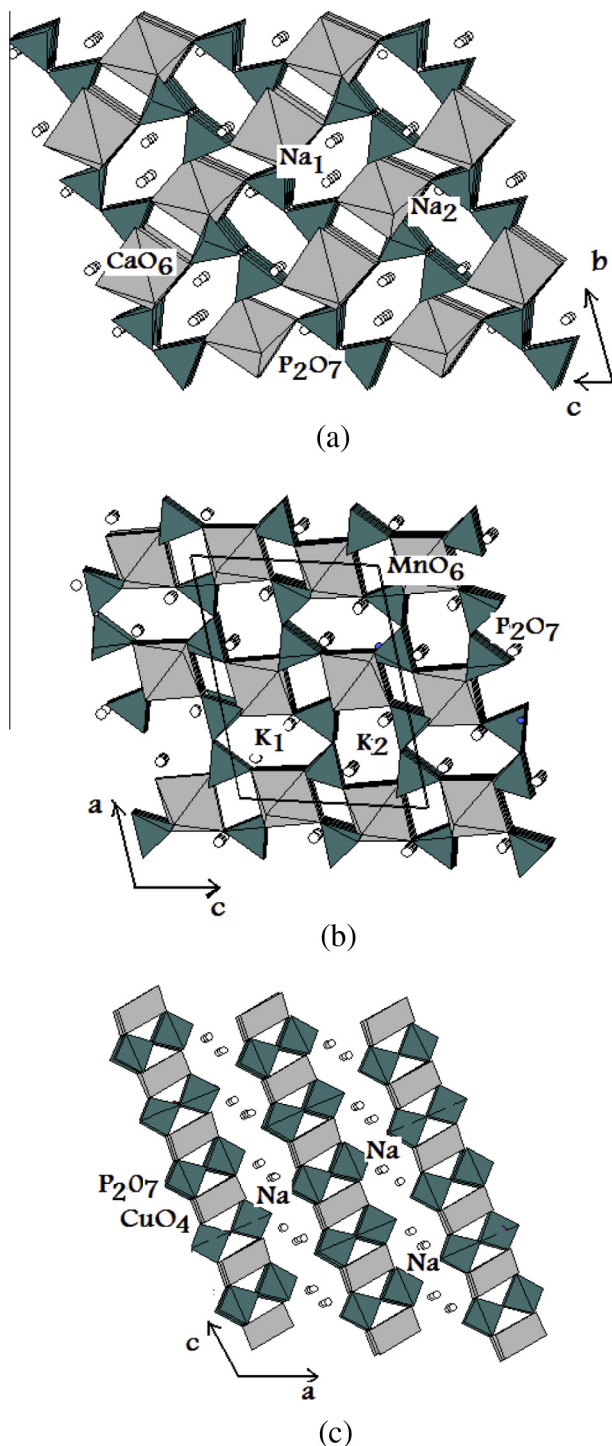


Figure 1 Projection view of (a) $\text{Na}_2\text{CaP}_2\text{O}_7$, (b) $\text{K}_2\text{MnP}_2\text{O}_7$, and (c) $\text{Na}_2\text{CuP}_2\text{O}_7$.

The powders were analyzed by X-ray powder diffraction, using a Siemens D-5000 diffractometer equipped with copper anticathode ($\lambda_{\text{K}\alpha} = 1.5406$). All diffractograms showed a good agreement with respective single crystal data (Bennazha et al., 1999; Elmaadi et al., 1994; Erragh et al., 1995).

2.2. Electrical properties

The conductivity measurements have been carried out using powder samples pressed to form pellets, with thickness 1 mm, and diameter 8 mm, sintered under the same operating conditions as for synthesis. The Compactness was close to 90% for all samples. In the case of vacuum evaporation, gold has been used as electrode material. The Au//diphosphate sample//Au devices were placed in a quartz measurement cell, degassed at 473 K for 2 h and filled with dry argon to avoid eventual oxidation of cell electrodes. The electrical properties were determined by complex impedance method (Bauerle, 1969), using a frequency response analyzer Solartron 1260.

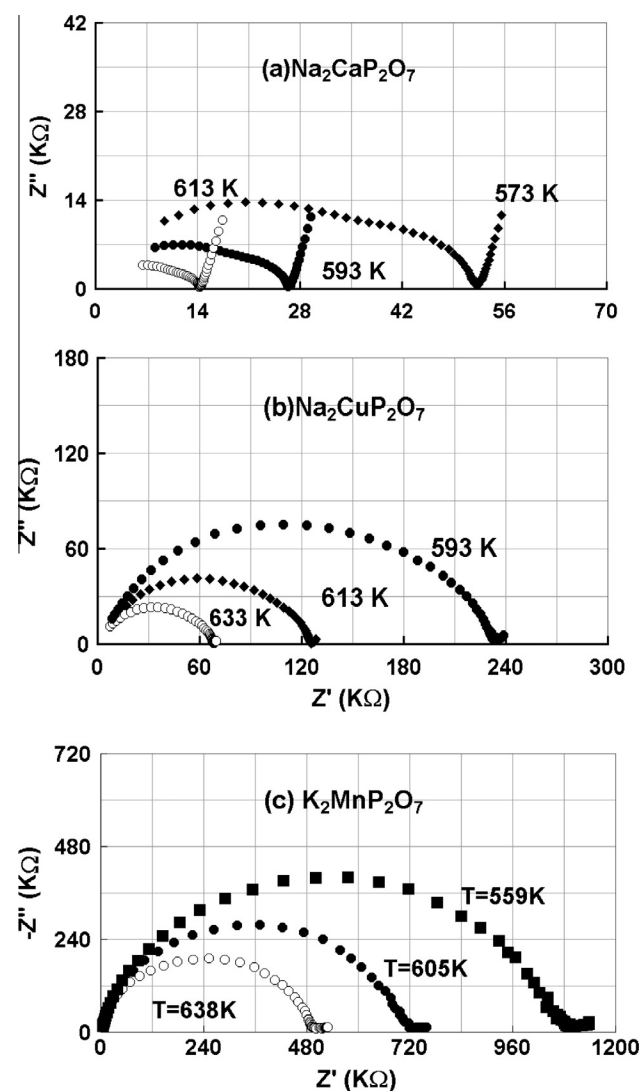


Figure 2 Complex impedance Cole-Cole plots of $Z''(\Omega)$ s. $Z'(\Omega)$ at various temperature for the three compounds (a) $\text{Na}_2\text{CaP}_2\text{O}_7$, (b) $\text{Na}_2\text{CuP}_2\text{O}_7$ and (c) $\text{K}_2\text{MnP}_2\text{O}_7$.

The frequency range was 10^{-1} – 10^6 Hz over the thermal interval 300–700 K in several temperature cycles. The electrical measurements were carried out automatically for temperature steps equal to 10° . For each temperature measurement, the sample was preserved for 30 min in order to reach its thermal equilibrium.

3. Results and discussion

3.1. Impedance hodographs

Impedance diagrams of $Z''(\Omega)$ as a function of $Z'(\Omega)$ i.e. Cole–Cole diagrams (Almond and West, 1983) are shown in Fig. 2a–c for $\text{Na}_2\text{CaP}_2\text{O}_7$ at 573, 593 and 613 K, $\text{Na}_2\text{CuP}_2\text{O}_7$ at 593, 613 and 633 K and for $\text{K}_2\text{MnP}_2\text{O}_7$ at 559, 605 and 638 K, respectively.

The spectra can be classified into two groups:

- Spectra relative to $\text{Na}_2\text{CaP}_2\text{O}_7$, which offer two depressed and distorted semi-circles at higher frequencies with a spike at lower frequencies. The presence of the inclined spike on the low frequency side of the semi-circles is characteristic of a polarization at the electrode–electrolyte interface.
- Spectra relative to $\text{Na}_2\text{CuP}_2\text{O}_7$ and $\text{K}_2\text{MnP}_2\text{O}_7$, which consist of a single arc, approximately a distorted semi-circle independent of the temperature. Absence of an inclined spike on the low frequency side of the semi-circles in the spectra of $\text{K}_2\text{MnP}_2\text{O}_7$ is attributed to the mixed ionic and electronic conductor.

3.2. Equivalent electric circuits

An equivalent circuit containing two, three or more elements may be modified in various combinations but still yields the same overall ac response. This leads to the notion that there is no unique equivalent circuit for a particular system. Thus, the challenge is the selection of the type of equivalent circuit to be used for the analysis and interpretation of the electrical behavior of a system. Usually, the equivalent circuit is selected based on the following:

- Intuition as to what kind of impedances is expected to be present in the studied system and whether they are connected in series or in parallel.
- Examination of the experimental data to determine whether the response is consistent with the proposed circuit.
- Inspection of R and C values obtained in order to check if they are realistic and their temperature dependence, if any, is reasonable.

An equivalent circuit widely used to represent bulk and grain boundary phenomena in polycrystalline materials consists of two parallel R_bC_b and $R_{gb}C_{gb}$ elements connected in series (Hodge et al., 1976). The determination of different electrical components of the circuit is best achieved using a combination of impedance and electrical modulus formalism since each parallel RC element gives rise to a semi-circle in the complex plan (Z'' vs. Z' ; M'' vs. M') or a Debye peak in the spectroscopic plots of the imaginary functions (Z'' ; M'' vs. $\log(f)$) Sinclair, 1995.

The response in the Z^* plane for a single parallel RC element has the form of a semi-circular arc passing through the origin. Its low frequency intercept on the real axis corresponds to the resistance R of the element. In practice, semi-circles associated with bulk relaxation processes in the Z^* plots of many conducting materials are found to be non ideal. Depressed semi-circles are obtained with their centers displaced below the real axis. There are two main reasons for such non-ideal behavior:

- The presence of a distribution in relaxation times within the bulk response (Howell et al., 1974).
- Distortion due to other relaxations, e. g. grain boundary relaxations, whose time constants are within two orders of magnitude of that of the bulk (Sinclair, 1995; Ming et al., 1995).

3.2.1. $\text{Na}_2\text{CaP}_2\text{O}_7$ sample

The Z^* hodographs obtained for the diphosphate $\text{Na}_2\text{CaP}_2\text{O}_7$ studied are consistent with the equivalent electric circuit shown in Fig. 2a. Two semi-circumferences of the $Z'' = f(Z')$ curve, which appear successively at decreasing frequency (Fig. 1a), are associated with relaxation processes characteristic of intragranular (R_bC_b) and intergranular ($R_{gb}C_{gb}$), respectively. The polarization phenomena at the electrode–electrolyte interface are represented by the C element.

For a given temperature, the values of R_b and R_{gb} parameters have been, at first, estimated from experimental spectra at

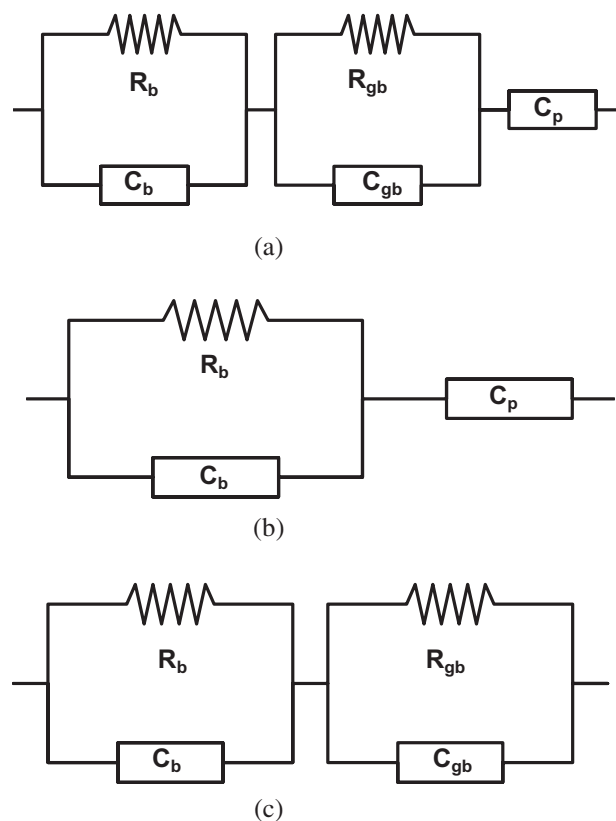


Figure 3 Equivalent circuit used to represent the electrical behaviour of (a) $\text{Na}_2\text{CaP}_2\text{O}_7$, (b) $\text{Na}_2\text{CuP}_2\text{O}_7$ and (c) $\text{K}_2\text{MnP}_2\text{O}_7$.

Table 1 Electrical values of the equivalent circuit parameters calculated for the compound $\text{Na}_2\text{CaP}_2\text{O}_7$.

T (°C)	R_1 (Ω) 10^{+5}	C_1 (F) 10^{-12}	n_1	R_2 (Ω) 10^{+5}	C_2 (F) 10^{-11}	n_2	C_3 (F) 10^{-7}	n_3
200	37.2	1.34	0.8	30.2	8.02	0.78	9.00	0.8
205	30.1	1.03	0.8	30.0	8.02	0.78	9.00	0.8
210	24.7	1.03	0.8	22.0	8.02	0.78	9.00	0.8
215	20.5	1.03	0.8	20.0	1.00	0.78	9.00	0.8
220	17.1	1.03	0.8	14.1	1.00	0.78	9.00	0.8
225	14.2	1.03	0.8	13.0	1.00	0.78	9.00	0.8
230	12.0	1.34	0.8	12.4	1.00	0.78	9.00	0.8
235	10.4	1.34	0.8	9.80	1.00	0.8	9.00	0.8
240	87.9	1.03	0.8	6.22	1.00	0.8	9.00	0.8
245	75.3	1.03	0.8	5.50	1.00	0.8	9.00	0.8
250	6.49	1.03	0.8	4.37	1.00	0.8	9.00	0.8
260	4.76	2.30	0.8	2.60	1.00	0.8	9.00	0.8
265	4.06	2.30	0.8	4.00	1.00	0.8	9.00	0.8
270	3.43	2.30	0.8	2.00	1.00	0.8	9.00	0.8
280	2.33	2.30	0.8	1.47	1.00	0.8	9.00	0.8
285	1.94	2.30	0.8	1.70	1.00	0.8	9.00	0.8
290	1.60	2.30	0.8	1.00	1.00	0.8	9.00	0.8
300	1.09	2.30	0.8	1.00	1.00	0.8	9.00	0.8
310	0.750	3.30	0.8	0.490	1.00	0.8	9.00	0.8
320	0.521	3.30	0.8	0.511	1.00	0.8	9.00	0.8
330	0.372	3.30	0.8	0.352	1.00	0.8	9.00	0.8
340	0.266	3.30	0.8	0.240	1.00	0.8	9.00	0.8
350	0.194	3.30	0.8	0.174	1.00	0.8	9.00	0.8
360	0.144	3.30	0.8	0.134	1.00	0.8	9.00	0.8

low frequency intercepts of each semi-circle with the real axis. For each relaxation process, the values of C_b and C_{gb} have been estimated from experimental points corresponding to the frequency $\omega_{\max}$ of the Z'' maximum. Indeed, $\omega_{\max}$, R and C for a parallel RC element are bound by the ($\omega_{\max}$, $RC = 1$) relationship. Recall that ω ($\omega = 2\pi f$) was the angular frequency.

The dispersive properties of different relaxation processes have been taken into account in the simulation of impedance spectra by including the complex capacitance C_i of each R_iC_i element in the form (Jonscher, 1983):

$$C_i = B_i \cdot (j\omega)^{n_i} - 1 (0 < n_i < 1)$$

A fitting approach for each temperature has been conducted by using complex non-linear least-squares fitting of both the real and the imaginary parts of $Z^*(\omega)$. LEVEM version 7.0 has been used for this research project (Macdonald, 1997). Typical fitting results of $\text{Na}_2\text{CaP}_2\text{O}_7$ sample at $T = 240, 300$ and 340 °C are illustrated in Fig. 3a, where the relative residuals are defined by the relationship (Ming et al., 1995):

$$\Delta_{\text{re}} = \frac{Z'_{\text{mes.}} - Z'_{\text{cal}}}{Z'_{\text{mes.}}} \text{ and } \Delta_{\text{im}} = \frac{Z''_{\text{mes.}} - Z''_{\text{cal}}}{Z''_{\text{mes.}}}$$

An optimum fit is obtained as the relative residuals were randomly distributed around the frequency axis. The relative errors were less than 5% in the measurement frequency range (Fig. 3a), which were in agreement with the experimental error. Therefore, an excellent agreement between experimental and theoretical calculation data has been established in a wide frequency range, confirming the validity of the equivalent electric circuit proposed.

Values of different electric parameters, at different temperatures, of the equivalent circuit determined after fitting were illustrated in Table 1. The R_i parameters vary with temperature

according to Arrhenius-type laws, while the B_i and the n_i parameters were relatively independent of temperature.

3.2.2. $\text{Na}_2\text{CuP}_2\text{O}_7$ sample

For this particular diphosphate, the complex impedance plan plot; Z^* , showed two depressed and overlapped semicircles followed by a tail at lower frequencies. The equivalent circuit proposed is composed of a series combination of two parallel RC elements in series (Fig. 2b). The displacement of each center of the experimental arcs below the real axis leads to conclude that the ideal resistive and capacitive circuit element is inadequate to describe the ac response of the sample. Consequently, the distributed impedance elements, and the constant phase

Table 2 Electrical values of the equivalent circuit parameters calculated for the compound $\text{Na}_2\text{CuP}_2\text{O}_7$.

T (°C)	R_1 (Ω) 10^{+5}	C_1 (F) 10^{-12}	n_1	C_2 (F) 10^{+7}	n_2
210	91.6	6.01	0.78	9.00	0.7
220	66.0	6.01	0.78	9.00	0.7
230	47.1	6.01	0.78	9.00	0.7
240	34.3	6.01	0.78	9.00	0.7
250	24.1	6.01	0.78	9.00	0.7
260	17.6	6.01	0.78	9.00	0.7
270	12.5	6.01	0.78	9.00	0.7
280	8.83	6.01	0.78	9.00	0.7
305	3.72	6.01	0.78	9.00	0.7
315	2.76	6.01	0.78	9.00	0.7
325	2.03	6.01	0.78	9.00	0.7
330	1.73	6.01	0.78	9.00	0.7
340	1.26	6.01	0.78	9.00	0.7
350	0.930	6.01	0.78	9.00	0.7
360	0.690	6.01	0.78	9.00	0.7

Table 3 Electrical values of the equivalent circuit parameters calculated for the compound $K_2MnP_2O_7$.

T (°C)	R_i (Ω) 10^{+5}	C_i (F) 10^{-12}	n_i	R_2 (Ω) 10^{+5}	C_2 (F) 10^{-9}	n_2
200	42.4	9.01	0.82	4.24	9.00	0.8
205	37.0	9.01	0.82	3.00	9.00	0.8
210	31.0	9.01	0.82	3.00	9.00	0.8
215	25.3	9.01	0.82	2.40	9.00	0.8
220	20.4	9.01	0.82	1.90	9.00	0.8
225	18.4	9.01	0.82	1.64	9.00	0.8
230	15.4	9.01	0.82	1.40	9.00	0.8
240	13.4	9.01	0.88	2.00	9.00	0.8
245	14.0	9.01	0.88	1.40	9.00	0.8
255	11.6	9.01	0.88	1.16	9.00	0.8
265	11.3	9.01	0.88	1.13	9.00	0.8
275	10.3	9.01	0.88	1.03	9.00	0.8
280	12.3	9.01	0.88	1.00	9.00	0.8
285	10.6	9.01	0.88	1.00	9.00	0.8
300	9.24	9.01	0.88	0.800	9.00	0.8
315	8.75	9.01	0.88	0.400	9.00	0.8
325	7.95	9.01	0.88	0.300	9.00	0.8
340	5.80	9.01	0.88	0.200	9.00	0.8

element have been introduced in order to fully characterize the data using two distributed parameters: Z_i in series with a $B_i(j\omega)^{n_i} - 1$. Both semi-circumferences of the $Z'' = f(Z')$ curve which appear successively at decreasing frequency are associated with relaxation processes characteristic of intragranular (R_bC_b) and intergranular ($R_{gb}C_{gb}$), respectively. No polarization phenomenon at the electrode-electrolyte interface was present, indicating that the compound is a mixed ionic-electronic conductor.

For each temperature, the values of R_i and C_i parameters have been estimated from experimental spectra. A fitting approach is followed by using complex non-linear least-squares fitting of both the real and the imaginary parts of $Z^*(\omega)$ with the same program (Macdonald, 1997). Typical fitting results from $Na_2CuP_2O_7$ sample at $T = 260, 300$ and 340 °C are presented in Fig. 3b.

An excellent agreement between experimental and theoretical calculation data has been obtained with a relative errors less than 5% in the measurement frequency range (Fig. 3b), confirming the validity of the equivalent electric circuit proposed. The values of different electric parameters are illustrated in Table 2. The R_i parameters vary with temperature according to Arrhenius-type laws, while the B_i and the n_i parameters were relatively independent on the temperature.

3.2.3. $K_2MnP_2O_7$ sample

For this diphosphate, the complex impedance plan plot; Z^* seems to be enough symmetrical. Taking into account this results and the absence of the inclined spike in the spectra, on the low frequency, characteristic of the polarization phenomena; the equivalent circuit proposed is constituted by parallel RC elements (Fig. 2c). The dispersive properties of different relaxation processes have been taken into account in the simulation of impedance spectra by introducing the complex capacitance $C = B_i(j\omega)^{n_i} - 1$. The electrical properties intragranular and intergranular in this compound appeared to be very close to each other. The fitting of the experimental data are followed in the same conditions as of the $Na_2CaP_2O_7$ and $Na_2CuP_2O_7$ samples. Typical fitting resulted of $K_2MnP_2O_7$ sample at $T = 285, 335$ and 365 °C are shown in Fig. 3c.

An optimum fit is obtained as the relative residuals were spreaded randomly around the frequency axis. The relative errors are less than 5% in the measurement frequency range (Fig. 3c), confirming the validity of the equivalent electric circuit proposed. Table 3 demonstrate the values of different electric parameters of the $K_2MnP_2O_7$ compound. As the crystalline $Na_2CaP_2O_7$ and $Na_2CuP_2O_7$ diphosphates, R parameter vary with temperature according to Arrhenius-type law, while B and n parameters are relatively independent of temperature.

3.3. Temperature dependence of electrical properties in $Na_2CaP_2O_7$, $Na_2CuP_2O_7$ and $K_2MnP_2O_7$

The temperature dependence of conductivity σ deduced from R_b is shown in Figs. 4a–c for the $Na_2CaP_2O_7$, $Na_2CuP_2O_7$ and $K_2MnP_2O_7$ for a temperature range from 473 K to 673 K. The graphs consist of two linear segments, each of which involving a behavior of Arrhenius-type, $\sigma.T = \sigma_0 \exp(-\Delta E \sigma / kT)$. The activation energies relative to both temperature intervals for each diphosphate, $(\Delta E \sigma)_I$ and $(\Delta E \sigma)_{II}$ are illustrated in Table 4. For the two compounds $Na_2CaP_2O_7$ and $Na_2CuP_2O_7$, the crossing at increasing temperature from low temperature regime to high temperature one is accompanied by a small increase of activation energy. In contrast, in the case of $K_2MnP_2O_7$, the activation energy decreases from the low temperature regime to high temperature.

Using the complex modulus formalism $M^* = 1/\varepsilon^* = j(\omega C_0)Z^*$; where C_0 is the vacuum capacitance of the empty measuring cell. An analysis of ac impedance data of $Na_2CaP_2O_7$, $Na_2CuP_2O_7$ and $K_2MnP_2O_7$ was carried out in order to determine the conductivity relaxation parameters. Considering an equivalent electric circuit composed of two parallel RC elements associated in series, the modulus plot gives emphasis to the element with the smallest capacitance where as the impedance plot highlights that with the largest resistance. Consequently, the M^* formalism can determine grain boundary phenomena, electrode polarization and other interfacial effects in solid electrolytes (Bauerle, 1969; Sinclair, 1995). Frequency dependence of the normalized imaginary

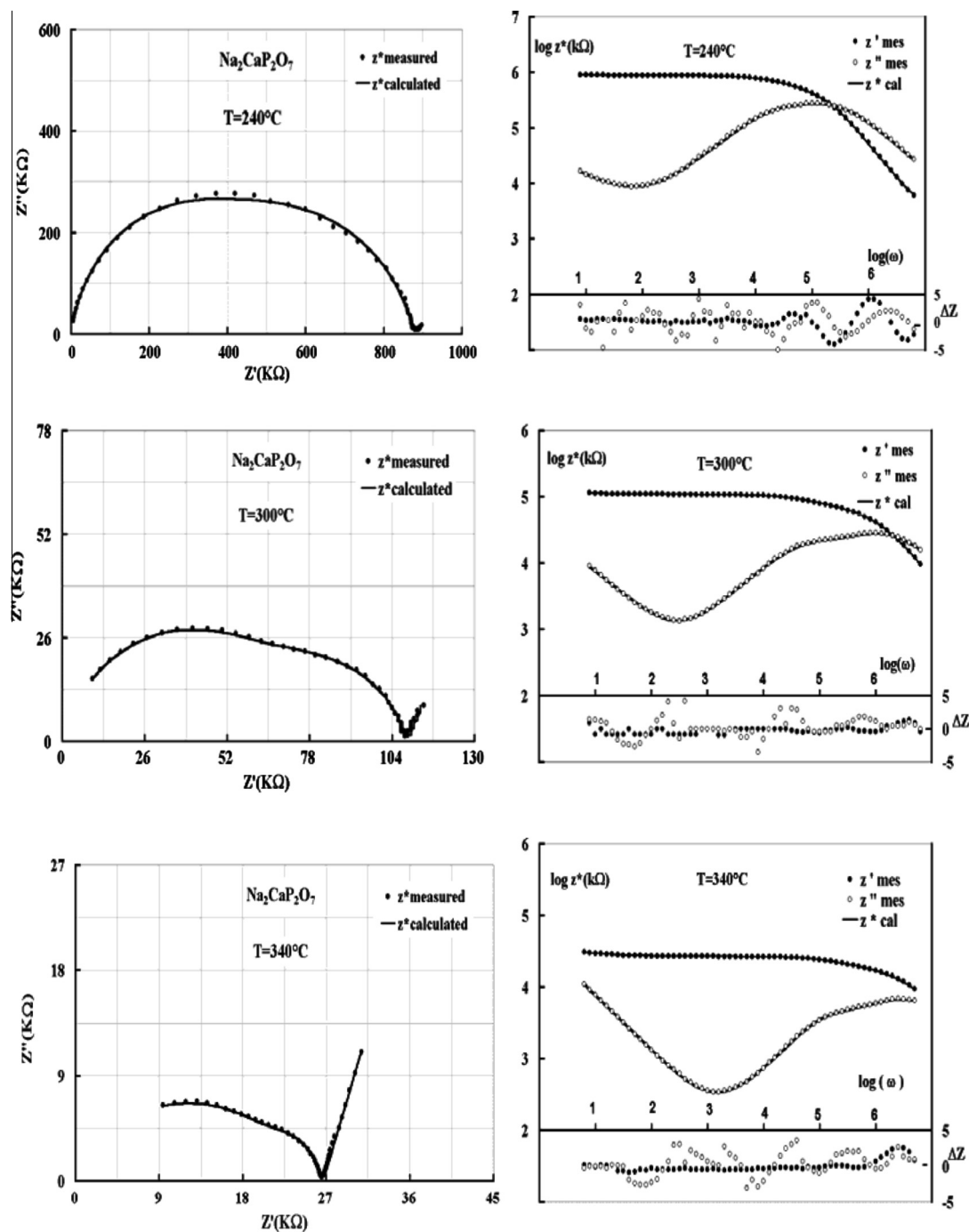


Figure 4a Impedance complex plane plot measured and calculated and relative residuals of the diphosphate $\text{Na}_2\text{CaP}_2\text{O}_7$ at $T = 513 \text{ K}$, $T = 573 \text{ K}$ and $T = 613 \text{ K}$, using the equivalent circuit of Fig. 2a.

part of M^* , $M''/M''_{\max}$, for $\text{Na}_2\text{CaP}_2\text{O}_7$, $\text{Na}_2\text{CuP}_2\text{O}_7$ and $\text{K}_2\text{MnP}_2\text{O}_7$ at different temperature, is shown in Fig. 5. The non-symmetric of curves $M''/M''_{\max}$ is in agreement with non exponential behavior of the electrical function, which is well described by the Kohlrausch function $\varphi(t) = \exp[-(t/\sigma)^\beta]$ with $0 < \beta < 1$ (Ngai and Martin, 1989; Howell et al., 1974). The σ and β parameters of the stretched exponential function are the conductivity relaxation time and the Kohlrausch exponent respectively. The smallest is the value of β , and the largest is attributed to the deviation of the relaxation with respect to a

Debye-type relaxation ($\beta = 1$). The frequency range, where the peak occurs, is indicative of the transition from short-range to long-range mobility at decreasing frequency and is defined by the condition $\omega\tau_\sigma = 1$ where τ_σ is the most probable ion relaxation time (Patel and Martin, 1992). The energy values ΔE_f were extracted from ρ frequency ($f_P = 1/2\pi\tau_\sigma$), data relative to $M''_{\max}$. The full width at half-height (FWHH) of the $M''/M''_{\max}$ spectrum is clearly wider than the breadth of Debye peak (1.14 decades) resulting in a value $\beta = 1.14/\text{FWHH}$ for the Kohlrausch exponent. For each material, β may be consid-

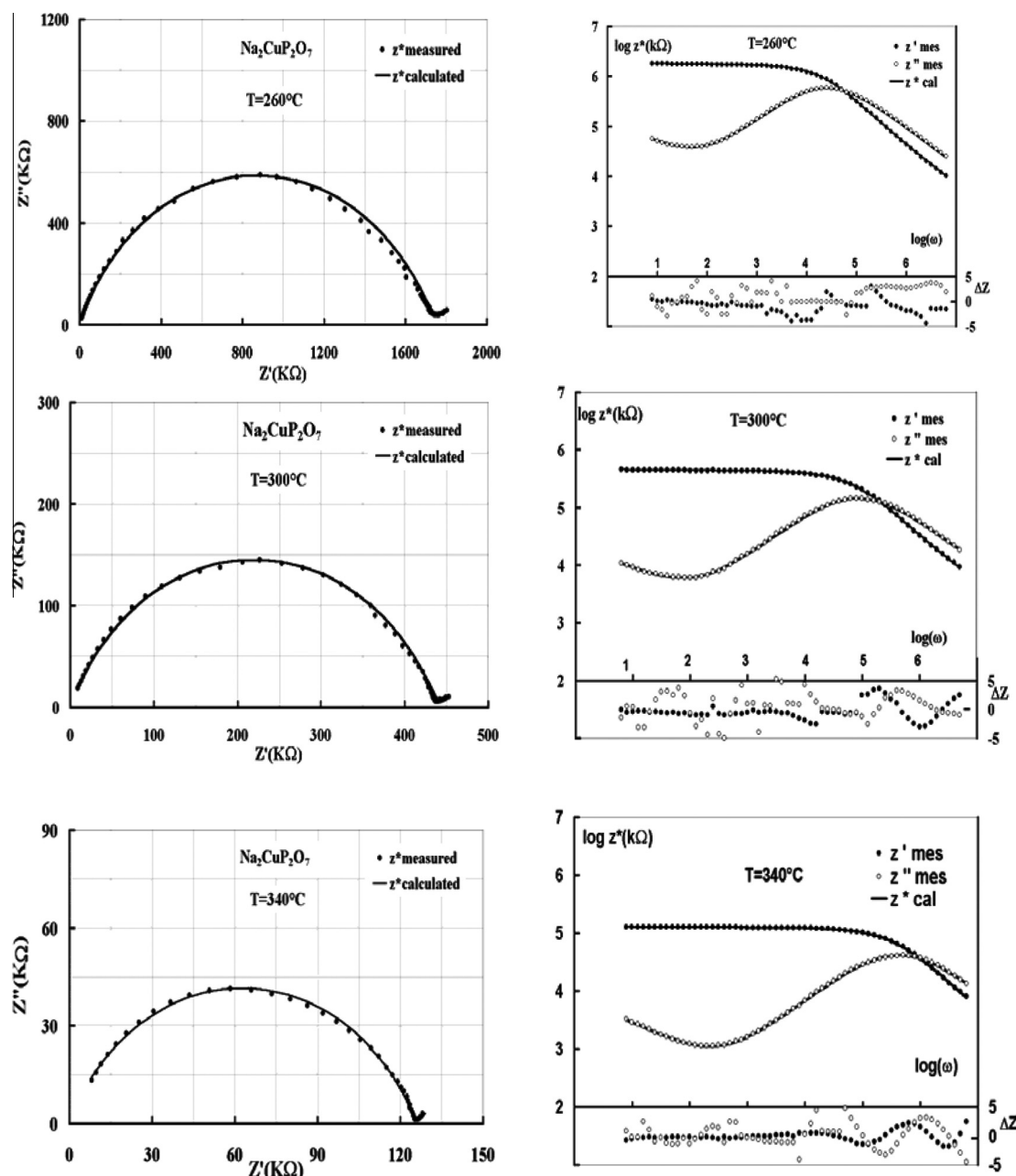


Figure 4b Impedance complex plane plot measured and calculated and relative residuals of the diphosphate $\text{Na}_2\text{CuP}_2\text{O}_7$ at $T = 533, 573$ and 613 K, using the equivalent circuit of Fig. 2b.

ered as temperature-independent in the studied temperature range. The β values obtained for the three materials under investigation are reported in Table 4. The values of β relative to the compounds $\text{Na}_2\text{CaP}_2\text{O}_7$ and $\text{Na}_2\text{CuP}_2\text{O}_7$ are relatively equal and are smaller than that corresponding to $\text{K}_2\text{MnP}_2\text{O}_7$. As the temperature increases, modulus peak maxima relative to each material under investigation shift to higher frequencies. The temperature dependence of the f_p frequency relative to $M''_{\max}$ for the $\text{Na}_2\text{CaP}_2\text{O}_7$, $\text{Na}_2\text{CuP}_2\text{O}_7$ and $\text{K}_2\text{MnP}_2\text{O}_7$ is reported in Figs. 4a–c. The activation energies determined from the impedance (ΔE_σ) and modulus (ΔE_f) spectra are close enough to suggest that the charge carriers in the three phases studied is probably due to a hopping mechanism (Chowdari and Gopalakrishnan, 1987) (See Fig. 6).

3.4. Correlation between electrical and structural properties in $\text{Na}_2\text{CaP}_2\text{O}_7$, $\text{Na}_2\text{CuP}_2\text{O}_7$ and $\text{K}_2\text{MnP}_2\text{O}_7$

The conductivity properties inside the two phases $\text{Na}_2\text{CaP}_2\text{O}_7$ and $\text{Na}_2\text{CuP}_2\text{O}_7$ can be considered as ionic. The Differential Scanning Calorimetry (DSC) analysis of the two compounds $\text{Na}_2\text{CaP}_2\text{O}_7$ and $\text{Na}_2\text{CuP}_2\text{O}_7$ has been conducted over the temperature range 298–673 K (temperature range studied by the ac conductivity). DSC thermograms do not present any phase transition or other thermal phenomenon. The results suggest that the phenomenon of the change in the slope observed in the plot of $\log \sigma T$ against reciprocal temperature, for the two compounds $\text{Na}_2\text{CaP}_2\text{O}_7$ and $\text{Na}_2\text{CuP}_2\text{O}_7$, is not due to a phase transition but probably to the crystallographic structure.

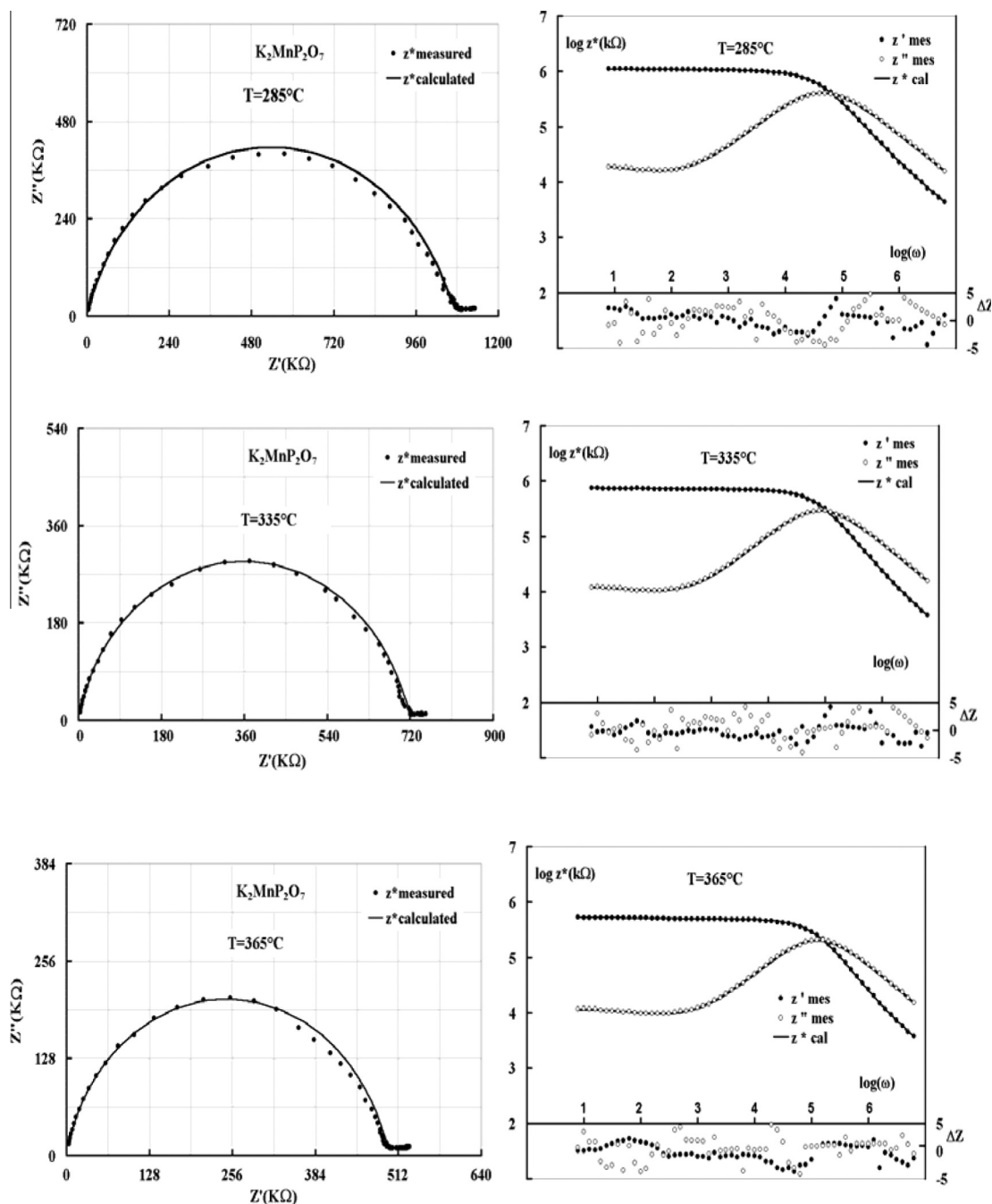


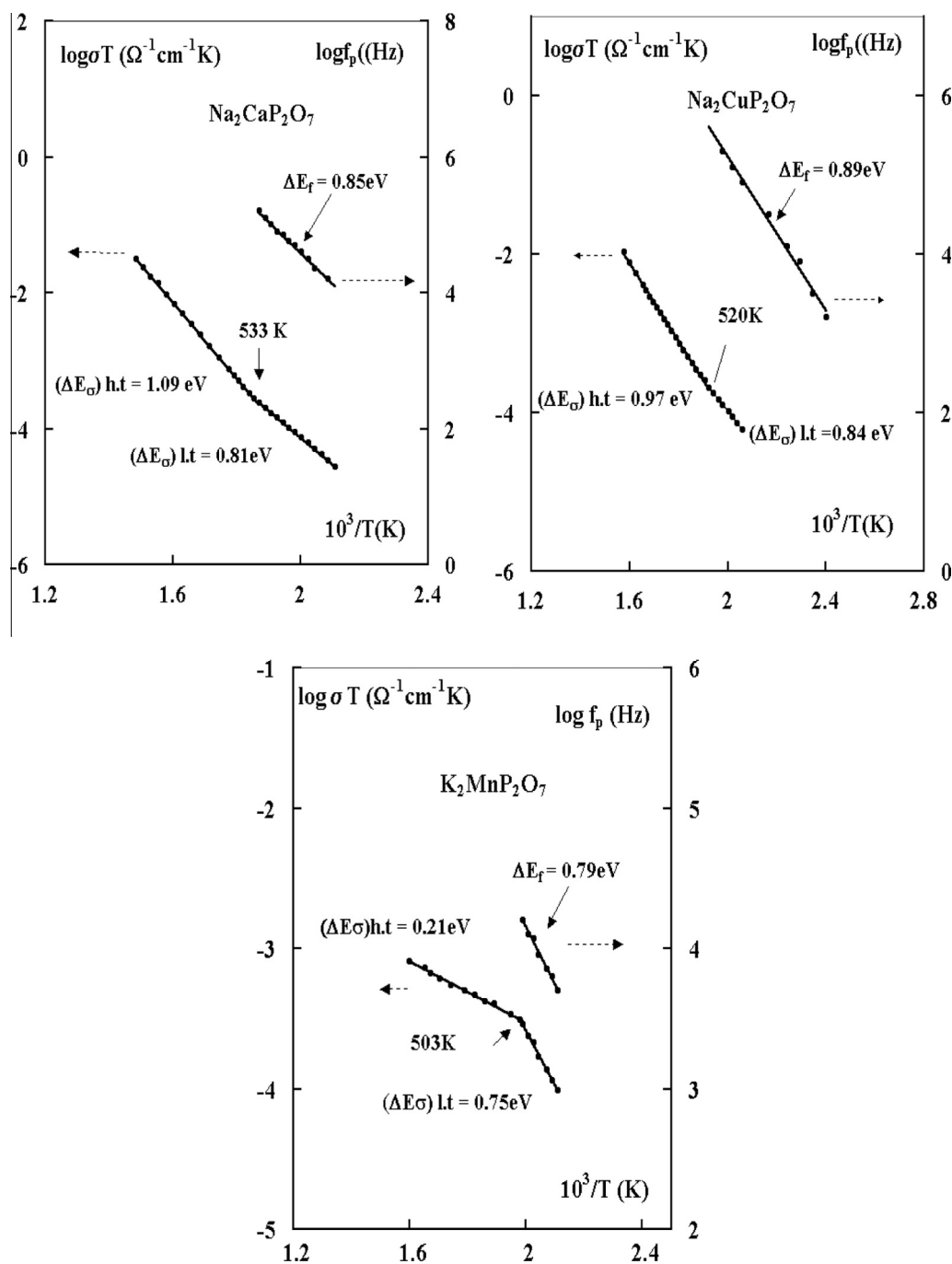
Figure 4c Impedance complex plane plot measured and calculated and relative residuals of the diphosphate $K_2MnP_2O_7$ at $T = 558, 608$ and 638 K, using the equivalent circuit of Fig. 2c.

Indeed, the transport properties inside the two phases $Na_2CaP_2O_7$ and $Na_2CuP_2O_7$ are respectively associated with the displacement of Na^+ ions in the tunnels seen according to the $[1\ 0\ 0]$ direction and in the space of interlayer seen according to $[0\ 1\ 0]$ and $[1\ 0\ 0]$ directions. For $Na_2CaP_2O_7$, the sodium ions occupy two crystallographic sites $Na^+(1)$ and $Na^+(2)$. Thus, the first segment of weak activation energy is attributed to motion of $Na^+(1)$ ions which are free in the center of their respective tunnels. Whereas the second segment of high activation energy is due, in addition to $Na^+(1)$ ions, to the contribution of $Na^+(2)$ ions which are rather wedged with polyhedra

CaO_6 and P_2O_7 and require more thermal energy to become mobile. The activation energy measured over the temperature 533 K is the average between the hopping energy of ions $Na^+(1)$ and $Na^+(2)$. For the compound $Na_2CuP_2O_7$, we have one kind of sodium cation according to its single crystallographic site. Each cation is surrounded by six oxygen atoms. The thermal activation can cause a motion of the P_2O_7 groups which influence the movement of the cations Na^+ neighbors and modify the behavior of ionic conductivity. The conductivity in the compound $K_2MnP_2O_7$ is rather of electronic nature. This electronic conductivity found may result from a charge

Table 4 Electrical parameters of the three compounds $\text{Na}_2\text{CuP}_2\text{O}_7$, $\text{Na}_2\text{CaP}_2\text{O}_7$ and $\text{K}_2\text{MnP}_2\text{O}_7$.

	$\log \sigma$ ($\Omega^{-1} \text{cm}^{-1} \text{K}$) ± 0.2	ΔE_{σ} (eV) ± 0.02	ΔE_f (eV) ± 0.02	T_r (K) ± 10	β
$\text{Na}_2\text{CuP}_2\text{O}_7$					
Low temp.	3.66	0.84	0.89	520	0.62
High temp.	5.7	0.97	—		
$\text{Na}_2\text{CaP}_2\text{O}_7$					
Low temp.	3.75	0.81	0.85	533	0.63
High temp.	6.69	1.09	—		
$\text{K}_2\text{MnP}_2\text{O}_7$					
Low temp.	4.13	0.75	0.79	503	0.67
High temp.	1.38	0.21	—		

**Figure 5** Temperature dependence of $\log \sigma$ versus reciprocal temperature for the three compounds $\text{Na}_2\text{CaP}_2\text{O}_7$, $\text{Na}_2\text{CuP}_2\text{O}_7$ and $\text{K}_2\text{MnP}_2\text{O}_7$.

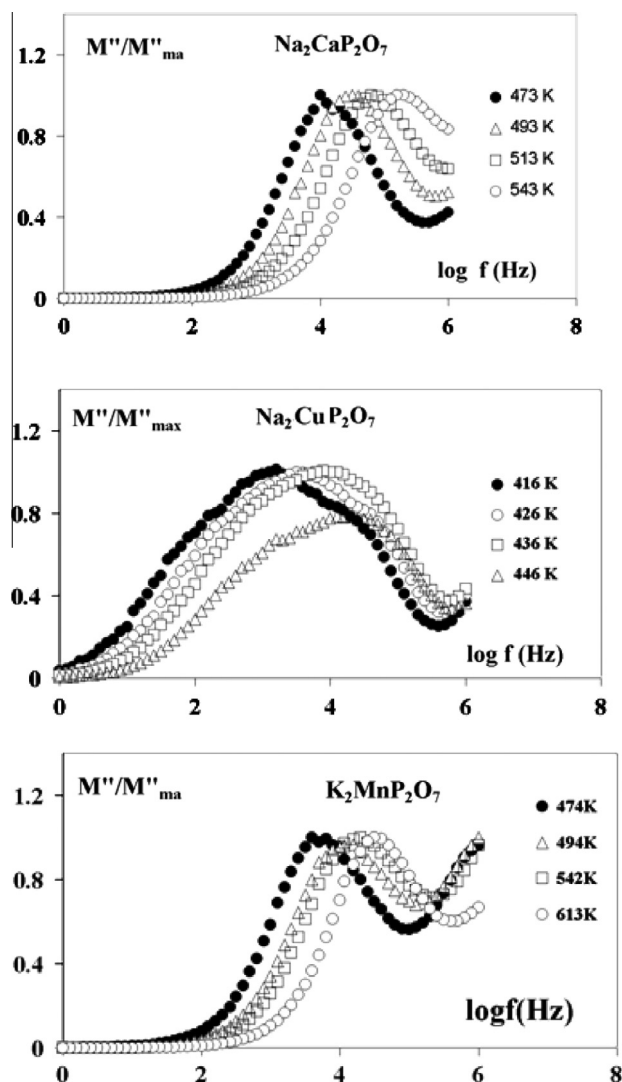


Figure 6 Normalized modulus, $M''/M''_{\max}$ versus $\log f$ at various temperature for of the three compounds $\text{Na}_2\text{CaP}_2\text{O}_7$, $\text{Na}_2\text{CuP}_2\text{O}_7$ and $\text{K}_2\text{MnP}_2\text{O}_7$.

carrier supported by the existence of the Mn element which has several oxidation states.

This compound is characterized by two mechanisms of ionic conduction. One with low temperatures, and an activation energy close to 0.71 eV and one with high temperatures, which energy is much lower and of the order of 0.21 eV. Such a phenomenon is also encountered in materials with tysonite structure type (El Omari et al., 1998a, 1998). These materials have three fluorine subnets. For low temperatures, only one sub-lattice of the three is mobile. In the contrary for high temperatures an exchange between the three networks is established.

4. Conclusion

The investigation of electrical properties of three diphosphates $\text{Na}_2\text{CaP}_2\text{O}_7$, $\text{Na}_2\text{CuP}_2\text{O}_7$ and $\text{K}_2\text{MnP}_2\text{O}_7$ in the combined Z^* and M^* formalisms has allowed us to confirm that $\text{Na}_2\text{CaP}_2\text{O}_7$

and $\text{Na}_2\text{CuP}_2\text{O}_7$ are moderate ionic conductors, which originates from Na^+ ions hopping respectively in the tunnels seen according to the $[1\ 0\ 0]$ direction and in the space of inter-layer seen according to $[0\ 1\ 0]$ and $[1\ 0\ 0]$ directions. However, $\text{K}_2\text{MnP}_2\text{O}_7$ is a mixed ionic-electronic conductor, which can be explained by an electron hopping supported by the transition element Mn with several oxidation states.

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