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Equivalent Circuit and AC conductivity of $Sr_{1.75}Co_{0.25}P_2O_7$ compound

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ABSTRACT

$Sr_{1.75}Co_{0.25}P_2O_7$ compound was prepared by the solid-state reaction method. The impedance spectroscopy measurements were performed in the frequency and the temperature range of (209 Hz–1 MHz) and (622–704 K), respectively. Besides, the impedance spectra were fitted to an equivalent circuit consisting of series combination of grains and grain boundary. The AC conductivity for grain contribution is interpreted using the universal Jonscher's power law. The approximation type OLPT model explains the universal behavior of the s exponent. The mechanism of conduction is probably due from the displacements of the Sr^{2+} ion in the tunnel-type cavities.

Keywords: ionic conductivity, ceramic compound, pyrophosphate, impedance spectroscopy

1. INTRODUCTION

The open-framework metal phosphates, characterized by their high ionic conductivity, have been extensively studied, which might find applications such as prospective materials in technology, viz. in electronic devices and as solid electrolytes with high thermal resistance and as potential devices in space application, sensors, solid-state laser materials, piezoelectrics, luminescence, ceramics, catalysis, adsorption, ionic conductors and magnetic materials [1–7]. During the last years, there have been many studies of the compounds with general formula ABP2O7 (A and B : divalent ions) due to their luminescent, dielectric, semiconductor, catalytic, magnetic, fluorescent, ion exchange, electrical, mechanical properties and their chemical and/or thermal resistance [7–10].

In the present paper, we report the results of the impedance spectroscopy, the temperature and frequency dependence of the electrical conductivity and the dielectric properties of Sr1.75Co0.25P2O7 compound.

2. Results and discussions

2.1. Electrical impedance analysis

The impedance spectroscopy is one of the most experimental techniques to analyze the charge transport processes in the grain and grain boundary of solids [11]. This technique allows the estimation of resistivity and capacitance [12, 13].

Figures 1 shows the plot of (–Z′′) versus (Z′) at different temperatures for Sr1.75Co0.25P2O7 compound. All impedance exhibits some dispersion instead of a centered semicircle on the real axis, which indicates a non-Debye type of relaxation [14]. Besides, the shape of diagrams suggests that the electric response is composed of two semicircles where the simulated Nyquist plots with equivalent circuit elements at different temperatures show accordance between the calculated lines and the experimental data, which indicates that the suggested equivalent circuit describes the pellet - electrolyte interface reasonably well . This circuit is modeled by the combination series of grain and grain boundary elements. The first consists of parallel combination of resistance (Rg) capacitance (Cg), whereas the second consists of parallel combination of resistance (Rgb) and a constant phase (CPEgb), the impedance of the capacity of the fractal interface CPE is given by the following equation[15,16] :

$$Z_{CPE} = \frac{1}{Q(j\omega)^{\alpha}} \quad (1)$$

where Q indicates the value of capacitance of the CPE and α is the fractal exponent. Further (Eq. (1)) shows that as α = 1, ZCPE = 1/jQω, involving a pure capacitance, and as α= 0, ZCPE = 1/Q, a pure conductance.

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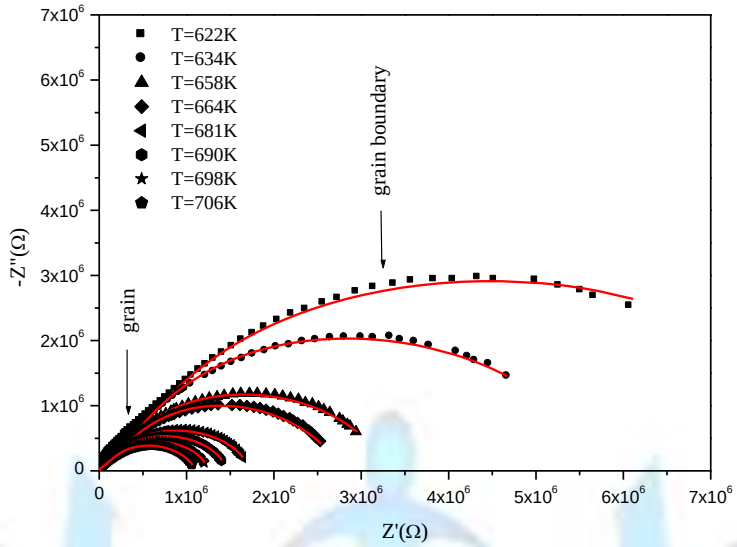

Fig 1: Plots of the impedance data at different temperatures for the $Sr_{1.75}Co_{0.25}P_2O_7$ compound

The fitting parameters obtained by the equivalent circuit corresponding to the grain and grain boundary are listed in Tab.1. It is evident that the grain resistance (Rg) is much lower than the grain boundary one. Because the latter dominates the resistance in the equivalent circuit, the semicircle of bulk is masked in a limited frequency range at higher temperature. The higher boundary resistance can be construed by the fact that the atomic arrangement near the grain boundary region is disordered, resulting in a serious increase in electron scaling [17].

Table 1 : The extract parameters for the circuit elements

T(k)	$R_g(\Omega)$	$C_g(10^{-11}F)$	R_{gb} (Ω)	α	$Q(10^{-10}F)$
622	341449	3.539	8076779	0,8201	2.179
634	238739	3.444	5556469	0.807	2.206
658	164801	3.124	3120263	0.821	2.153
664	145471	3.095	2623560	0.824	2.137
681	110079	2.969	1619303	0.829	2.228
690	95272	3.067	1372277	0.824	2.394
698	87387	3.066	1164984	0.826	2.385
706	78946	3.179	1023557	0.821	2.578

Figure 2 shows the frequency dependence of Z' and -Z'' at 698 K. An excellent agreement between the experimental (scatter) and theoretical curve (line) of the real and imaginary impedance was shown. Fitted values (grain, grain boundary) parameters, determined using the Zview software for all temperatures. All fitted curves at each temperature show good compliance of the calculated lines with the experimental data, confirming that the suggested equivalent circuit describes the crystal–electrolyte interface reasonably well.

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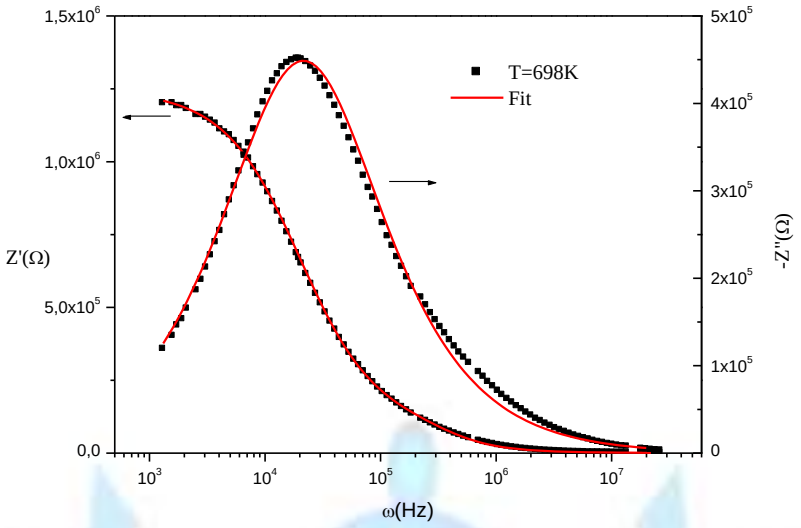

Fig. 2. Variation of Z' and –Z" with angular frequency at 698 K.

The curves -Z ″ = f (Z ′) are plainly separated and have the classic evolution of conductivity depending on temperature. Indeed, any rise in temperature is accompanied with a decrease in resistance. The dc conductivity of grain/grain boundary was calculated from the following equations:

$$\sigma_g = \frac{e}{R_g S} \quad (1)$$

$$\sigma_{gb} = \frac{R_g S}{R_{gb} S} \times \frac{C_g}{C_{gb}} \quad (2)$$

where e and S are, respectively, the thickness and the area of the pellet.

The temperature dependence of the grain conductivity rg and grain boundary conductivity rgb is shown in Fig. 3 and represented in the form of $Ln(\sigma_{dc}T)$ versus 1000/T. $Ln(\sigma_{dc}T)$ increases linearly with increasing temperature, proving that the conduction in the material is characterized by the Arrhenius law:

$$\sigma_{g,gb} \times T = \sigma_{g0,gb0} e^{\frac{-E_{g,}}{kT}} \quad (3)$$

The bulk (E_g) and the grain boundary bulk (E_{gb}) activation energies were 0.89 and 0.96 eV, respectively.

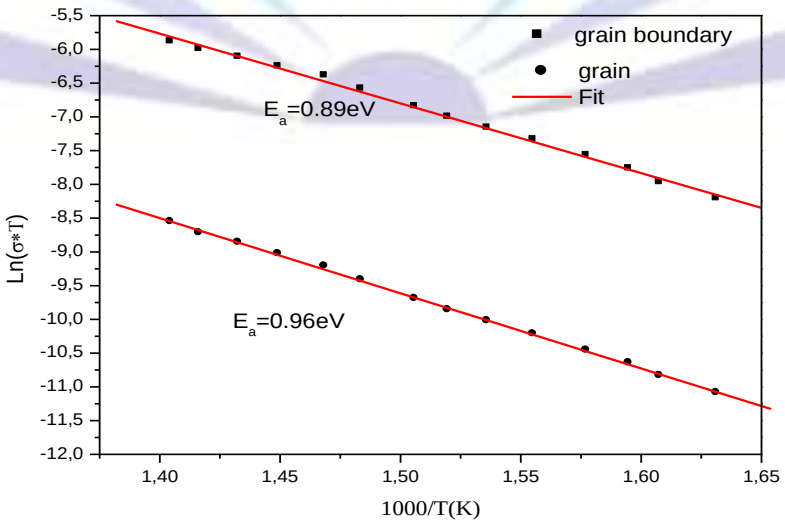

Fig. 3. Variation of the Ln(σg,.gb*T) versus 1000/T.

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2.2 AC electrical conductivity

The a.c. conductivity study gives information on the time dependent movement of charges. The complex conductivity can be given as:

$$\sigma^{*}_{AC}(\omega, T) = \frac{e}{l}\left(\frac{Z^{*}(\omega)}{(Z'^{2}+Z''^{2})}\right) = \sigma'_{AC}(\omega) + j\sigma''_{AC}(\omega) \quad (4)$$

The real and the imaginary parts of the total AC conductivity, $\sigma'_{AC}(\omega, T)$ and $\sigma''_{AC}(\omega, T)$ are calculated using the following expressions:

$$\sigma'_{AC}(\omega, T) = \frac{e}{l}\frac{Z'}{(Z'^{2}+Z''^{2})} \quad (5)$$

$$\sigma''_{AC}(\omega, T) = \frac{e}{l}\frac{Z''}{(Z'^{2}+Z''^{2})} \quad (6)$$

where e, l, Z' and Z″ are the thickness, the cross-sectional area and the real and the imaginary parts of complex impedance.

Frequency dependence of real part of AC conductivity in Sr1.75Co0.25P2O7 at different temperatures is shown in Fig.4. As illustrated, three parts are observed in this plot for this reason the classical equation of Jonscher ($\sigma'_{AC} = \sigma_{DC} + A\omega^{s}$) does not allow us to explain the behavior of our experimental data [18, 19].

Another equation is proposed which gives better agreement with experimental values, and the developed equation is called the equation of Jonscher [20]:

$$\sigma'_{AC}(\omega) = \frac{\sigma_{s}}{1+\tau^{2}\omega^{2}} + \frac{\sigma_{\infty}\tau^{2}\omega^{2}}{1+\tau^{2}\omega^{2}} + A\omega^{s} \quad (7)$$

where σ_s is conductivity at low frequencies, σ_∞ is an estimate of conductivity at high frequencies, $\omega=2\pi f$ is angular frequency, τ represents the characteristic relaxation time, A is a constant that is temperature dependent, and s is power law exponent, where 0<s<1.

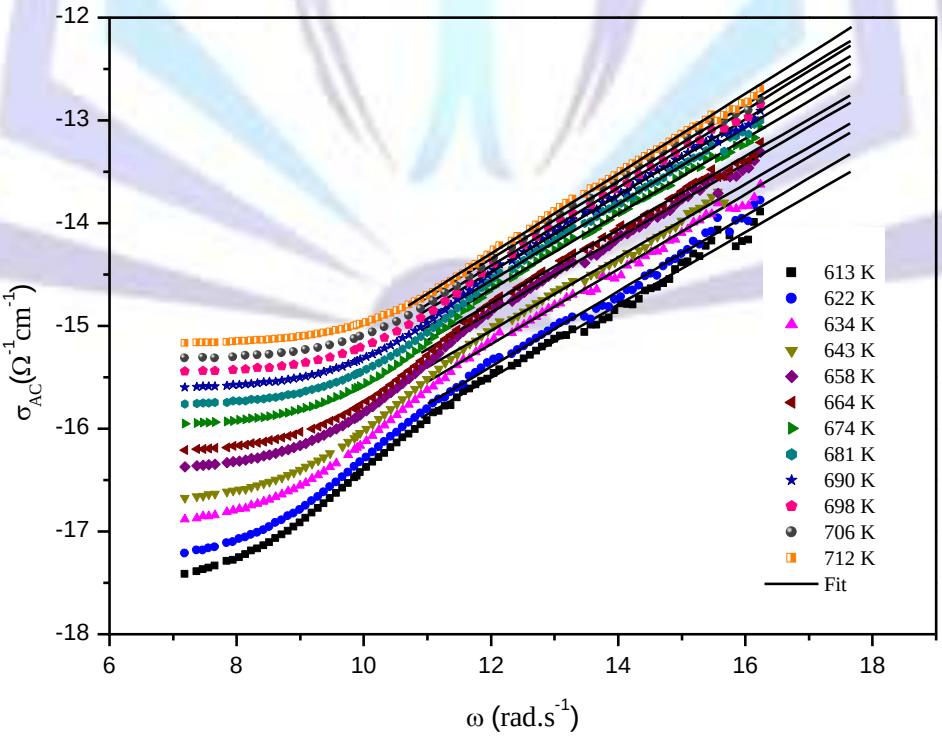

Fig. 4. Angular frequency dependence of the AC conductivity at various temperatures

The s represents the degree of interaction between mobile ions with the environments surrounding them, and A determines the strength of polarisability. The temperature dependence of frequency exponent s was investigated to understand the conduction mechanism in $Sr_{1.75}Co_{0.25}P_2O_7$. A linear fit was performed for high frequencies (Fig.4), the values of exponent s lie in the range 0.35 – 0.39. As shown in Fig. 5, s decreases to a minimum value for T ~ 640K and then increase.

Various theoretical models for AC conductivity have been predicted to explain the temperature dependence of s. As illustrated in Fig. 5, it is apparent that OLPT mechanism could operate for this compound [21]. The mechanism of conduction is probably due from the displacements of the Sr^{2+} ion in the tunnel-type cavities.

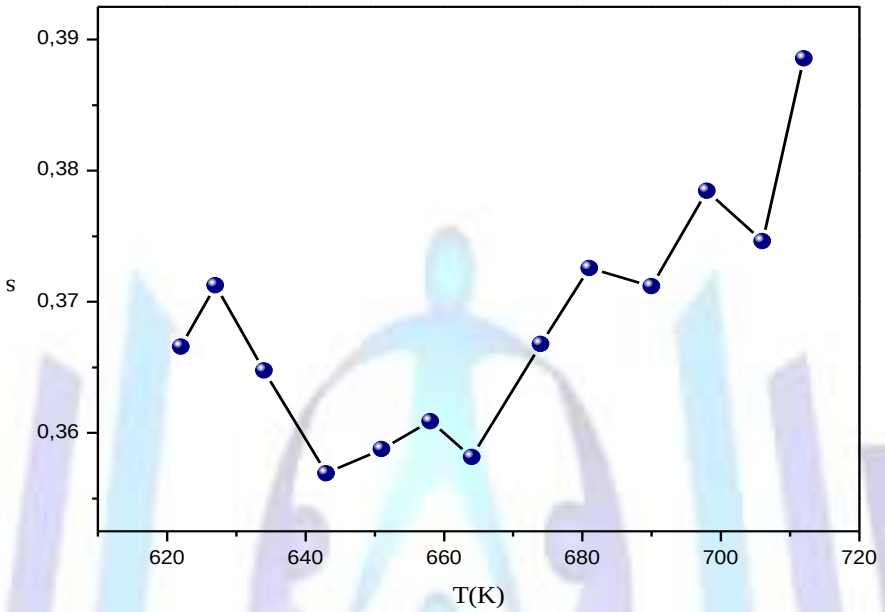

Fig. 5. Variation with temperature of both exponents s.

3. Conclusion

$Sr_{1.75}Co_{0.25}P_2O_7$ pyrophosphate compound was synthesized by the traditional method of ceramics preparation. Two semicircles are observed in impedance plot indicating the presence of two relaxation processes in the compound associated with the grain and grain boundary. The bulk (Eg) and the grain boundary bulk (Egb) activation energies were 0.89 and 0.96 eV, respectively. The AC conductivity for grain response is interpreted using the universal Jonscher's power law. Temperature dependence of the exponent s suggests that the mobility of the charge carrier is due to OLPT model in the investigated material.

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