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Dielectric properties of Li$^+$-exchanged mixed Fe–Cr oxide pillared phosphate

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Abstract

The dielectric properties of mixed Fe–Cr oxide-pillared α-zirconium phosphate and derivatized Li$^+$-exchanged have been studied by impedance spectroscopy. The pure Fe–Cr pillared material exhibits low electronic conductivity and presents only a dielectric relaxation. However, the Li$^+$-exchanged sample is an ionic conductor and subtracting the dc contribution, a dielectric relaxation at low frequency is observed. The Li$^+$ ions distribution presents a two-potential-well system; the ions localized at small pores cannot be displaced over long distances and their short hopping transitions determine the dielectric properties. On other hand, only a fraction of the ions located in large pores are free and can be displaced over long distances and the remainders are fixed and can only make short displacements. These ions behave like jumping dipoles and produce a dielectric relaxation at low frequencies and high temperatures. © 1997 Elsevier Science S.A.

Keywords: Dielectric; Pillared; Zirconium phosphate; Lithium exchanged; Iron oxide; Chromium oxide

1. Introduction

Mixed Fe–Cr oxide pillared α-zirconium phosphate is a porous solid which presents very low electronic conductivity [1]. Its structure consists of uniform pores containing residual P–OH acid groups capable of exchanging protons with other cations. In a previous paper [1] we have studied the ion conduction and the dielectric loss in Li$^+$ mixed Fe–Cr oxide pillared α-zirconium phosphate in order to determine the different displacements of Li$^+$ across the porous structure. Two different exchange sites were found for lithium ions [2,3], one localized in mesopores and the other in micropores, constituting a two-potential-well system. Lithium ions can only make long displacements through large pores. These displacements are responsible for the conducting properties. The hopping transitions into small pores determine the dielectric properties. However, the dc conductivity perturbs the dipolar relaxation and it is an obstacle to the study of the dielectric relaxation processes [4]. Subtracting the conductivity effects allows us to remove undesired physical effects (like dc conductivity) and it is an important step in order to make a good description of dielectric relaxation [5]. The aim of this paper is to study the influence of the conduction contribution in the dipolar relaxation in these materials in order to isolate the dipolar relaxation in pure mixed Fe–Cr oxide pillared α-zirconium phosphate and in the Li$^+$-exchanged derivative.

2. Materials and experimental methods

Mixed Fe–Cr oxide-pillared α-zirconium phosphate and the Li$^+$-exchanged derivative were prepared as

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described elsewhere [1]. Pellets of 13 mm in diameter and 1 mm in thickness were prepared at 6 MPa. Opposite faces of disc-shaped samples were coated with gold by a vapor deposition method. Platinum electrodes were used. The dc current conductivity was measured by means of a PA meter/D.C. The voltage source was controlled by a computer. The ac electrical behaviour of the pellet was monitored using a Solartron 1260, also computer controlled. The electrical response was measured in the $1-10\times10^6$ Hz range. The temperature range was between 473 and 773 K, and it was measured by means of a platinum thermometer; the temperature did not change more than 1% during the measurement. Experimental data were corrected by software and the influence of connecting cables and other parasite capacitances were eliminated.

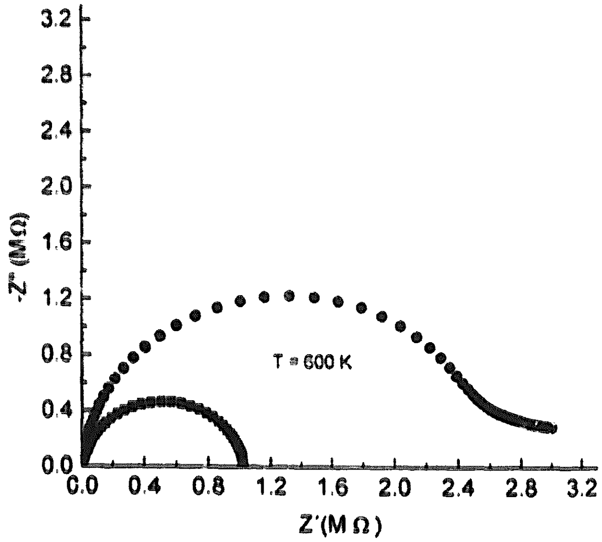

Fig. 1. Complex impedance plot: (■) Li⁺, 0%; (○) Li⁺, 100%.

3. Experimental results and discussion

Data directly measured as complex impedance Z^* were converted into complex conductivity σ^*, electric modulus M^* and complex permittivity ϵ^*, using the relations:

$$\sigma^*(\omega)=Z^*(d/S),\ M^*=j\omega C_0 Z^*,\ \epsilon^* = 1/(j\omega C_0 Z^*) \qquad (1)$$

where S is the area of the Pt electrode, d is the thickness of the sample, C_0 is the vacuum capacitance and $j=(-1)^{1/2}$.

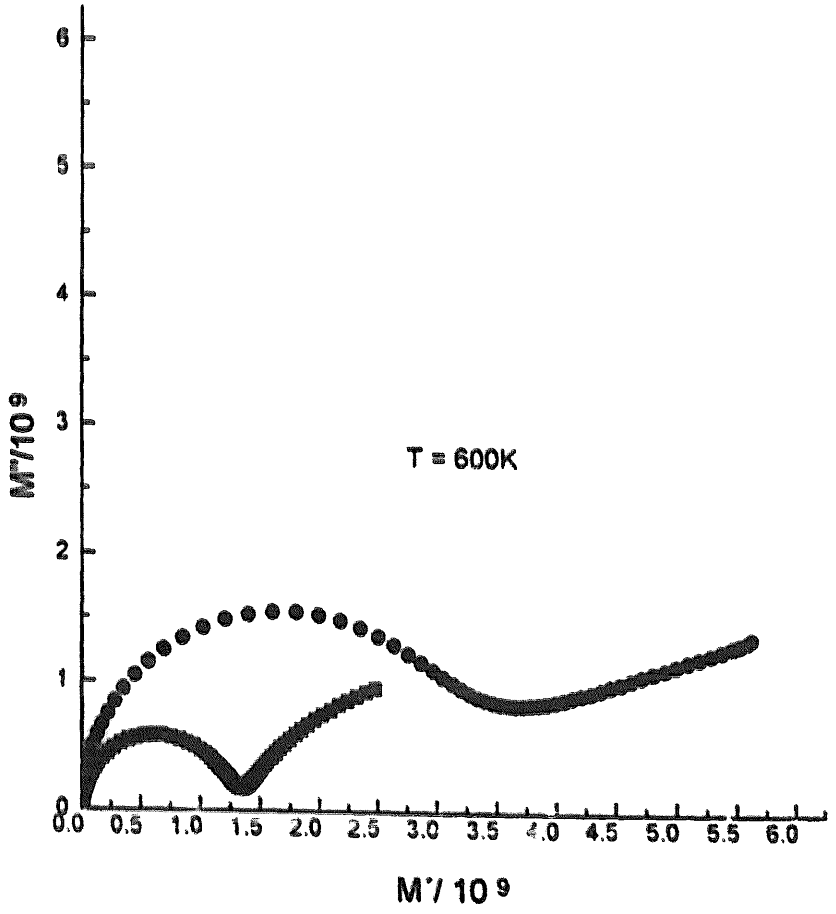

Fig. 2. Complex modulus plot: (■) Li⁺, 0%; (○) Li⁺, 100%.

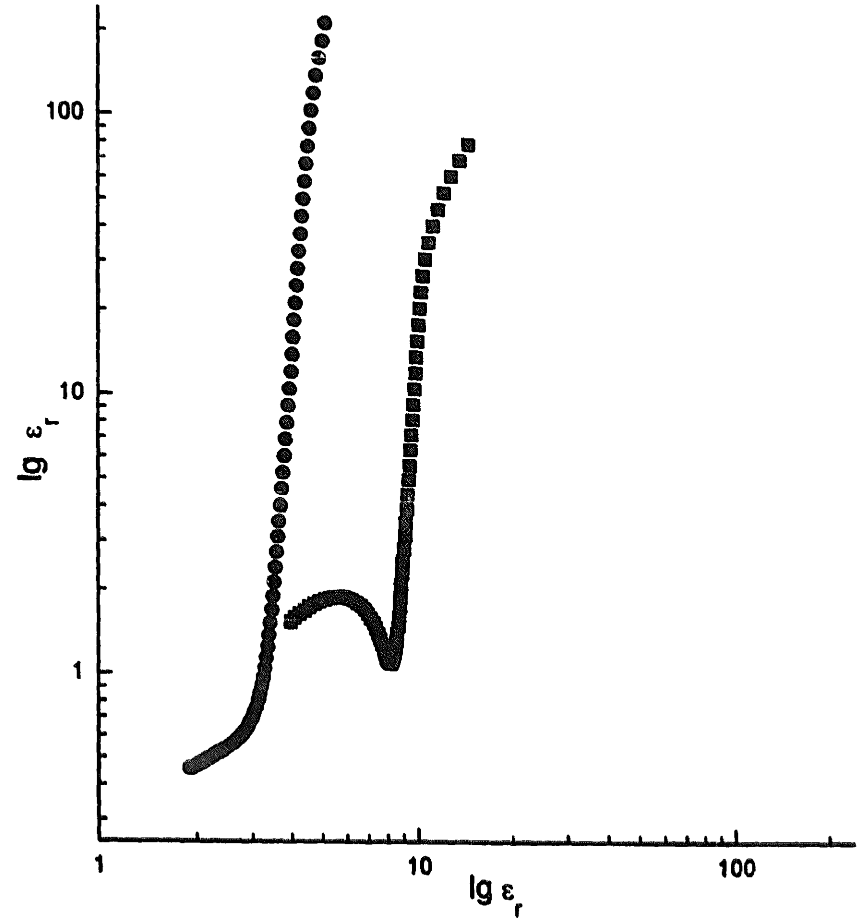

Fig. 3. Complex permittivity plot: (●) Li$^+$, 0%; (■) Li$^+$, 100%.

Typical complex impedance Z^* plots are shown in the Fig. 1. At each temperature, only one depressed arc could be observed. While the complex impedance plots point out those elements with the largest resistance, the electric modulus plots highlight those with smallest capacitance. Fig. 2 presents a typical modulus plot. As $M^* = 1/\epsilon^*$, the smallest semi-circle in the complex electric modulus plot corresponds to the bigger capacitance.

The dependence of permittivity or susceptibility on temperature and frequency allows us to obtain valuable information about the link between the microscopic and macroscopic dielectric mechanism occurring in an ionic conductor. Fig. 3 shows the complex permittivity for the pure mixed Fe–Cr sample and the Li$^+$-exchanged compound. Fig. 4 presents the real and imaginary components of permittivity vs. frequency for both samples. Their behaviour is characteristic of systems with hopping carriers.

For a better understanding of the charge motions, we need to distinguish relaxation and long-range motions. In some cases, the $\epsilon'' = f(\epsilon')$ recorded spectra give evidence of a well-shaped semi-arc of a circle and a low frequency straight line. This is observed for many ionic conductors because the relaxation arises from large dipoles and on the other hand, the conduction loss takes place at low frequency. In this case, subtraction of the conduction loss is necessary to obtain, from Cole–Cole plots, a visible separation between 'free charges' and 'dipolar' contributions.

The Havriliak and Negami function (HN) [6] with a conductivity term includes the equations of Debye, Cole–Cole and Cole–Davidson and permits the removal of the effects of the dc conductivity and the dipolar relaxation and is the most general model of the relaxation process. The equation is as follows:

$$\epsilon^*(\omega) = \epsilon' - j\epsilon'' = -j\left(\frac{\sigma_{dc}}{\epsilon_0 \omega}\right)^n + \sum_{k=1}^{p}\left[\frac{\Delta\epsilon_k}{\left(1 + (j\omega\tau_k)^{\alpha_k}\right)^{\beta_k}} + \epsilon_{\infty k}\right] \qquad (2)$$

where σ_{dc} is the direct conductivity, ω the angular frequency and ϵ_0 denotes the vacuum permittivity. The first term represents the dc conductivity and the others, the dielectric relaxation. The increment, at low frequency, in ϵ'' is due to the conductivity term. The slope of the increment is determined by the

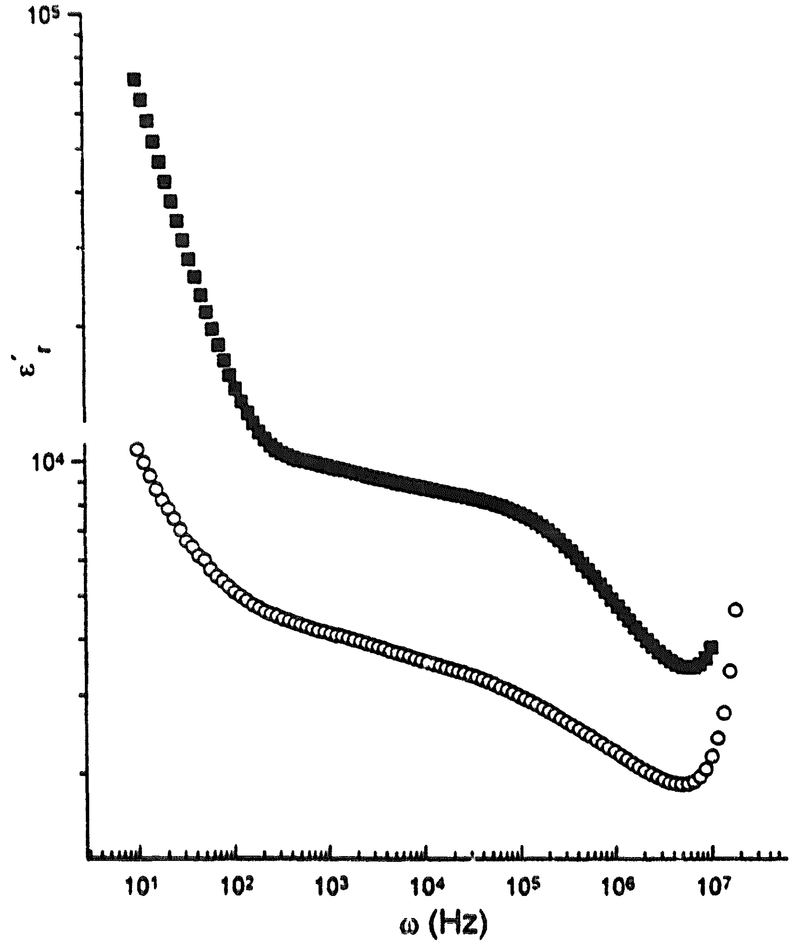

Fig. 4. Dielectric permittivity vs. frequency: ε', (○) Li^+ 0%; ε', (■) Li^+, 100%.

exponential factor n, which, in general, is equal to 1. In each relaxation term, $\Delta\epsilon$ is the difference between the static and infinity permittivity. $\Delta\epsilon$ is also proportional to the area below the ϵ'' relaxation peak. The value of ϵ' at infinity frequencies is determined by ϵ_∞. τ specifies the relaxation time. For high values of α and β, the maximum frequency of the relaxation peak in ϵ'' is approximately situated at $1/(2\pi\tau)$. The width parameter α specifies the slope of the low frequency side of the relaxation in ϵ''. β is the asymmetry parameter, $=\alpha\beta$ gives the slope of the high frequency side of the relaxation in ϵ''. When α and β are equal to 1 the HN function becomes the Debye model. A fitting approach in the temperature region between 673 and 773 K is followed by using a non-linear least-squares fitting of both the real and imaginary part of $\epsilon \times (\omega)$ [7].

Both compounds in all the studied temperature ranges present only a dielectric relaxation but now we can subtract the first term from the experimental data and separate the conductivity contribution from the relaxation contribution. For the pure mixed Fe–Cr sample there are no strong changes in the dielectric spectra, because this material exhibits a very low electronic conductivity and there is no ionic conductivity (Fig. 5). A new fitting to the new dielectric spectra present very similar results. However, the Li^+-exchanged compound shows a new dielectric relaxation at low frequencies for the highest temperature ($T > 573$ K) range; this new dielectric relaxation implies short displacement by the Li^+ ions (Fig. 6). The Li^+ ions are localized in mesopores and micropores. Micropore Li^+ ions cannot make long displacements because the routes across the small pores are broken, and these are responsible for the dielectric relaxation at high frequencies [1]. However, Li^+ ions located in large pores can make long displacements. Because the activation energy of the hopping rate of the mobile ion and the activation energy of the direct current conductivity are very close [1], only a small, but fixed, fraction (independent of temperature) of them is essentially free, and most of the carriers are bound at specific defect sites. However, the immobile ions can make short displacements and new dipoles are induced by the shift of the fixed ions in the micropores from the center of their geometrical sites, i.e. from the negative charge center of gravity.

4. Conclusions

The fitting of the Havriliak and Negami function (HN) with a conductivity term to the experimental

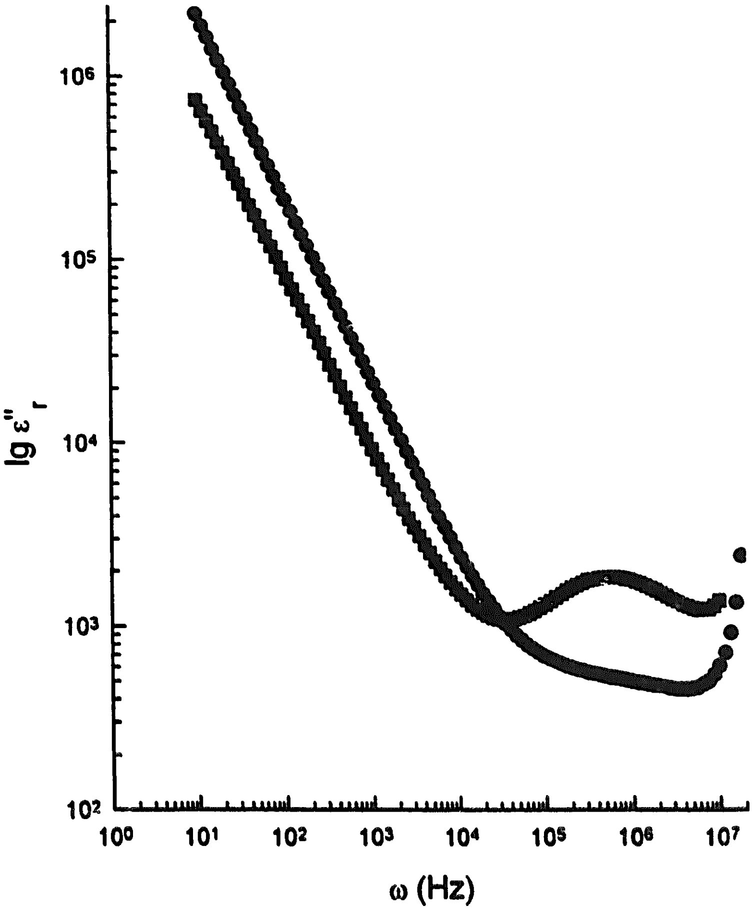

Fig. 5. Cole–Cole plot without conductivity term for pure mixed Fe–Cr. oxide pillared α-zirconium phosphate.

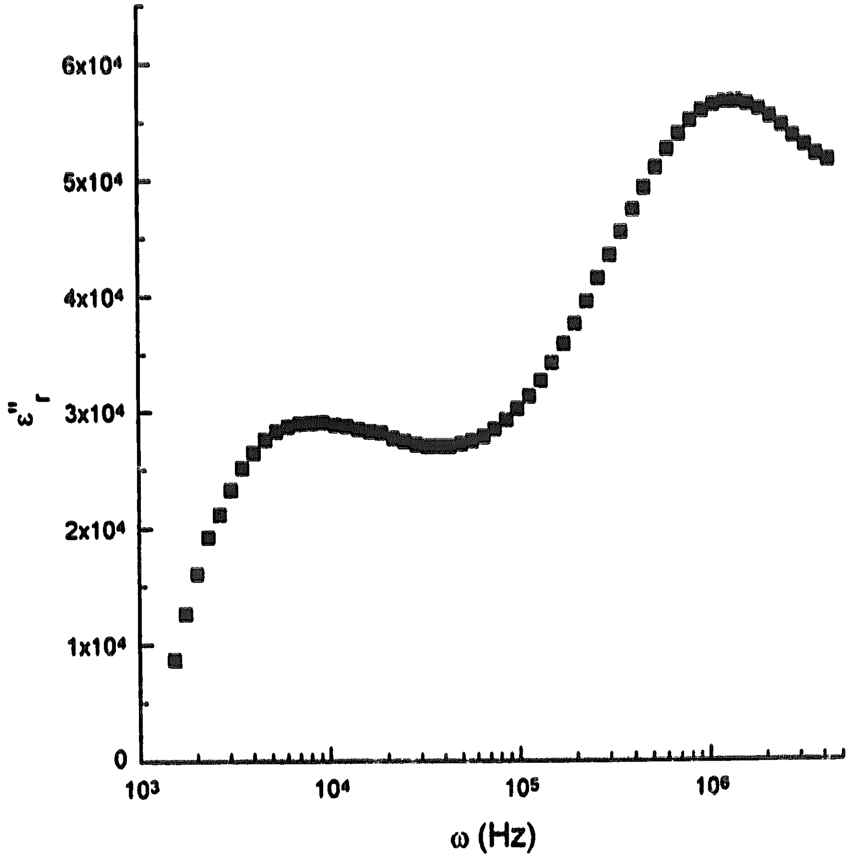

Fig. 6. Cole–Cole plot without conductivity term for Li⁺-exchanged mixed Fe–Cr. oxide pillared α-zirconium phosphate.

data allows subtraction of the conductivity contribution from the relaxation contribution and isolation of the dielectric relaxation. The pure mixed Fe–Cr oxide pillared α-zirconium phosphate is a material with a very low electronic conductivity and presents only a dielectric relaxation. The deconvolution of the electrical relaxation does not change the dielectric spectra. However, the Li^+-exchanged mixed Fe–Cr oxide pillared α-zirconium phosphate is an ionic conductor and subtracting the dc contribution enables us to discover a dielectric relaxation at low frequency. The Li^+ ion distribution presents a two-potential-well system; the ions localized at small pores cannot make long displacements and their short hopping transitions determine the dielectric properties. On the other hand, only a fraction of the ions located in large pores are free and can make long displacements and the remainders are fixed and can only make short displacements. These ions behave like jumping dipoles, and produce a dielectric relaxation at low frequencies and high temperatures.

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