ORIGINAL ARTICLE

Variations in β(T)-function due to addition of LiI-4AgI system

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Abstract

Impedance spectroscopy measurements of the LiI-4AgI samples, in the frequency range 20 Hz–1 MHz, and in the temperature range between 353 K and 378 K were made. Both pure and lithium-doped silver iodide showed blocking phenomena in the electrodes and the grain boundary. The blocking phenomena allowed a change in the transport properties of the pure compound in respect to the doped compound as the temperature varied. The curves of electrical modulus in the LiI-4AgI system show asymmetric peaks corresponding with a weak correlation between mobile ions in the diffusion process. The electrical conductivity in the AgI-LiI system can be described using a stretched relaxation function of the Kohlrausch-Williams-Watts (KWW) type. We speculat e that the phase of lithium dissolved in the silver iodide favors the formation of islands that disperses the conductivity due to the modification of the relationship among the microscopic energies: microscopic energy and migration energy.

Keywords: Electrical modulus; Ionic conductivity; Silver iodide; Lithium iodide; KWW function.

Introduction

The high diffusion of ions in the so-called superionic or fast-ion conductor materials can be seen in the superionic phase for temperatures $T \geq T_t$, where T_t is the transition temperature from low-conducting to high-conducting phases. The influence of mobile ions such as Na^+, Li^+, Ag^+ [1,2], among others, has been studied in these systems. The phase transition is characterized by an abrupt increase in ionic conductivity, a low activation energy, a latent heat typical for a first-order transition, a crystalline structure with vacancies available for mobile ions, and, in general, a change in the symmetry of the lattice. For these materials the structural disorder, below the melting point, is important for the increase of the ionic diffusion rate when either it is heated or a voltage is applied.

One of the most used experimental techniques to characterize the dynamics of ionic transport is the so-called impedance spectroscopy. In order to study the dielectric

properties of materials using the impedance spectroscopy technique, an impedance bridge is used. It provides conductance (G), capacitance (C), and phase angle (θ) measurements as a function of the angular frequency ω [3]. All the experimental information about electric relaxation at a given temperature is found in $G[\omega]$ and $C[\omega]$. These physical quantities are transformed in the complex permittivity $\varepsilon^\star[\omega]$, complex conductivity $\sigma^\star[\omega] = j\omega\varepsilon^\star[\omega]$, complex resistivity $\rho^\star[\omega] = 1/\sigma^\star[\omega]$, and complex electrical modulus $M^\star[\omega] = 1/\varepsilon^\star[\omega]$ [4].

Electric answer due to ion dynamics

By applying a Heaviside step function to the electric displacement vector $\boldsymbol{D}$, we have that for $t > 0$ the internal electric field $\boldsymbol{E}$ decreases due to the ion conventional hopping mechanism. This condition is expressed mathematically introducing the $c_m[t]$ function [5,6], that defines the electric field change with time:

$$E[t] = c_m[t]E[0] \tag{1}$$

$c_m[t]$ represents the relaxation of $\boldsymbol{E}$ at the interior of the material when a step function is applied to $\boldsymbol{D}$, $E[0]$ is the value of $\boldsymbol{E}$ at the instant $t > 0$:

$$E[0] = \frac{D_0}{\varepsilon_0 \varepsilon_\infty} \tag{2}$$

where ε_0 is the electrical permittivity of vacuum and ε_∞ is the electrical permittivity at the high-frequency limit.

The time derivative of (1) is:

$$\frac{dE[t]}{dt} = \frac{D_0}{\varepsilon_0 \varepsilon_\infty} \frac{dc_m[t]}{dt}. \tag{3}$$

By denominating

$$\Phi_m[t] = -\frac{dc_m[t]}{dt} \tag{4}$$

as the relaxation function and integrating the Eq. (3)

$$\boldsymbol{E}[t] = \frac{1}{\varepsilon_0 \varepsilon_\infty} \left(\boldsymbol{D}[t] - \boldsymbol{D}_0 \int_0^t \Phi_m[t']dt' \right) \tag{5}$$

In the Eq.(5), the notation $E[t]$ and $D[t]$ are defined over the whole interval $-\infty < t < \infty$.

Fourier transform of (5) is:

$$\boldsymbol{E}[\omega] = \frac{\boldsymbol{D}[\omega](1 - \Phi_m[\omega])}{\varepsilon_0 \varepsilon_\infty} \tag{6}$$

where $\Phi_m[\omega]$ is the electrical susceptibility.

From (6) and $\boldsymbol{D}[\omega] = \varepsilon_0 \varepsilon[\omega]\boldsymbol{E}[\omega]$, the electrical modulus is:

$$\boldsymbol{M}^\star[\omega] = \boldsymbol{M}_\infty(1 - \Phi_m[\omega]) \tag{7}$$

being $\boldsymbol{M}_\infty \equiv 1/\varepsilon_\infty$. For the case of an assembly of dipoles or ions non-correlated or Debye behavior ($c_m[t] \sim e^{-t/\tau}$), the electrical modulus would be:

$$\boldsymbol{M}^\star[\omega] = \boldsymbol{M}_\infty \left(1 - \int_0^\infty \left\{ -\frac{de^{-t/\tau}}{dt} e^{-j\omega t} \right\} dt \right) \tag{8}$$

with $j = \sqrt{-1}$.

The solution of (8) gives the spectrum of $\boldsymbol{M}^\star$ [7]:

$$\boldsymbol{M}^\star[\omega] = \boldsymbol{M}_\infty \left(1 - \frac{1}{1 + j\omega\tau}\right) \qquad (9)$$

For the case of some compounds that do not follow the Debye type behavior, i.e., when the interactions between the ions and the structural disorder are taken into account, Havriliak-Negami proposed a susceptibility function of the form [8]:

$$\Phi_{m,\text{HN}}[\omega] = \frac{1}{[1 + (j\omega\tau_{\text{HN}})^\alpha]^\gamma} \qquad (10)$$

where the exponents α, γ and the characteristic time τ_{HN} are chosen in such a way that they satisfy the experimental data which are asymmetric curves of slope different from one for the right branch, therefore expression (7) may be rewritten as:

$$1 - \frac{\boldsymbol{M}^\star[\omega]}{M_\infty} = \mathfrak{F}\left[\frac{\partial c_m[t]}{\partial t}\right] \qquad (11)$$

where the new susceptibility must be equal to the susceptibility for the Debye case, multiplied by the time distribution function:

$$\Phi_{m,\text{HN}} = \rho[t]\frac{1}{1 + j\omega\tau} \qquad (12)$$

carrying out the inverse transform:

$$c_m[t] = e^{-(t/\tau)^\beta}[T] \qquad (13)$$

That is, a stretched relaxation function of the Kohlrausch-Williams-Watts (KWW) type [9,10]. Thus the expression (8) takes the form

$$\frac{\boldsymbol{M}^\star[\omega]}{\boldsymbol{M}_\infty} = \left(1 - \int_0^\infty \left\{-\frac{\partial e^{(-t/\tau)^\beta}}{\partial t} e^{-j\omega t}\right\} dt\right) \qquad (14)$$

This is the expression used to fitting experimental data.

Preparations of samples

Polycrystalline AgI powder were recrystallized using the solution technique with high-purity reagents [11] starting from 99.99% (Aldrich) high-purity compound. Pure single crystals of 0.5 cm in diameter were achieved. The obtained single crystals were subjected to thermal treatment at 413 K during 24 hours before the measurements to eliminate the γ-phase. The single crystals of chemical composition LiI-4AgI were prepared using the same method, mixing AgI and LiI Aldrich compounds of 99.99% in purity. During the recrystallization process, both AgI and LiI compounds do not react between them. The AgI and LiI compounds are combined forming a mix. Other phases in the formed crystals are not presents. The effect upon activation energy is produced by proximity among LiI and AgI compounds, by principle of conservation of mass all amount of the compounds of AgI and LiI used for the mix at the finish of process of recrystallization in the same initial.

The monocrystalline samples were painted with silver paint on their parallel faces. The impedance spectroscopy measurements were carried out in the LCR meters HP 4284A and HP 4284A in the range of frequencies from 20 Hz to 1 MHz for a temperature range from 200 K to 400 K. The measurements were carried out under N_2 gas flow ensuring a controlled atmosphere.

Results and discussions

Figure 1 shows the dependence on the frequency of real part of ac conductivity $\sigma'[\omega]$ for LiI-4AgI crystals obtained by impedance spectroscopy measurements below the superionic transition in the range temperature from 258 K to 350 K. A potential dependence is observed at the highest frequencies and a cut frequency that separates the dc regime from the dispersive regime that increases with temperature. At low frequencies and high temperatures, ionic conductivity decreases due to the processes that happen in the frontier between the ionic conductor and the electrodes. The diminution effect of conductivity is greater in the AgI samples doped with Li, than in the pure AgI this is explainable due to a greater grain boundary effect. The values of dc conductivity are obtained from the plane regions of the isotherms of conductivity at the lowest frequencies. The solid lines are the best adjustments to experimental data.

In Figure 2, the curves of the imaginary part of the electrical modulus are shown as a function of the frequency for various temperatures, of the LiI-4AgI sample. An asymmetric peak is observed, which was adjusted by expression (14), with a stretched relaxation function (13) KWW type. The solid lines in the figure represent better adjustment to the KWW relaxation function, from which the β parameter was obtained.
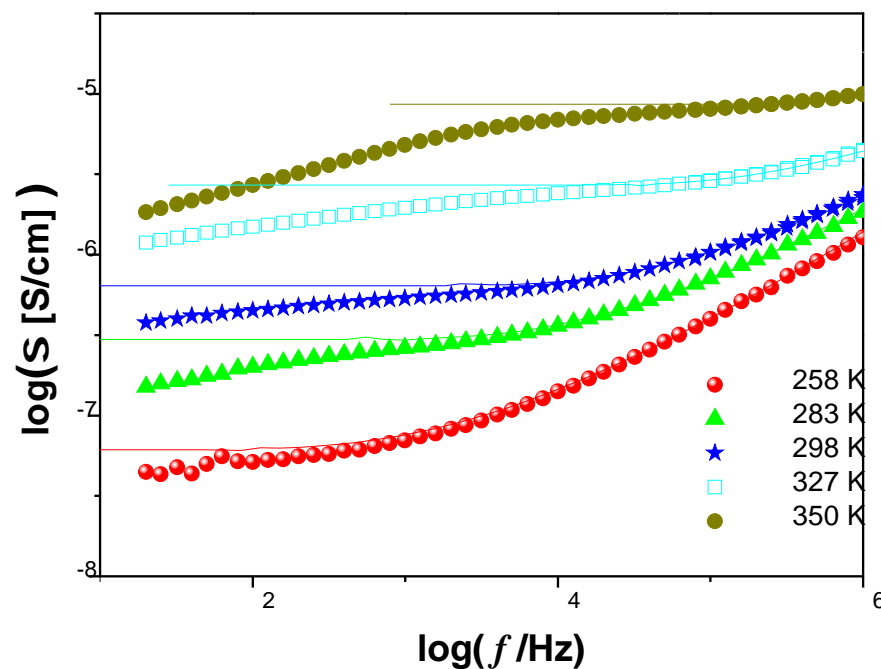

Fig. 1. Real part of the electrical conductivity as a function of frequency for LiI-4AgI at temperatures 258 K (red), 283 K (green), 298 K (blue), 327 K (cyan), and 350 K (dark yelow).
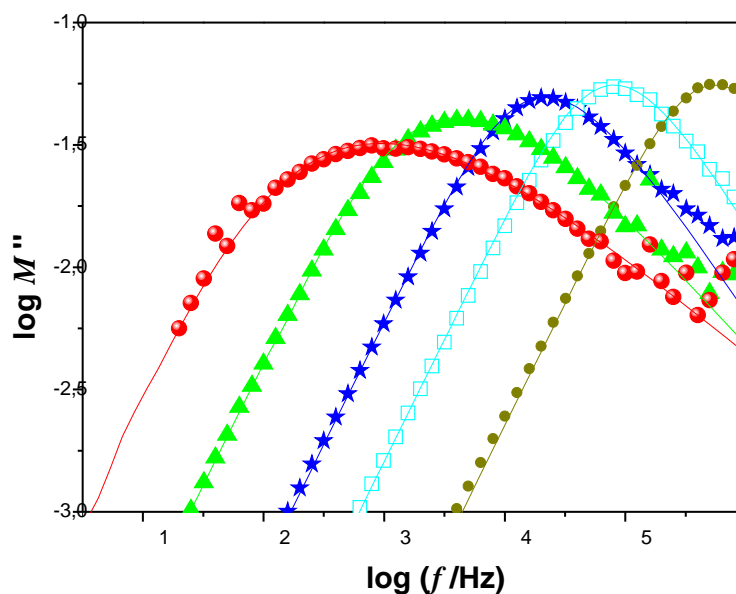
Fig. 2. Dependence of frequency of the real part of the electrical modulus for LiI-4AgI at temperatures 258 K (red), 283 K (green), 298 K (blue), 327 K (cyan), and 350 K (dark yelow).

In Figure 3, dependence of the $\beta[T]$ function is represented with temperature T for the AgI and LiI-4AgI systems. This function has been obtained starting from the slopes of the right branch of the curves of the imaginary part of the electrical modulus. The continuous line represents the behavior of the $\beta[T]$ function for the pure AgI. The changes observed in the behavior of $\beta[T]$ for the LiI-4AgI system, with respect to the AgI compound, are the consequences of the addition of the lithium phase to the pure AgI compound. The activation energies for the pure AgI and for the LiI-4AgI are similar; however the values of $\beta[T]$ are different. This fact suggests that the addition of the lithium phase would bring as a consequence the variation of microscopic energy and, consequently, a variation of the migration energy according with the coupling model [10].

This is due to the presence of the non-conductor phase of LiI dispersed at nanometric level in the conductor phase of AgI which would favor the local ordering of Ag^+ ions increasing slightly the microscopic energy. This observation confirms the hypothesis that the addition of the LiI phase would produce a decrease in the positional disorder of the sub-lattice of silver ions, with which the correlations at a given temperature would decrease with respect to the pure AgI [12].
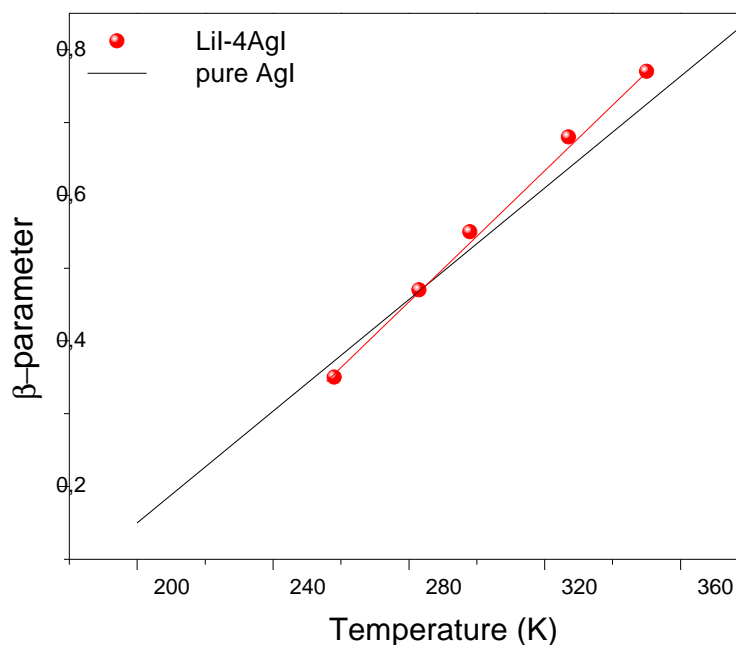
Fig. 3. Dependence of $\beta[T]$-function with temperature T for both pure AgI and LiI-4AgI systems. The continues solid line representes the behavior of $\beta[T]$-function for the pure AgI compound.

Conclusions

In this work, we have researched the existence and importance of the ion-ion correlation effects on the relaxation of electrical conductivity of doped AgI crystals with Lithium Iodide at close temperatures and below the superionic transition.

It was found that correlations between mobile ions decrease when the concentration of the LiI doping phase increases. The experimental evidence suggests that the inclusion of the lithium phase in the AgI, favor the decoupling of interaction between the silver ions, and the sub-lattice of fixed iodide ions, remaining the constant activation energy for the silver ions, with a value of 0.50 ± 0.02 eV.

The decoupling of interaction between mobile ions can be due to the modification of relation among the microscopic energies.

Acknowledges

References

[1]Peña Lara D, Vargas RA, Correa H. Solid electrolyte transition and conductivity in 0.1NaI-0.9AgI, *Solid State Ionics*, 175: 451–453, 2004.
doi:10.1016/j.ssi.2004.03.039

[2]Lozano CA, Correa H, Peña Lara D, Vargas RA. Superionic transition of the NaI-AgI System, *Physica Status Solidi(b)*, 245(12): 2 791–2 793, 2008.
doi: 10.1002/pssb.200844134

[3] León C, Lucia ML, Santamaria J, Sánchez-Quesada F. Universal scaling of the conductivity relaxation in crystalline ionic conductors, *Physical Review B*, 57: 41–44, 1 998.
doi: 10.1103/PhysRevB.57.41

[4] Hippel AR von. Editor Dielectric materials and applications The Technology Press of MIT and John Wiley & Sons, Inc., New York Chapman & Hall, Ltd., London, 1954.

[5] Funke K. Jump relaxation in solid electrolytes, *Progress in Solid State Chemistry*, 22: 111–195, 1993.
doi: 10.1016/0079-6786(93)90002-9

[6] Bötcher CJF, Bordewijk P. Theory of Electric Polarization Vol. II, *Elsevier Scientific Publishing Company*, 1980.

[7] Rivera AC. Movilidad iónica en conductores superiónicos. Tesis de doctorado, *Universidad Complutense de Madrid*, Facultad de Ciencias Físicas, Instituto de Ciencia de Materiales de Madrid, Madrid, España, 2003.

[8] León C. Relajación de la conductividad eléctrica en conductores iónicos cristalinos. Tesis de doctorado, *Universidad Complutense de Madrid*, Facultad de Ciencias Físicas, Instituto de Ciencia de Materiales de Madrid, Madrid, España, 1 997.

[9] Jonscher AK. Dielectric Relaxation in Solids, *Chelsea Dielectrics* Press, London, 1983.

[10] Ngai KL, Jonscher AK, White CT. On the origin of the universal dielectric response in condensed matter, *Nature*, 277: 185–189, 1979.
doi:10.1038/277185a0

[11] Kruempelmann J, Mariappan CR, Schober C, Roling B. Electrochemical double layers at the interface between glassy electrolytes and platinum: Differentiating between the anode and the cathode capacitance, *Physical Review B*, 82(22): 22–203, 2010.
doi: 10.1103/PhysRevB.82.224203

[12] Correa H, Vargas RA, García-Barriocanal J, Rivera A, Santamaría J, León C. Electrical conductivity relaxation in lithiun doped silver iodide, *Journal of European Ceramic Society*, 27: 4 297–4 300. 2007.
doi:10.1016/j.jeurceramsoc.2007.02.148

Variaciones en la función β(T) - por la adición del sistema LiI-4AgI

Resumen. Se tomaron medidas de espectroscopía de impedancia de muestras de LiI-4AgI en el rango de frecuencia de 20 Hz-1 MHz y en el rango de temperatura entre 353 K y 378 K. Tanto el litio puro como el litio dopado con ioduro de plata mostraron fenómenos de bloqueo en los electrodos y la frontera de grano. Los fenómenos de bloqueo permitieron un cambio en las propiedades de transporte del compuesto puro respecto del compuesto dopado a medida que variaba la temperatura. Las curvas del módulo eléctrico en el sistema LiI-4AgI muestran picos asimétricos correspondientes a una débil correlación entre iones móviles en el proceso de difusión. La conductividad eléctrica en el sistema AgI-LiI se puede describir usando una normalización de la función de relajación del tipo Kohlrausch-Williams-Watts (KWW). Especulamos que la fase de litio disuelto en ioduro de plata favorece la formación de islas que dispersan la conductividad debido a la modificación de la relación entre las energías microscopias: energía microscópica y energía de migración.

Palabras clave: módulos eléctricos; conductividad iónica; ioduro de plata; ioduro de litio; función KWW.

Variações na função β(T) devido a adição do sistema LiI-4AgI

Resumo. Foram realizadas medidas de espectroscopia de impedância de amostras de LiI-4AgI na faixa de frequência de 20 Hz - 1 MHz e na faixa de temperatura entre 353 e 378 K. Tanto o lítio puro como o lítio contaminado com iodeto de prata mostram fenômenos de bloqueio nos eletrodos e nos limites do grão. Os fenômenos de bloqueio permitiram uma mudança nas propriedades de transporte do composto puro em respeito ao composto contaminado, à medida que se variava a temperatura. As curvas do módulo elétrico no sistema LiI-4AgI mostraram picos assimétricos correspondentes a uma correlação débil entre íons móveis no processo de difusão. A condutividade elétrica no sistema AgI-LiI pode ser descrita utilizando uma normalização da função de relaxação do tipo Kohlrausch-Williams-Watts (KWW). Especulamos que a fase de lítio dissolvida em iodeto de prata favorece a formação de ilhas que dispersam a condutividade devido a modificação da relação entre as energias microscópicas: energia microscópica e energia de migração.

Palavras-chave: módulos elétricos; condutividade iónica; iodeto de prata; iodeto de lítio; função KWW.

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