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Ionic conductivity relaxation studies in $RbAg_4I_5$ crystal with nano-sized AgI particles

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Abstract –The "filler-effect" on silver-ion dynamics, due to the presence of AgI nanoparticles has been investigated by means of admittance spectroscopy measurements near the γ to β-phase transition of $RbAg_4I_5$ at 120 K. The complex ionic conductivity is well described by a power-law dependence according to $\sigma = \sigma_0(1+(\omega/\omega_p)^n$ at intermediate and high-frequency ranges. In the low-temperature regime the spectra is dominated by the sample/electrode interface, due to the high bulk resistance of the sample, so σ_0 was calculated from the end point of the portion of the spectra attributed to this electrode-effect. The Arrhenius plots of the temperature variation of σ0 show activation energy, E_σ, which depends on temperature that increases as the temperature increases toward the transition temperature. The electric modulus plots have been fitted using the KWW's expression, $\exp(-(t/\tau)^\beta$ showing a decrease of n as the temperature increase toward 120 K, thus indicating that correlation effects among mobile silver ions increases, which is contrary to what is expected in a superionic phase transition, which occurs at 209 K in $RbAg_4I_5$. This effect near 120 K is attributed to a change in the conductivity regime, such that at lower temperature the main contribution is due to the crystalline grain surface conduction where the defect formation is favored. As the temperature increases the conductivity propagates toward the interior of grains involving a greater sample volume. This behavior suggests that the observed increase in the n-exponent value, and therefore the increase in correlations among silver ions is caused by the transition from surface to bulk grain conductivity when the temperature is increased toward the γ to β-phase transition of $RbAg_4I_5$ surface.

Among ionic compounds, rubidium silver iodide in its α-$RbAg_4I_5$ phase (above 209 K under normal pressure) is a typical example of a silver-ion superionic conductor with highly disordered structure. Upon cooling, the α -phase (cubic) transforms into the rhombohedral β-$RbAg_4I_5$ phase at 209 K and into the trigonal γ-$RbAg_4I_5$ at 121 K [1]. The α-to-β transition is accompanied by only a small change in the rhombohedral angle (to 90.10°± 0.05°) and no change in the cell dimension and contents.
We have measured the specific heat near the α-to-β phase transition which is characterized by a lambda-shape critical behavior (Fig. 1). The data appear to be fitted fairly well by the following power law equations

$$c_p = \begin{cases} A_-|\epsilon|^{-\alpha'} + B_-, & \epsilon \to 0^- \\ A_+|\epsilon|^{-\alpha} + B_+, & \epsilon \to 0^+ \end{cases}$$

where $\epsilon = (T/T_c - 1)$ is the reduced temperature.

Measurements of the ionic conductivity and the specific heat close and below the γ-to-β first-order transition of $RbAg_4I_5$ establish an accurate proportionality between the interaction enthalpy of the mobile Ag-ion defects, h, and the product nE_A ,where $\beta = 1 - n$ is the Kohlrausch stretching exponent for the conductivity relaxation, and $E_A = d\ln(\sigma_0)/d(T^{-1})$ is the dc conductivity activation energy. In Fig. 2 we compare $c_p = dh/dT$ with $d(nE_A/dT)$. In other words, we have verified that the apparent activation energy $E_A(T)$ includes, besides the true microscopic energy "barrier" for independent ionic motion, βE_A (according to the coupling model [3]), a contribution from the enthalpy of the mobile AgI defects, h due to their thermal generation and the interaction among them.

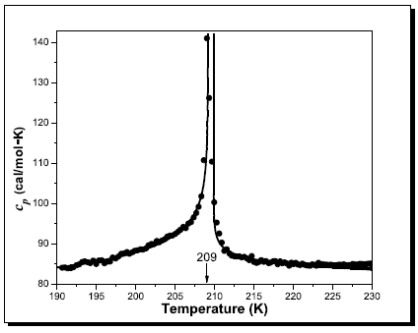

Figure 1: The specific heat of $RbAg_4I_5$. The second-order transition at 209 K has a critical exponent α′ = α = 0.086 ± 0.02, which is close to an Ising-like phase transition.

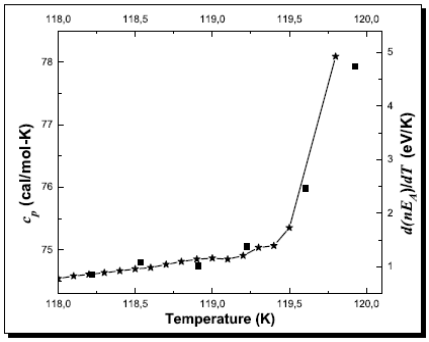

Figure 2:. The derivate of migration energy as a function of T is proportional to heat specific of the $RbAg_4I_5$. Only the range of temperature between 117.5 K and 119.8 K was calculated. The behavior of dE_m/dT is similar to $c_p(T)$.

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