

Measurement of Termic and Electric Properties of the System $x\text{AgI}-(1-x)\text{NH}_4\text{I}$ at High Temperatures

¹J.A. Trujillo, ¹A. Garcia-Muriel and ²R.D. Ortiz

¹Grupo Global Institute of Cyber Intelligence and Security (GICIS),
Universidad de Cartagena, Cartagena de Indias, Colombia

²Grupo ONDAS, Universidad de Cartagena, Cartagena de Indias, Colombia

Abstract: The technique of spectroscopy of impedances have be used to measure electric conductivity and in the range of temperature of 300 and 500 K. This technique it is used to study the nature of the processes of ionic conduction in solids. Using the system binary $x\text{AgI}-(1-x)\text{NH}_4\text{I}$ with concentrations of 0.6 and 0.8, like I model of study. A jump in the conductivity in the $x\text{AgI}-(1-x)\text{NH}_4\text{I}$ system with concentrations $x = 0.6$ and $x = 0.8$ for $T = 406\text{ K}$ and $T = 400\text{ K}$, respectively which is reduced when exchanged NH_4^+ for Ag^+ was observed AgI in the cooperative effects due to interaction of ion-ion and ion-network. The jump observed with the technique of impedance spectroscopy in this agglomerate is due to the presence of phases of AgI and corroborated with the technique of differential scanning calorimetry observed an absorption peak corresponding to phase α and β of AgI heat.

Key words: Electrical conductivity, phase transitions, solid electrolytes, calorimetry, corroborated

INTRODUCTION

According to the investigations, at ambient temperature the ionic solids have very small conductivities, $<10^{-6} (\Omega\text{cm})^{-1}$ therefore, the movement of ions through the glass practically does not exist. However, when an ionic solid melts, the ions separate or dissociate because of the thermal movement and can move freely through the liquid mass which consequently implies an increase in their conductivity (Trujillo, 2003). It has been observed that the substitution of host atoms by other ions produces increase in the conductivity, one of the purposes of this research is to explore further in this direction using the binary system $x\text{AgI}-(1-x)\text{NH}_4\text{I}$ with concentrations of $x = 0.6$ and 0.8 (Trujillo *et al.*, 2008). It should be noted that an ionic conductor to be useful as a solid electrolyte in a battery, not only must have high conductivity but also despicable electronic conduction, to avoid that the battery is short-circuit. AgI is one of the most investigated solid ion conductors. With the increase in temperature, this ionic conductor achieves an extremely high ionic conductivity ($\sigma \approx 0.1-1.0 \Omega^{-1}\text{cm}^{-1}$) in the phase (α -AgI over 420 K) comparable to liquid electrolytes, although a long range of crystallinity is still shown structure bcc (Lara *et al.*, 2004).

MATERIALS AND METHODS

Experimental: In this researcher the system $x\text{AgI}-(1-x)\text{NH}_4\text{I}$ with concentrations of 0.8 and 0.6 was

analyzed. Silver Iodide (AgI) Ammonium Iodide (NH_4I) and Potassium Iodide (KI) with 99.9% purity were used as reagents. All reagents were supplied by Sigma-Aldrich.

Sample preparation: These systems were prepared by slow evaporation under a pressure of 1 Atm to 30°C with molar concentrations of $x = 0.6$ and 0.8 . Were weighed in an analytical balance, Scientech SA525D, high precision (10^{-4} g) the powders were mixed and then pulverized in a mortar until a homogenous mixture was obtained. The solution was kept in a covered glass Hood with the purpose of keeping the solution free of impurities and a constant relative humidity of $45 \pm 5\%$. Once the crystals were obtained it was necessary to keep them free of moisture in a dry and closed environment and in this way to avoid their decomposition and contamination. To achieve this the crystals were introduced into test tubes and then into a glass bell (of 250 mL) which contains in its interior silica gel a substance which is very hygroscopic and which keeps the environment inside the bell free from moisture (Chandra, 1981; Trujillo *et al.*, 2011).

RESULTS AND DISCUSSION

The results obtained in the measurement of electrical conductivity show anomalies evidencing the existence of phase transitions in the investigated compounds and in addition to observing a similar behavior of all solid electrolytes base on the silver iodide associated with the

appearance of ionic states in the subnet of Ag^+ . Figure 1 shows the logarithm of the electrical conductivity as a function of the inverse of the temperature for the pure AgI sample.

It can be seen that there is a transition at 420 K with a conductivity change of three orders of magnitude. This transition is confirmed by the DSC heating curve (Fig. 2). Previous studies on electrical conductivities have also shown that pure AgI has some transition anomalies around 420 K but the electrical conductivity has been in the order of $1 (\Omega \text{ cm})^{-1}$ (Trujillo *et al.*, 2008, 2016). For system $x\text{AgI}-(1-x)\text{NH}_4\text{I}$ with concentration of 0.6 the anomaly is presented in 400 K (Fig. 3).

The differential scanning calorimetry results for 0.6 are shown in Fig. 4 where a transition was found at 395 K (Trujillo *et al.*, 2010). For system $x\text{AgI}-(1-x)\text{NH}_4\text{I}$ with concentration of 0.8 a scan of the logarithm of the electrical conductivity is shown as a function of temperature. Where it presents a transition in 406 K (Fig. 5). The differential scanning calorimetry results for the concentration of 0.8 are shown in Fig. 6 where a transition was found at 409 K (Table 1).

Table 1: Transition temperatures

| $x\text{AgI}-(1-x)\text{NH}_4\text{I}$ | $T_i(\text{K})$ IS | $T_i(\text{K})$ DSC |
|--|--------------------|---------------------|
| $x = 1$ | 420 | 421 |
| $x = 0.8$ | 406 | 409 |
| $x = 0.6$ | 400 | 395 |

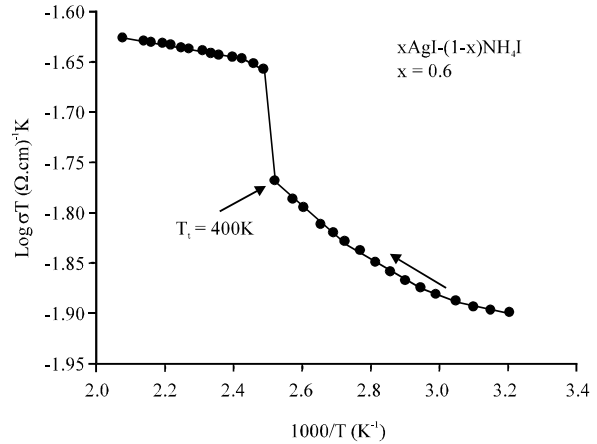


Fig. 3: Transition temperature (for 0.6AgI-0.4NH₄I)

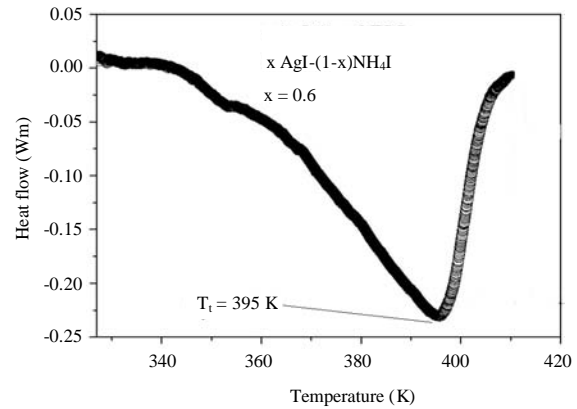


Fig. 4: DSC heating curve for (0.6AgI-0.4NH₄I)

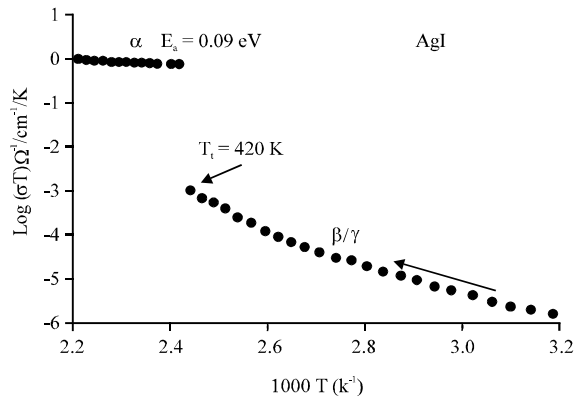


Fig. 1: Transition temperature for AgI

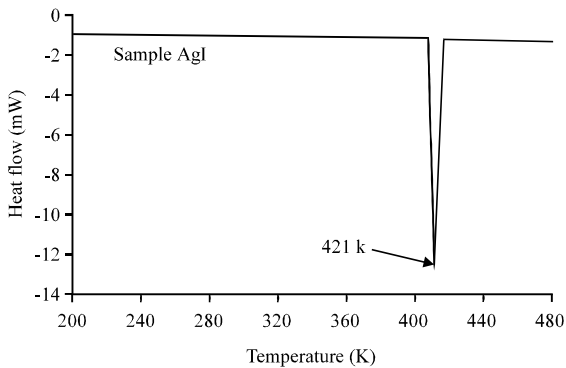


Fig. 2: DSC heating curve for AgI

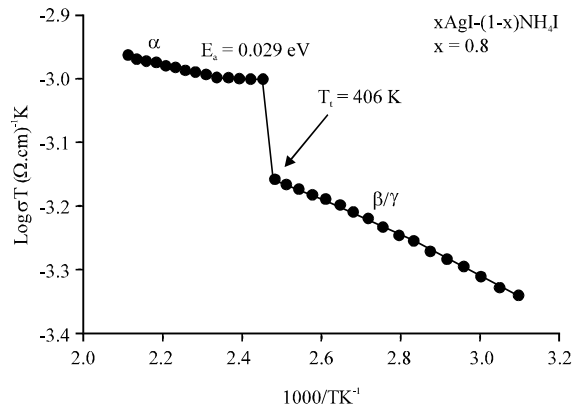


Fig. 5: Transition temperature for (0.8AgI-0.2NH₄I)

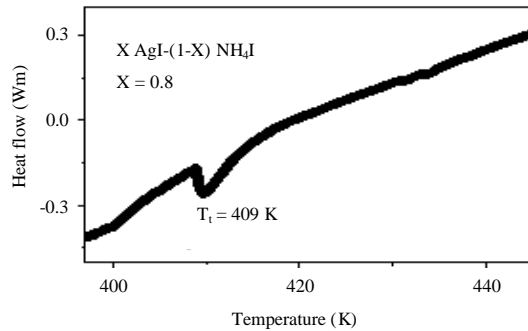


Fig. 6: DSC heating curve for (0.8AgI-0.2NH₄I)

CONCLUSION

We find that the high temperature phase α -AgI in solid solution in combination with another phase (MI, $M = \text{NH}_4$) has high conductivity of the order of $(0.1\ (\Omega\text{ cm})^{-1})$ and a rather simple structure (bcc). The conductivity jump occurring at the structural transition temperature β/γ -AgI (ss)- α -AgI(ss) (ss = solution solid) abrupt changes in the conductivities at the transition temperatures in 420, 400 and 406 K are observed in Fig. 1, 3 and 5 corroborating these transitions with measures of differential calorimetry of sweep as a function of the temperature. Figure 2, 4 and 6 with transition temperatures in 421, 395 and 409 K. Obviously, the transition temperature is run towards lower values with the concentration of the dopant.

REFERENCES

- Chandra, S., 1981. Superionic Solids, Principles and Applications. North-Holland Publisher, Amsterdam, Netherlands,.
- Lara, D.P., R.A. Vargas and H. Correa, 2004. Solid electrolyte transition and conductivity in 0.1 NaI-0.9 AgI. Solid State Ionics, 175: 451-453.
- Trujillo, J.A., M.A. Garcia and J.F. Jurado, 2010. [Electrical and thermal analysis of the system $x\text{AgI}-(1-x)\text{LiI}$ above room temperature]. Colomb. J. Phys., 42: 406-409 (In Spanish).
- Trujillo, J.A., 2003. Effects of other ions on the transport of agen crystals. Ph.D Thesis, Universidad del Valle, Cali, Colombia.
- Trujillo, J.A., A. Garcia, E.E. Quinonez, R.D. Ortiz and A.M. Marin, 2016. Thermal, electrical and structural characterization of MI-AgI ($M = \text{Na}, \text{Li}$) systems above room temperatures. J. Eng. Appl. Sci., 12: 2709-2716.
- Trujillo, J.A., E.E. Quinones, L.E. Cortes and R.A. Vargas, 2008. Transitions of phase and ionic conductivity in the systems $x\text{AgI}-(1-x)\text{KI}$ y $x\text{AgI}-(1-x)\text{AgBr}$ at high temperatures. Colomb. J. Phys., 40: 132-135.
- Trujillo, J.A., J. Acevedo and E. Ortiz, 2011. [Electrical conductivity of $x\text{AgI}-(1-x)\text{LiI}$ and $x\text{AgI}-(1-x)\text{NaI}$ systems at high temperatures]. Colomb. J. Phys., 43: 753-756 (In spanish).