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Thermal, Electrical and Structural Characterization of MI-AgI (M = Na, Li) Systems above Room Temperatures

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Abstract: The thermal (DSC) and electrical (IS) and structural (XRD) behavior of MI-AgI (M = Na, Li) systems were investigated for temperatures above 300 K. The slow evaporation method was used to synthesized samples under concentrations given by the relationship: xAgI-(1-x) NaI and xAgI-(1-x) LiI with x = 0.8. The characterization results reveal how the AgI conductivity jump at T = 420 K, this was reduced when the Li+or Na+was interchanged for Ag+ion due to the cooperative effects of ion-ion and ion-lattice interactions. The transition temperature of the system decreased as the doping concentration was increased. The reached conductivities (>10-4 S/cm) and the low activated energy values (lower than those found with AgI) show the importance of xAgI-(1-x)LiI systems, allowing a wider knowledge of the behavior of solid conductors developed based on silver iodide compounds.

Key words: Phase transition, X-ray diffraction, ionic conductivity, system, energy

INTRODUCTION

Ionic materials based on silver salts have demonstrated great ionic mobility and potential usein technological applications such as fuel cells, batteries and electrochromic devices (Kim and Honma, 2005). Silver Iodide (AgI) is one of the most widely studied superionic systems, selected usually as control unit to evaluate new solid state ionic conductors in the range of 223-423 K Ionic conduction depends strongly on the operating temperature, below 300 K, conductivities are $<10^{-7}\Omega^{-1}cm^{-1}$, showing low ion mobility in the crystal structure. However when ionic solids are melted because of the gained thermal energy, ions becomes free to move through the liquid mass increasing their conductivity from one to five order of magnitude.

Silver iodide is an especially case because has shown high ionic conductivities ($>10^{-4}$ S/cm) when are thermally stabilized in electrolytic baths operated near room temperatures. Extensive efforts have been made to increase AgI conductivities; one of the approaches is to incorporate different ions (Cu and Li) into the lattice of AgI (Ocampo *et al*., 2011; Johan *et al*., 2011; Hassan and Hakimi, 2011; Kartini *et al*., 2014). Despite these efforts, more researches are needed to improve doping techniques and understanding of properties changes to produce improved materials. Most of the tested AgI microstructures have been developed based on crystal materials such as LiI, NaI and Al_2O_3 (Jurado *et al*., 2003; Zapata, 2009; Trujillo *et al*., 2008) in which their atomic particles are stable enough to form a strong crystal lattice structure. In this sense, the objective of this investigation is to compare the effects on AgI conductivity when it sis doped with different concentrations of Na and Li, using the slow evaporation method (Kittel, 1976).

MATERIALS AND METHODS

Experimental: The 0.8AgI-0.2NaI and 0.8AgI 0.2 LiIsystems were prepared using silver iodide (AgI), sodium iodide (NaI), Lithium Iodide (LiI) and potassium iodide (KI). First, NaI and LiI powder reagents were properly weighted, sprayed and blended together in a KI saturated solution with 99.9 % purity, until a homogenized mixture was obtained. Then, the mixture was covered with a bell-glass in which underwent through a slow evaporation process at 1 atm and 304 K to finally get a strong crystal free of impurities. The formed crystals were placed in test tubes stored in an oven at 323 K and 45+5% relative humidity to avoid contamination and chemical decomposition (Acevedo, 2010; Trujillo *et al*., 2008).

All the samples were structurally characterized using X-ray diffraction to verify the degree of purity and

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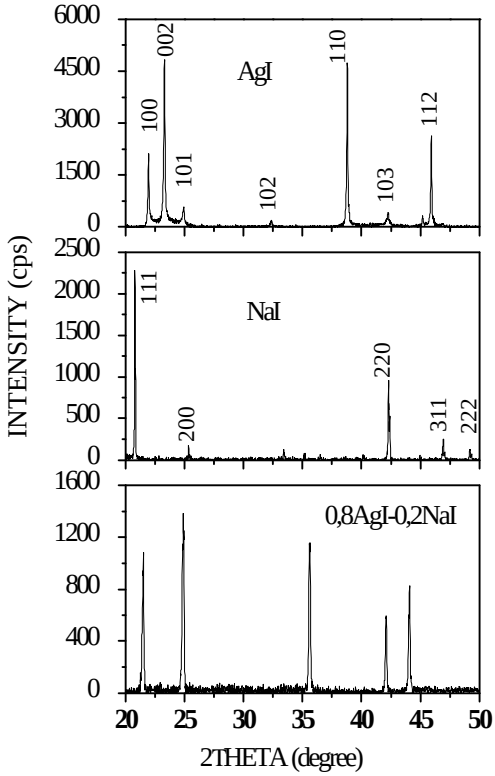

Fig. 1: Power X-ray diffraction patterns at 300 K

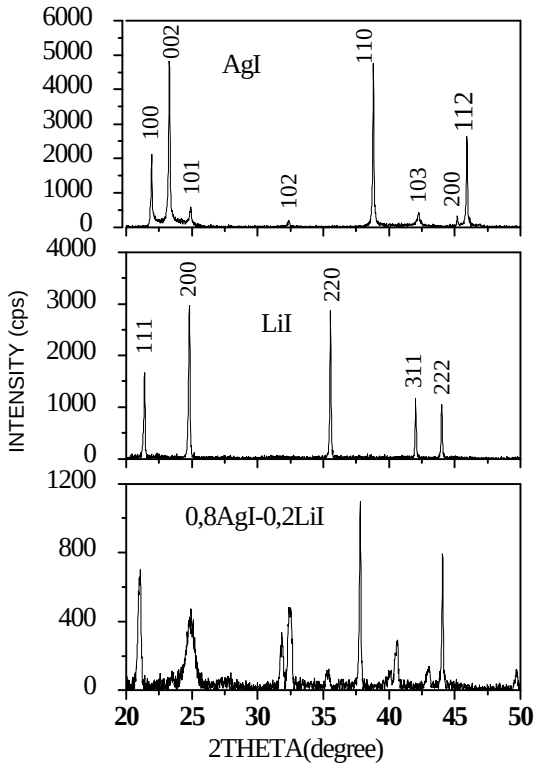

Fig. 2: Power X-ray diffraction patterns at 300 K

crystallization of each phase (Jurado *et al*., 2003). The X ray equipment was as a PAN analytical diffractometer with a Cu Kα radiation and a Θ-Θ parallel beam geometry, 20-50 as it shown in Fig. 1 and 2Θ range, at a sampling velocity of 56 steps per seconds with a 0.013° step increment.

Figure 1 shows the X-ray diffractograms of the 0.8 AgI-0.2 NaI samples taken at room temperature. It can be observed that several diffractions are comparable to those obtained for pure AgI and NaI samples but differing in intensities. These differences in intensity are due to the different amounts of NaI and AgI used in each system. In the same way, Fig. 2 shows that some diffractions obtained for 0.8 AgI-0.2 LiI systems are similar to those obtained for pure AgI and LiI, respectively. The intensity reduction and the slight displacement of the maximum absorption points (Fig. 1 and 2) are consequences of the defects created by the replacement of Ag for Na and Li ions, respectively that differ from each other in atom size.

Thermal analyses of the samples were carried out using a Differential Scanning Calorimeter (DSC 2920) in the temperature range of 300-450 K. The blank and crystal samples were independently heated but kept under the exact same temperature. A temperature sensor was inserted in each sample to automatically control the added heat transfer rate (Zapata, 2009).

Impedances Spectroscopy (IS) analyses were carried out using a solartron 1260 instrument in the frequency range from 10^{-6} Hz to 32 MHz.

RESULTS AND DISCUSSION

Figure 3 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. 4). 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 $(\Omega.cm)^{-1}$ (Trujillo *et al*., 2008).

Figure 5 shows the results of the impedance spectroscopy analysis conducted for the 0.8 AgI-0.2 NaI system. It indicates a transition at 397 K with electrical conductivities in the order of 10^{-6} $(\Omega\ cm)^{-1}$. Similar results were obtained with the DSC analysis in which the transition was obtained at 396 K (Fig. 6).

Figure 7 shows the IS traces found for the LiI system. It reveals that there is transition temperature at 395 K which produces an electrical conductivity change from

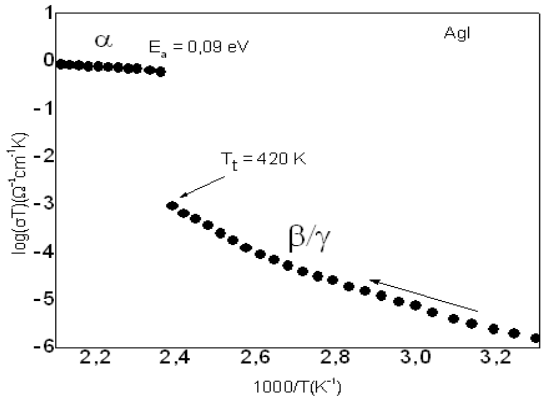

Fig. 3: Transition temperature for AgI

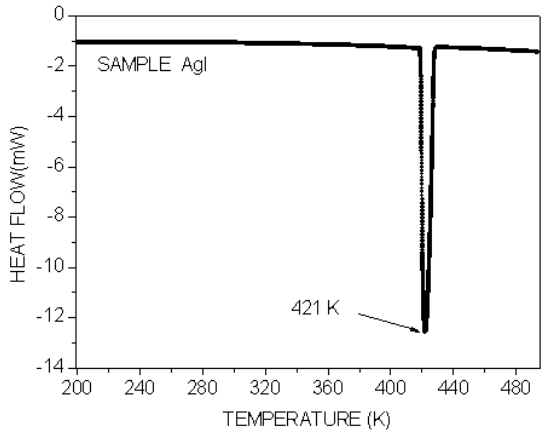

Fig. 4: DSC heating curve for AgI

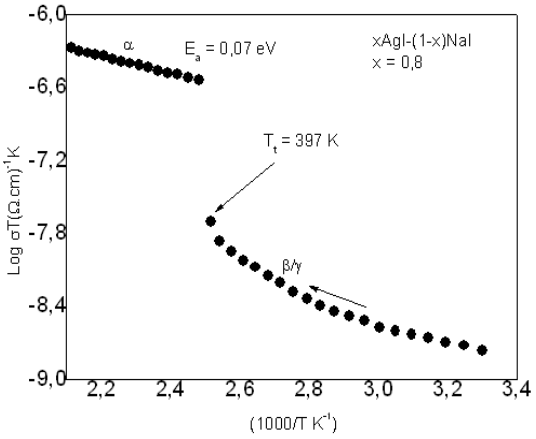

Fig. 5: Transition temperature for 0.8AgI-0.2NaI

10^{-4}-10^{-2}(Ω cm)$^{-1}$. This result was confirmed with the DSC heating curve (Fig. 8) at 399 K. The change in

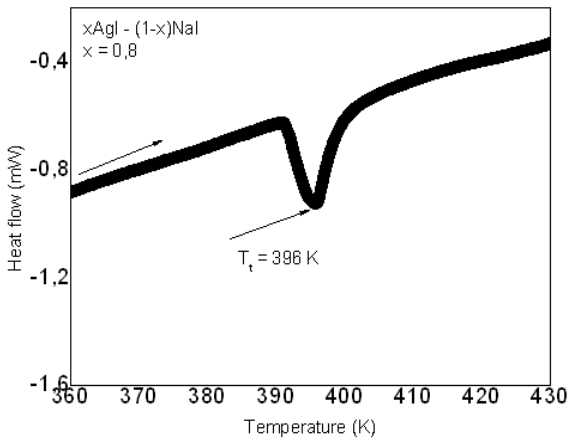

Fig. 6: DSC heating curve for 0.8AgI-0.2NaI system

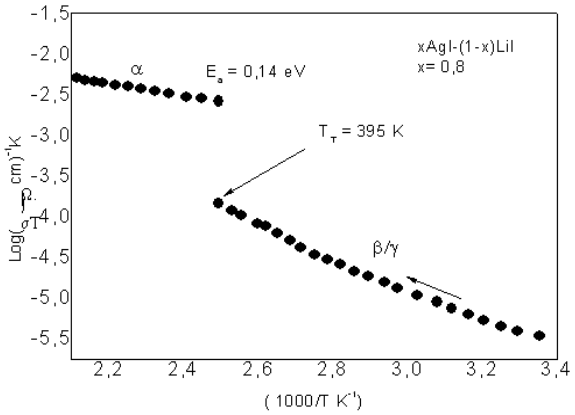

Fig. 7: Transition temperature for 0.8AgI-0.2LiI

electrical conductivity is probably due to cooperative effects of ion-ion and ion-crystal lattice interactions. The two studied systems showed at least one order of magnitude change in conductivity at the given transition temperature. However, the 0.8 AgI-0.2 NaI had an electrical conductivity 10-6 times whereas the 0.8 AgI 0.2 LiI was 10^{-2} times lower than those found for AgI.

The activation energy for each system was estimated using the Arrhenius model. The associated transition temperature of the superionic phase of silver iodide, decreases as the NaI and LiI dopant concentrations increases. In the meantime, the conductivity decreased about two orders of magnitude with dopant concentrations. These effects reveal that extrinsic conductivity prevails before and after the transition temperature due to the presence of interstitial Li ions in the crystal lattice (Chandra, 1981; Garcia and Trujillo, 2010) (Table 1).

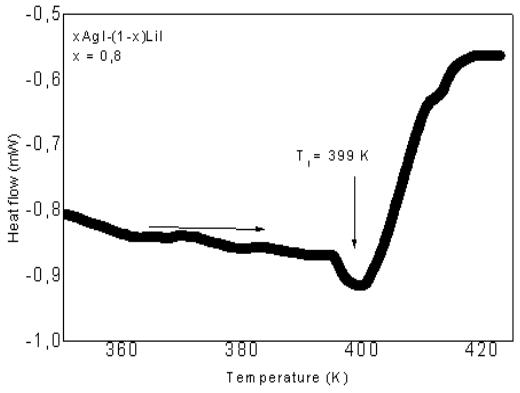

Fig. 8: DSC heating curve for the 0.8AgI-0.2LiI system

Table 1: Transition temperatures and activation energies

MI-AgI	T_t(K) IS	T_t(K) DSC	E_a(eV)
M = Na	397	396	0.07
M = Li	395	399	0.14
AgI	420	422	0.09

CONCLUSION

The IS results show that the xAgI-(1-x)LiI ionic conduction is similar to those obtained for the pure AgI system in the superionic phase. The DSC results shows that the transition temperature decreases as the Na and Li doped concentration increases, indicating that the interactions between ions and the crystal lattice have been modified because of the Na and Li addition.

From the activation energy graphs, it can be observed that the α-AgI pure phase in the range $T>T_t$ had greater conductivity than those obtained for the doped with Li, Na, alkaline salt systems. However, the transition temperature decreases as Na, Li concentrations increases. The Na doped system gave conductivities values in the order of 10^{-6} $(\Omega.cm)^{-1}$ which are not appropriate for ionic conductors.

In the other hand, the LiI doped system is a good candidate to be used as electrolytic device with conductivities in theorder of 10^{-2} $(\Omega.cm)^{-1}$. LiI doped system were more thermally stable than the physical mixture of NaI and AgI systems which could indicate that the extrinsic conductivity prevails before and after the conductivity transition due to the interstitial Li ions.

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