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STUDIES EFFECT ON STRUCTURAL RELAXATION OF THE x(AgI+KI)+ (1-x)NH_4I SYSTEM BASE ON THERMAL MEASUREMENTS

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ABSTRACT

Structural phase transitions in the x(AgI+KI)+(1-x)NH_4I system, allowed quantifying the structural relaxation of the phases: β→α:$NH_4Ag_4I_5$ andβ→α: KAg_4I_5respectively, being correlated with the NH_4I content and with the presence of the glass phase within the compound. It is noticed the importance of having a first thermal treatment of the compound, in order to erase the thermal history. The spontaneous liberation of the residual enthalpy is achieved by using a T_a=308 K isotherm for a two-hour time span. Based on the obtained data, it is presented the phase diagram for variations from *x*=0.45 to 0.95.

Keywords: ion conductor, structural relaxation, vitreous state, phase transitions.

INTRODUCTION

Silver iodide in the alpha phase (T>420 K)(Grupa 2010, Tomaev *et al*. 2014, Valov *et al.* 2012,) is considered to be the prototype, of the named superionic materials or fast ion conductor, since it has a conductivity close to a 1.0 Scm^{-1}, being this value comparable to liquid electrolyte (Cocharane *et al.* 1971, Vonnehut *et al.*) This has driven a technological interest to develop solid electrolytes that could be used in appliances such as power transformers and storage devices, among others (Tomaev *et al.* 2012).

There are many experimental and theoretical reports that show the great advances around studies related to lattice and load transportation dynamics. For example, the compounds named ammonium halide, present several phase changes related to possible configurations of NH^+_4tetrahedral groups, in the crystalline lattice. When the compound is cooled down to temperatures below room temperature, it shows a second order phase transition close to 198 K (Vargas *et al.* 2003), being accompanied by other transitions that allow differentiating three vitreous states, which are correlated to the ammonium content coexisting to temperatures below 100 K (Shuvalov *et al.* 2000). The transition temperatures have been modulated with the substitution of the NH_4^+ ionic groups by K^+ o Ag^+ions (García *et al.* 1997, Mata *et al.* 2002).

In 1949, Vonnegut (Vonnegut *et al.*) proposed a method to dissolve AgI, using as a solvent a mixture of NH_4I and acetone, being proven just until 1973, that the AgI compound is dissolved in acetone in the state of enlarged polarity by NH_4I (Blair *et al* 1973). The methodology in this study was extended by using acetonitrile as a solvent with KI compound. It was found in the dissolution, that the host structure may present several structural relaxation processes, which might be directly correlated to the Ag:NH_4 factor. It has also been proven that the direction of the ammonium group affects the order-disorder of the polarization state, due to the presence of vitreous phases within the AgI structure.

On the other hand, the presence of NH_4^+ groups in the host structure encourages the conformation of Frenkel defects. This new environment favors the Ag+ ion mobility to jump among interstitial sites within the disorganized structure, whereas the ammonium - substituent ions of the Ag^+ sites, remain almost immobile in the lattice. This fact produces a decrease in the number of load carriers of the system. In this paper it was synthesized the x(AgI+KI)+(1-x)NH_4I crystalline compound. Thermal measurements allowed to study the effects of structural relaxation correlated with the thermal treatment and to the content of NH_4I. The results are interpreted according to the vitreous state prompted by the positional disorder of the NH_4^+ group.

EXPERIMENTAL DETAILS

The x(AgI+KI)+(1-x)NH_4I compound, was synthesized through the dissolution method. As precursors there were used: NH_4I, KI, and AgI with a 99.9% purity. In order to increase the polarity and to achieve the AgI dissolution, we started from a 40 ml solution of acetonitrile and KI, for a Ag:K molar reaction of 1:1 and adding NH_4I to the resulting solution, for different molar percentages in weight. The solution was mixed strongly by a time of two hours and after that, the solvent is extracted into a silica gel -desiccator, during four days approximately. The crystallites are selected manually. They are cleaned and are stored in an environment without dampness.

The thermal measurements of the x(AgI+KI)+(1-x)NH_4Icrystalline compounds, were carried out by using a (DSC-Q200) differential scanning calorimeter by the "National Instrument" brand and by utilizing the temperature modulation mode (MDSC). The sample mass was between 10 to 15 mg and they were enclosed into aluminum containers. The measurements were taken by following the standard procedure for structural relaxation. Annealing temperature o starting temperature of the process was T_a=308 K. The annealing times (t_a) varied between 0 and 2 h, respectively. The maximum or resting

temperature of the measurement wasT_0=543 K. For all of the samples it was established an isotherm of (543 K) for one minute, to start the cooling. The heating speed was of 5 K/min and the cooling speed was of20 K/min in a flow of 50 ml/min of nitrogen.

ANALYSIS AND RESULTS

Figure-1 shows the MDSC measurement of the x(AgI+KI)+(1-x)NH_4I compound for x=0.4. The three endothermic peaks are associated to the presence of structural phase transitions (first order): Being the first one around 419 K, itis related to the $\beta\rightarrow\alpha$:AgI transition. This phase is attributed to the part of AgI that does not react during the process. Being the second one close to 483 K, it is associated to the $\beta\rightarrow\alpha$: KAg_4I_5transition and being the third one about 510 K, it is connected to the $\beta\rightarrow\alpha$: $NH_4Ag_4I_5$ phase transition. The results are coherent to what it was reported by Topol (Topol *et al.* 1968). In the report, it is also mentioned the presence of a eutectic stage with the same temperature, than the one for the β-αstructural transition forKAg_4I_5 around 512 K, for a 70% content of AgI.

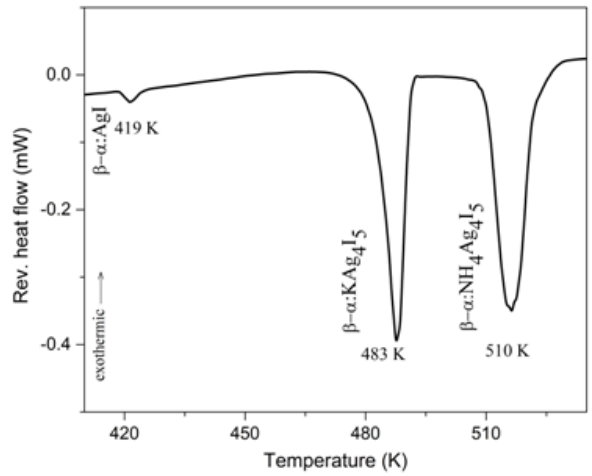

Figure-1. Cooling MDSC curves of 0.6(Ag+KI)+0.4NH_4I for annealing t_a=2h.

Figure-2 shows the thermo grams for the x(AgI+KI)+(1-x)NH_4I crystalline compound for x=0.60 for different annealing times. The HT curve that was identified corresponds to the first measurement. This initial measurement ensures erasing the thermal history of the compound. The displacement of the position of the maximum of the

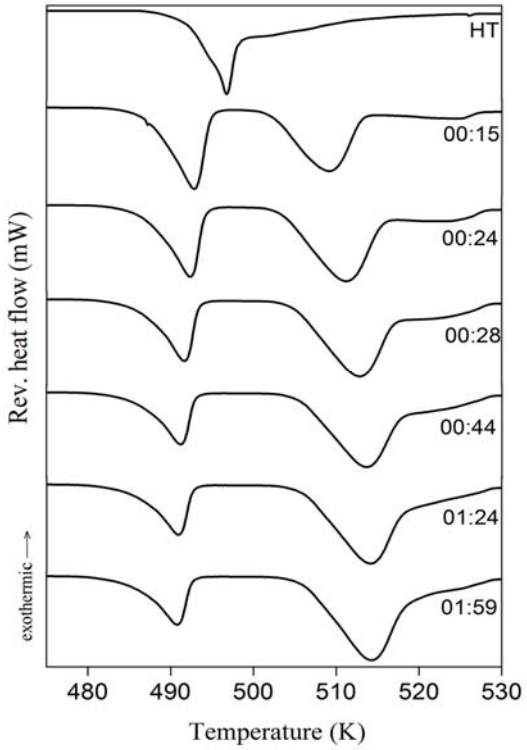

Figure-1. Cooling MDSC scan showing heat latent of transition from β→α:AgI, β→α: KAg_4I_5 and β→α:$NH_4Ag_4I_5$ in 0.6(AgI+KI)+0.4NH_4I for several annealing times t_a. HT curve corresponds to their first measurement.

peaks is related to the dependence on the structural transition and on the annealing for the phases: $\beta\rightarrow\alpha$: AgI, $\beta\rightarrow\alpha$: KAg_4I_5 and$\beta\rightarrow\alpha$: $NH_4Ag_4I_5$, respectively. The highest temperature peak is associated to the $\beta\rightarrow\alpha$: $NH_4Ag_4I_5$ phase transition. These results are coherent to the reports presented by Vargas (Vargas *et al.* 1977) and Swaminathan (Swaminathan *et al.* 1994) for a synthesized compound from saturated solutions of KI. The reports show that the measurements were taken after cooling suddenly the compound. Figure-3 shows the variation of reversible heat flow with an average temperature from 475 to 530 K, and molar concentrations of$x$=0.50, 0.60, 0.65, 0.70, 0.80, 0.90 and0.95, respectively, for annealing times: t_a= 0 h and2 h. The peak located in the lowest temperature zone is related to the $\beta\rightarrow\alpha$: KAg_4I_5transition and the peak located in the highest temperature zone is related to the $\beta\rightarrow\alpha$: $NH_4Ag_4I_5$ transition phase. For x>0.70 (Figure-3), the thermo grams show that both transitions overlap. This overlapping suggests the presence of a temperature zone for which there is a phases coexistences (KAg_4I_5 and $NH_4Ag_4I_5$) and that they are correlated with the NH_4I content. For the x values above 0.90 and0.95, the position of the maximum of the only peak is very close to the temperature of the only phase $\beta\rightarrow\alpha$: KAg_4I_5 transition phase. The structural relaxation existent in the individual phases for$\beta\rightarrow\alpha$: KAg_4I_5 and$\beta\rightarrow\alpha$: $NH_4Ag_4I_5$

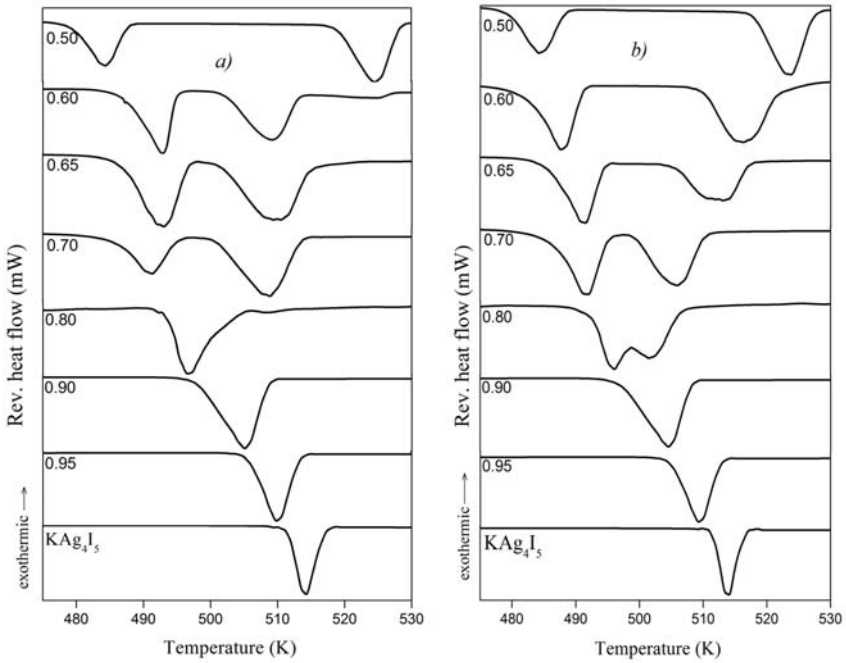

Figure-2. Cooling MDSC for x(AgI+KI)+(1-x)NH_4I for x=50, 60, 65, 70, 80, 95 and 100%. Annealing time a) t_a=0h, b) t_a=2h respectively.

is assessed with the shift of the position of the maximum of the peaks, according to the corresponding transition. This tendency is typical in vitreous systems that are caused by a fast cooling of 20 °C/minhence, there is an spontaneous liberation of a residual enthalpy energy at a annealing temperature of T_a=308 K.

The presence of the $NH_4Ag_4I_5$ phase in the compound causes probably a structural relaxation, mainly because of the direction disorder NH^+_4 ions and it is correlated to the percentage of the NH^+_4 presence; i.e. the higher the content of ammonium, the wider the relaxation is, implying an increase of the vitreous phase. For the discussion on the structural relaxation for the compound, it is adopted a formalism presented in (Hanaya *et al.* 1994), where the position of the maximum of the peaks vs. the annealing time are graphed.

Figure-4 shows the tendency of the position of the maximum of the peaks of Figure-3 with the annealing time. The presence of phase changes: $\beta\rightarrow\alpha$: AgI, $\beta\rightarrow\alpha$: $NH_4Ag_4I_5$ and$\beta\rightarrow\alpha$: $KAg_4I_5$for contents of x=0.60 and 0.70, showed the same tendency. For the $\beta\rightarrow\alpha$: AgIy$\beta\rightarrow\alpha$: KAg_4I_5phases, it is decreasing and it stabilizes for annealing times close to 2 h, whereas for the $\beta\rightarrow\alpha$: NH_4Ag_4I phase, the tendency is increasing and it tends to stabilize for annealing times close to 1 h.

The results show a vitreous response in these compounds, which are considered to be crystalline, emerging in hysteretic behaviors in conductivity measurements, when comparing conductivity curves during the cooling and heating (Rodriguez *et al.* 2010), without taking into account the spontaneous evolution of the system towards a balanced state. The results also glimpse that the effect is caused by the presence of NH_4I within the compound, which fosters reversible changes enhanced by the thermal treatment. One of the contributions of this research is that, for the right interpretation of the thermal measurements, as well as for the structural relaxation of thex(AgI+KI)+(1-x)NH_4I compound, it is necessary to carry out a previous thermal treatment, in order to erase the thermal history and to allow the system reaching a thermal balance.

Figure-5 shows the phase diagram obtained from MDSC measurements for at$_a$=2 hannealing time. Which is time enough for the compoundto reach the thermal balance state? When comparing the results of this research with the ones reported by (Swaminathan *et al.* 1994) it is concluded that the results by Swaminathan *et al.* correspond to a measurement without a previous thermal treatment and it is only reported the structural relaxation for two annealing temperatures. Other important contribution of the results presented in this paper, infers that the

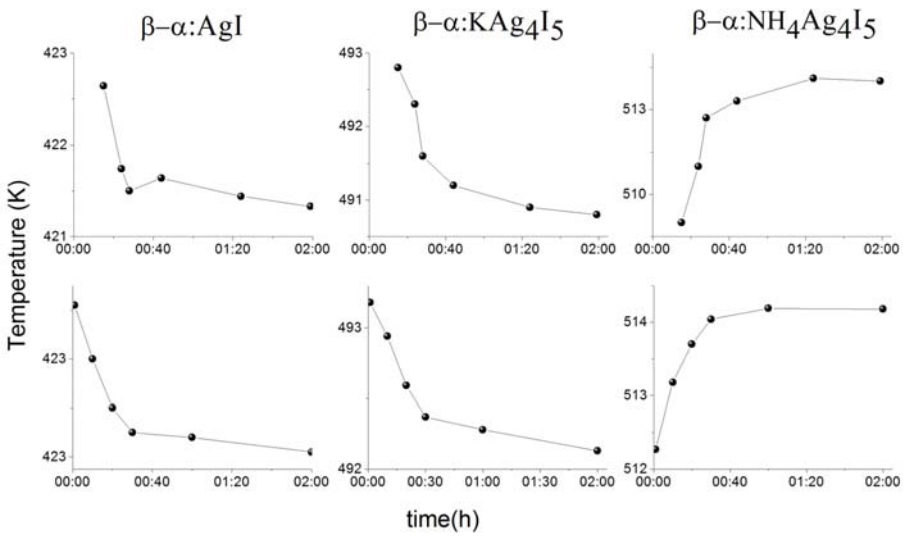

Figure-3. Plot showing variations of transition temperature forβ→ a: AgI and β→ a: $KAg_4I_5$the x(Ag+KI) + (1-x)NH_4I_5 compound: a) up x=60%, b) down x= 65%.

systematic treatment over the x(AgI+KI)+(1-x)NH_4I compound, allows to assess the dynamic of the presence of both of the phases: $NH_4Ag_4I_5$ and KAg_4I_5respectively. These results lead to controvert the position that the saturated solution of KI is inert to the reaction that was presented in (Bradley *et al.* 1967).

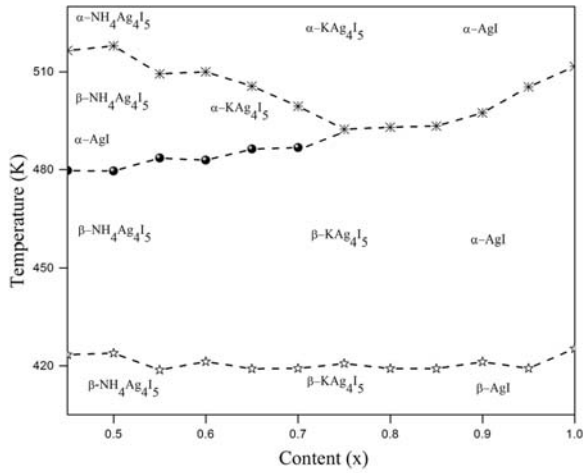

Figure-4. Experimental phase diagram for x(AgI+KI)+(1-x) NH_4I constructed from DSC measurements. Solid lines in the figure are a guide for the eyes.

CONCLUSIONS

The ionic crystalline compound x(AgI+KI)+(1-x)NH_4I for*x*=0.60, when increasing the temperature, shows the presence of three structural transitions: $\beta \rightarrow \alpha$: AgI, $\beta \rightarrow \alpha$: KAg_4I_5 and$\beta \rightarrow \alpha$: $NH_4Ag_4I_5$, respectively. For different *x* values and for the temperature zone of 470 and 530 K, showed dependence on the phase transitions $\beta \rightarrow \alpha$: KAg_4I_5 and$\beta \rightarrow \alpha$: $NH_4Ag_4I_5$with the annealing time. The thermo grams showed that while the annealing (tempering) time was increased, both transitions approach to each other and overlap. The only resulting peak moves towards the transition temperature of the KAg_4I_5 phase, being close to 514.1 K. This behavior proves that the saturated solution of KI used with the solvent, cooperates with the potassium in the configuration of the KAg_4I_5 phase. The structural relaxation presented in the compound is correlated to the annealing time and to theNH_4I content. The results presented in this paper infer that the transition reported by V. S. Swaminathan *et al* correspond to a thermal response of the compound for a first thermal treatment, therefore, the thermal history of the material has not been previously erased. It is presented a phase diagram for the x(AgI+KI)+(1-x)NH_4Isystem, conformed form MDSC measurements, for a t_a=2 hannealing time. For this annealing time, it is ensured that the system has reached its thermal balance state.

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