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: \( \beta \rightarrow \alpha: NH_4AgI_4 \) and \( \beta \rightarrow \alpha: KAg_4I_5 \) respectively, 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 0.2.

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 \( NH_4^+\)tetrahedral groups, in the crystalline lattice. When the phase changes related to possible configurations of the compounds named ammonium halide, present several to lattice and load transportation dynamics. For example, reports that show the great advances around studies related transformers and storage devices, among others (Tomaev et al. 2012).

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 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 \( x(AgI+KI)+(1-x)NH_4I \) crystalline 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 was $T_0=543$ 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 of 20 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)NH₄I 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, it is 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 $\beta\rightarrow\alpha$: KAg₄I₅ transition and being the third one about 510 K, it is connected to the $\beta\rightarrow\alpha$: NH₄Ag₄I₅ 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 $\beta\rightarrow\alpha$ structural transition for KAg₄I₅ around 512 K, for a 70% content of AgI.

Figure-2 shows the thermo grams for the $x$(AgI+KI)+(1-x)NH₄I 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 peaks is related to the dependence on the structural transition and on the annealing for the phases: $\beta\rightarrow\alpha$: AgI, $\beta\rightarrow\alpha$: KAg₄I₅ and $\beta\rightarrow\alpha$: NH₄Ag₄I₅ in 0.6(AgI+KI)+0.4NH₄I for several annealing times $t_a$. HT curve corresponds to their first measurement.

**Figure-1.** Cooling MDSC scan showing heat latent of transition from $\beta\rightarrow\alpha$: AgI, $\beta\rightarrow\alpha$: KAg₄I₅ and $\beta\rightarrow\alpha$: NH₄Ag₄I₅ in 0.6(AgI+KI)+0.4NH₄I for several annealing times $t_a$. HT curve corresponds to their first measurement.

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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/min hence, there is a spontaneous liberation of a residual enthalpy energy at a annealing temperature of $T_a=308$ K.

The presence of the NH$_4$Ag$_4$I$_5$ 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$_4$Ag$_4$I$_5$ and $\beta\rightarrow\alpha$: KAg$_4$I$_5$ for contents of $x=0.60$ and $0.70$, showed the same tendency. For the $\beta\rightarrow\alpha$: AgI, $\beta\rightarrow\alpha$: KAg$_4$I$_5$ phases, it is decreasing and it stabilizes for annealing times close to 2 h, whereas for the $\beta\rightarrow\alpha$: NH$_4$Ag$_4$I 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 hysteresic 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$_4$I 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 the $x$(AgI+KI)+(1-x)NH$_4$I 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 $t_a=2$ h annealing time. Which is time enough for the compound to 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
systematic treatment over the $x(\text{AgI} + \text{KI}) + (1-x)\text{NH}_4\text{I}$ compound, allows to assess the dynamic of the presence of both of the phases: $\text{NH}_4\text{Ag}_4\text{I}_5$ and $\text{KAg}_4\text{I}_5$ respectively. 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).

CONCLUSIONS
The ionic crystalline compound $x(\text{AgI} + \text{KI}) + (1-x)\text{NH}_4\text{I}$ constructed for $x = 0.60$, when increasing the temperature, shows the presence of three structural transitions: $\beta \rightarrow \alpha$: $\text{AgI}$, $\beta \rightarrow \alpha$: $\text{KAg}_4\text{I}_5$ and $\beta \rightarrow \alpha$: $\text{NH}_4\text{Ag}_4\text{I}_5$, respectively. For different $x$ values and for the temperature zone of 470 and 530 K, showed dependence on the phase transitions $\beta \rightarrow \alpha$: $\text{KAg}_4\text{I}_5$ and $\beta \rightarrow \alpha$: $\text{NH}_4\text{Ag}_4\text{I}_5$ 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 $\text{KAg}_4\text{I}_5$ 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 $\text{KAg}_4\text{I}_5$ phase. The structural relaxation presented in the compound is correlated to the annealing time and to the $\text{NH}_4\text{I}$ 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 $x(\text{AgI} + \text{KI}) + (1-x)\text{NH}_4\text{I}$ system, conformed form DSC measurements for a $t_a = 2$ h annealing time. For this annealing time, it is ensured that the system has reached its thermal balance state.

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