PHASE BEHAVIOUR OF THE (1-X)CSHSEO$_4$ –XKHSEO$_4$ BINARY SYSTEM

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Abstract

Modulated differential scanning calorimetry (MDSC), thermogravimetric analysis (TGA) and electrical impedance spectroscopy (EIS), were used to study the thermal and electrical properties of the (1−x)$CsHSeO_4$-x$KHSeO_4$ binary system in the concentration range x = 0.0 – 0.7. The sample $CsHSeO_4$ was prepared using Cs_2CO_3 and H_2SeO_3 (Aldrich), by a solution technique, followed by a slow evaporation at room temperature in presence of $CaCl_2$. For the $KHSeO_4$ sample, we used K_2CO_3 and H_2SeO_3 (Aldrich) following the same procedure. Pure $CsHSeO_4$ (x = 0.0) shows three endothermic anomalies at around 80, 130 and 172°C, respectively. The three anomalies of $CsHSeO_4$ are affected by the $KHSeO_4$ content, specially the second anomaly which tends to disappear as the $KHSeO_4$ content increases. The TGA curves show that all the samples start to lose weight above 120°C, indicating possible dehydration reactions similar to those found in alkaline acid salts, phosphate and sulphates that may explain the highly proton-conducting phases found in these compounds at high temperatures, which reached values of the order of 10^{-2} $(\Omega \cdot cm)^{-1}$.

Keywords: *Solid protonic conductors, Binary systems of acid salts, Dehydration reaction.*

Resumen

La calorimetría diferencial de barrido modulado (MDSC), el análisis termogravimétrico (TGA) y la espectroscopia de impedancia eléctrica (EIS), fueron utilizadas para estudiar las propiedades térmicas y eléctricas del sistema binario (1−x)$CsHSeO_4$-x$KHSeO_4$, en un rango de concentraciones x = 0.0 – 0.7. La muestra $CsHSeO_4$ fue preparada usando Cs_2CO_3 y H_2SeO_3 (Aldrich), por técnicas de soluciones y posteriormente secados gradualmente a temperatura ambiente en presencia de $CaCl_2$. Para la muestra $KHSeO_4$, usamos K_2CO_3 y H_2SeO_3 (Aldrich) desarrollando el procedimiento anterior. La muestra pura $CsHSeO_4$ (x = 0.0) muestra tres anomalías endotérmicas alrededor de 80, 130 y 172°C, respectivamente. Las tres anomalías del $CsHSeO_4$ son afectadas por el contenido de $KHSeO_4$, en especial la segunda anomalía que tiende a desaparecer a medida que se incrementa el contenido de $KHSeO_4$. Las curvas del TGA presentan en todas las muestras el inicio de una pérdida de peso alrededor de los 120ºC, indicando unas posibles reacciones de deshidratación, similares a las que se han propuesto para las sales ácidas alcalinas, fosfatos y sulfatos que pueden explicar ampliamente las fases de conducción protónica encontradas en estos compuestos a altas temperaturas, las cuales fueron del orden de 10^{-2} $(\Omega \cdot cm)^{-1}$.

Palabras Claves*: Conductores protónicos sólidos, Sistema binario de sales ácidas, Reacción de deshidratación.*

1. INTRODUCTION

The family $MHXO_4$ (M = K, Rb, Cs, NH_4 and X = S, Se) forms a group of materials which is characterized by presenting conductivities of ionic type. The crystal formed by $CsHSeO_4$ presents two anomalies at around 80 ºC and 128 ºC Yokota *et al*.[1] and Luspin *et al*.[2], respectively. The anomaly at 128 ºC, studied in the crystal is characterized by a structural transition from a monoclinic phase at ambient temperature to a superionic tetragonal phase Luspin *et al*.[2]. The existence of other transitions in this crystal has not been clearly established Checa *et al*.[3].

On the other hand, the crystal formed by $KHSeO_4$ presents two anomalies at around 140ºC and 170ºC, respectively. Studies carried out on this crystal showed orthorhombic symmetry with hydrogen bond around each SeO_4 Ivanov *et al*.[4] and Baran *et al*.[5] ion.

In a solid solution Baranov *et al*.[7] of these two compounds, the reorganization of the lattice periodicity generates defects that, under the control of the proper thermodynamic phase equilibria, results in a new compound that facilitates through its hydrogen bond network the exchange and the jumps needed in the transport of the charge carriers Zouari *et al*.[6].

The hydrogen bond network exhibits interesting physical phenomena as ferroelectricity, ferroelasticity and the proton conductivity Baranov *et al*.[7,8]. However, the superionic conductivity is of special attention due to its possible technological applications. In H-bonded crystal the electric charge is transported by protons in a hopping process between different hydrogen bonds. These types of jumps are thermally activated in absence of an external applied electric field. At high temperatures, the protonic exchange is activated to a high level and the result is a conductivity called superionic. At low temperatures, the jumps are not so frequent due to the small probabilities of the thermal activation. In the last few years, new combinations of hydrogen sulfate-phosphates Haile *et al*.[9] and Stiewe *et al*.[10], and selenate-phosphates Troyanov *et al*.[11] have being synthesized and characterized structurally. The physical properties previously mentioned are strongly correlated with the phase transitions of acid salts that are of special interest. The superprotonic phases observed in the last years in a great number of such combinations as: $Cs_3(HSO_4)_2(H_2PO_4)$ Haile *et al*.[12], $Cs_3(HSO_4)_2(H_xS/PO_4)$ Haile *et al*.[13] and $Cs_2(HSO_4)(H_2PO_4)$ Chisholm and Haile [14], have presented very interesting properties.

Due to the above-mentioned previous results, in this work we used thermal and electrical treatment techniques that allowed us to visualize some changes in their phase equilibria and in protonic transport properties of the $(1-x)CsHSeO_4$- $xKHSeO_4$ binary system.

For the study of phase equilibria in the binary system one can calculate the formation enthalpy easily as it is proposed by Wunderlich [16] by means of the thermal conductivity constant *K,* the area under the peak in the diagram of heat flow vs. temperature of the MDSC curve, by using

$$\Delta H_f = K \cdot A \qquad (1)$$

K is also the variation of the heat flow with the temperature scan.

The electrical response of the binary system was used to determine the temperature dependence of its conductivity. In the DC regime, one can describe its temperature dependence empirically with the Arrhenius relation describes by:

$$\sigma(0) = \sigma_0 \exp\left[-\frac{E_A}{\kappa_B T}\right] \qquad (2)$$

From the least square fittings of the data to this model it is possible to calculate the activation energy E_A from the slope of the linear fitting to the plots $\mathrm{Ln}\,\sigma$ Vs. 1000/T .

2. EXPERIMENTAL

The $CsHSeO_4$ crystals were synthesized starting from the neutralization of the basic cesium carbonate salt, Cs_2CO_3 (Aldrich 99,9%), with the selenic acid H_2SeO_3 (Aldrich 99.998%) using an aqueous solution technique. The same procedure was used to synthesize $KHSeO_4$ using potassium carbonate K_2CO_3 (Aldrich 99.9%) and the selenic acid H_2SeO_3 (Aldrich 99.998%). After having carried out the neutralization process for a quantity of 10 grams of each compound the solutions were stored in an evaporator for a period of three to four weeks until obtaining the single crystals of $CsHSeO_4$ and $KHSeO_4$, respectively. The crystals were them macerated in independent mortars for 30 minutes, and mixed thoroughly by keeping in mind the necessary concentrations given in molar fraction of x = 0.0. - 0.7. Later on, each mixture of the binary system was again macerated by a period of 30 more minute and finally calcinated at 60°C for about three hours for each concentration.

The prepared concentrations were thermal analyzed by using the modulated differential scanning calorimetry MDSC 2920 analyzer, TA Instruments. The measurements were carried out using a rate of heating of 10ºC/min in the 30°C - 200ºC temperatures range; the samples were always in presence of a dry atmosphere of nitrogen N_2. The thermogravimetric analysis (TGA) was performed using an TA Instruments TGA 2050 analyzer, and the heating rate for this case was the same as that in the previous case, from a temperature of 60ºC up to 210ºC. Also, in both cases they were applied isotherm of 30 minutes above 100°C to minimize the influence of the superficial water in the samples.

The electrical impedance spectroscopy (EIS) was studied in a computer controlled Wayne Kerr 6420

LCR meter in the frequency range of 25 Hz -5 MHz to analyze the behavior of the electric conductivity of the material in the same range of temperature as that used in the thermal (MDSC) characterization, with the purpose of finding intrinsic relationships of the phase behavior by comparing these two quantities. The samples used in electrical characterization were prepared by uniaxial pressure to form pellets of 5 mm diameter and an approximate thickness of 1 mm, applying a pressure of 2,5 tons during a time of 10 minutes. These samples were deposited between two platinum electrodes in a home-made cell with controlled temperature. The impedances spectra were obtained in the isothermal mode, by increments of 10°C for each concentration. Before each electrical run, the sample chamber was evacuated to a pressure of $1{,}0\times10^{-2}$ millibars.

3. RESULTS AND DISCUSSION

Figure 1 shows the MDSC curves for the binary system (1-x)$CsHSeO_4$-x$KHSeO_4$. One can observe from the $CsHSeO_4$ curve two endothermic peaks at 80°C and 128°C, respectively, the second peak associated to a structural phase transition in agreement with previous reports Baranov *et al*.[15]. The samples with small content of $KHSeO_4$, x = 0.1 and 0.3, continue showing the same peaks as those for the pure salt, decreasing their intensity and enthalpy ΔH_f values, like it is shown in Table 1.

The results of MDSC for the combined salts show that the peak at around 128 ºC tends to disappear for $KHSeO_4$ concentrations greater than x = 0.5, while at about 140ºC it starts to increase another endothermic broad peak in the binary system, moving up to 160ºC which coincides with the of structural type phase transition of the $KHSeO_4$.

In Figure 2 the TGA the curves are shown for the binary system using the procedure that was described in the previous section. The curves show a dehydration of the salts expressed as a weight loss near the 120ºC, being bigger for concentrations x = 0,1 and x = 0,3. The weight loss is more pronounced for the concentrations x = 0,9 and x = 1,0 near 140ºC when the binary system presents more concentration of $KHSeO_4$. This weight loss coincides with the transition temperatures given by the MDSC curves.

Figure 3 shows the temperature dependence of the conductivity. We can observe that at low concentrations of $KHSeO_4$ and at about 128ºC, a step change in the conductivity data of approximately three orders of magnitude is apparent.

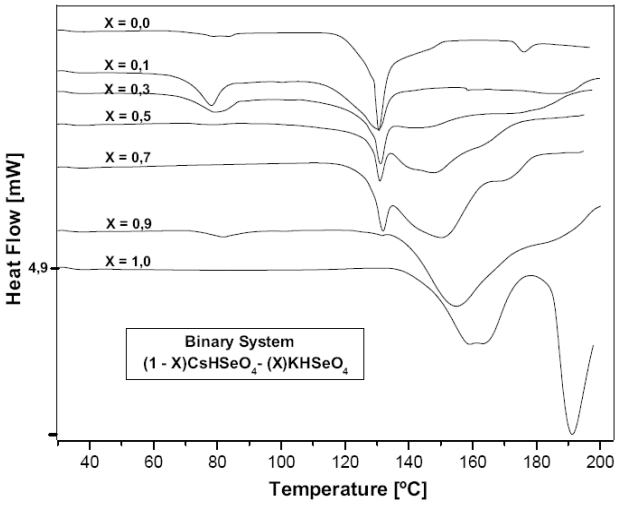


Figure 1. MDSC heating curves for various concentrations of the (1−x)$CsHSeO_4$-xKHSeO4 binary system.

Table 1. Enthalpies of the most important MDSC anomalies observed in the binary system (1−x)$CsHSeO_4$-x$KHSeO_4$.

Concentrations	*ΔH_f [J/g] at 128ºC*
x = 0,0	*32,23*
x = 0,1	*18,65*
x = 0,3	*8,79*
x = 0,5	*6,46*
x = 0,7	*5,84*
x = 0,9	*0,13*
x = 1,0	*0,00*

The step change of conductivity at about 128°C is related to the MDSC peak observed at around this temperature (see Figure 1) for x≤0.7. Notice that for x=0.7 the conductivity increase gradually across the transition region, thus indicating the absence of this transition. Also, it should be pointed out that the conductivity increases rapidly again above approximately 160°C where de second broad MDSC peak become apparent for higher concentrations of $KHSeO_4$ (see Figure 1), as well as the weight loss shown by the TGA results (see Figure 2).

Thus, the highly conducting phase shown above 160°C in all salt concentrations indicate the

presence of a liquid–like phase that promotes proton transport as high as of having a conductivity of the order of 10^{-2} $(\Omega \cdot cm)^{-1}$ at about 180°C.

This liquid phase might be the product of a thermal dehydration of the sample, whose reaction rate increases with increasing $KHSeO_4$ content. The dehydration reaction, accompanied by a dimerization of the product might well be described by assuming the decomposition reaction Pham-Thi *et al*.[17]:

$$2MHSeO_4 \rightarrow M_2Se_2O_{7(s)} + H_2O_{(v)} \qquad (3)$$

where s is solid phase, v is vapor phase, M=Cs or K

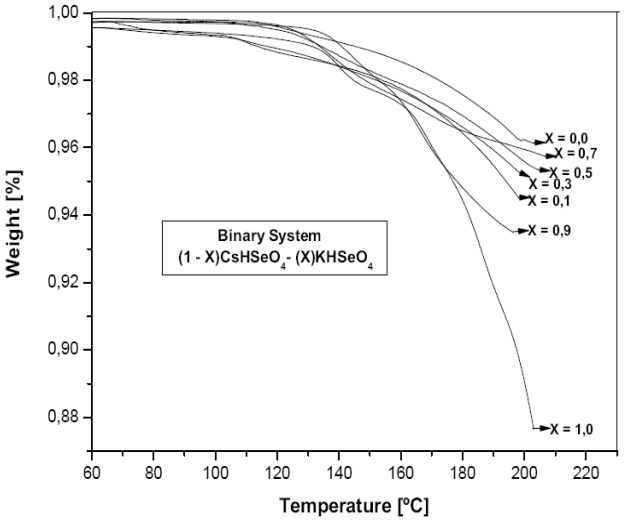


Figure 2. TGA heating curves for various concentrations of the (1−x)$CsHSeO_4$- x$KHSeO_4$ binary system.

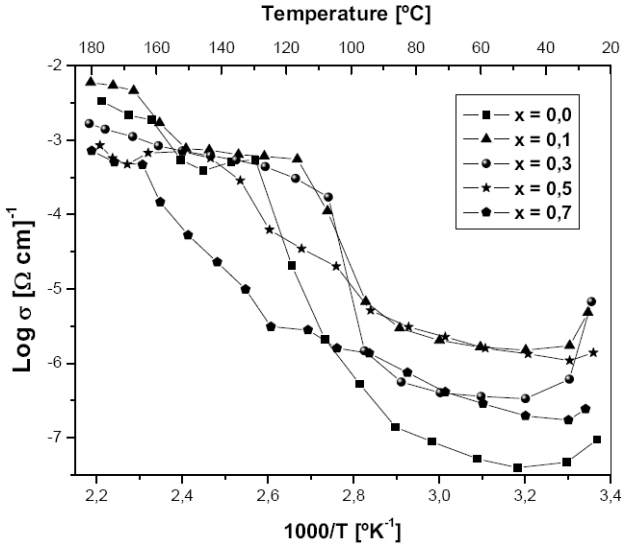


Figure 3. Temperature dependence of the conductivity data, in Arrhenius plots for the (1−x)$CsHSeO_4$-x$KHSeO_4$ system.

4. CONCLUSIONS

In summary, our results of MDSC, TGA and dc conductivity measurements to study the phase interrelationship in the (1-x)$CsHSeO_4$-x$KHSeO_4$ system clearly give evidence that the high-temperature phenomena observed in these acid salts, could be explained by a thermal dehydration like reaction (equation 3). Due to this, the endothermic peaks observed above 128°C for $CsHSeO_4$ rich concentrations and above 160°C for $KHSeO_4$ rich concentrations, as well as conductivities changes associated to superionic-like phase transitions, could be due to dehydration reactions, since they are accompanied by weight loss in the TGA curves.

5. ACKNOWLEDGEMENT

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