REVISTA COLOMBIANA DE FÍSICA, VOL. 37, No. 1. 2005

EFFECT OF DISPERSED Al_2O_3 AND S_iO_2 ON THE PHASE EQUILIBRIA OF NH_4HSO_4

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ABSTRACT

Differential scanning calorimetry (DSC), impedance spectroscopy (IS) and X ray diffraction were used to study the composite solid electrolytes (1-x)NH_4HSO_4-xAl_2O_3 ($x \leq 0.5$) and (1-x)NH_4HSO_4-xSiO_2 ($x \leq 0.7$). Alumina with grain size of 10 μm, pores size of ~6 nm and silica with grain size of 14 nm were used. The SiO_2 and Al_2O_3 particles have different effects on the NH_4HSO_4 thermal phase behaviour: the phase transitions of NH_4HSO_4 at 154 K and 420 K (melting point) were not affected by the silica doping, whereas in the (1-x)NH_4HSO_4-xAl_2O_3 composites, Al_2O_3 affects the enthalpy of both transitions such that the phase transitions at 154 K and at 420 K disappeared for $x \geq 0.3$. The DSC results shows that new morphological states are formed by the Al_2O_3 doping because new phase boundaries are observed below the melting point of AHS in the composites. The X-ray diffraction data also confirm that the composites with alumina becomes more amorphous as x increases reaching completion for $x \geq 0.3$. On the other hand, the dc-conductivity is only improved on adding either Al_2O_3 or SiO_2 to AHS in the solid phases of the composites. The results are discussed in terms of the influence of the dispersed second phase on the overall electrical response and phase behaviour of the composites.

1. Introduction

Ammonium hydrogen sulphate (AHS) belongs to the hydrosulphate of alkali metals that show a high temperature phase transition phenomena that have been investigated by several researchers. This family forms an interesting group of materials characterised by the presence of hydrogen bonding pattern between the HSO^-_4 tetrahedral ions [1]. These bonds are also responsible for the ferroelectric phase transitions found in ammonium and rubidium hydrogen sulphates [2,3]. From earlier dielectric measurements [2], it was inferred that AHS undergoes two phase transitions at normal pressure, at T_1=270 K (second order) and T_2 =154 K (first order), respectively. The phase behaviour of AHS have also been studied by thermal and electrical measurements [4,5]. In the high temperature phase (270K<T<420K), it has been claimed that some proton transport takes place in AHS [6].

On the other hand, heterogeneous doping has been widely used in order to improve the ionic conductivity. Two phase composites are usually obtained by doping an ionic conductor and a highly dispersed inert isolator, such as Al_2O_3, SiO_2, TiO_2, ZrO_2, etc [7-9]. Additional concentrations of defects in undersurface space caused by quasichemical reaction between surface atoms or ions of ionic salt and inert matrix have been attributed as the main reason for the ionic conductivity enhancement [7,8].

In this work we used mechanical treatment technique to obtain composites with different alumina and silica (specific surface area and porosity) concentrations in order to study the effect of dispersed Al_2O_3 and S_iO_2 on the physical properties of the NH_4HSO_4.

2. Experimental

Powders of NH_4HSO_4 (Merck), Al_2O_3 (Aldrich, grain size of 10 μm, pores size of ~6 nm) and SiO_2 (Sigma, grain size of 14 nm) were used as starting materials. The mixtures were treated in a mortar during 25 minutes and then calcinated during 1 hour at 410 K (close to the melting point of NH_4HSO_4). The thermal characterisation was carried out using a differential scanning calorimetric Mettler-Toledo DSC 30 with a low temperature cell in the temperature range from 120 K to 473 K. The electrical characterisation of the samples was done by impedance spectroscopy (IS) using the two electrodes configuration Ag|sample|Ag. The powder was uniaxially pressed ($1.5x10^5$ Pa) into disk-shaped pellets of 13 mm diameter and 1-2 mm thickness. The data were recorded in the frequency range between 5 Hz-13 MHz with an applied signal of 100 mV, using a computer controlled Hewlett-Packard 4192A LCR meter. The temperature was measured using a type K, alumel-chromel thermocouple situated as close as possible to the cell. The X-ray diffraction measurements were performed with a Philips powder diffractometer equiped with a high temperature attachment. Ni filtered CuK_α radiation was used.

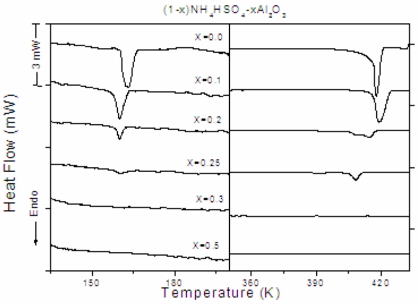

Fig. 1 *DSC curves for* (1-x)NH_4HSO_4-xAl_2O (x=0.0 - 0.5) composites from 135 K to 435 K heating rate of 5 K min^{-1} under a dry N_2 flux.

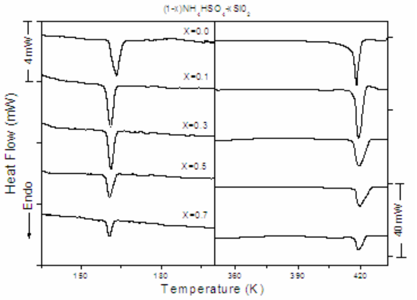

Fig. 2 *DSC curves for* (1-x)NH_4HSO_4-xSiO_2 (x=0.0 - 0.7) composites from 120 K to 473 K heating rate of 5 K min^{-1} under a dry N_2 flux.

Fig. 1 shows representative DSC curves for (1-x)NH_4HSO_4-xAl_2O_3 (x=0.0 - 0.5) composites from 135 K to 435 K using a heating rate of 5 K min^{-1} with a dry N_2 flux. The pure AHS salt, x=0.0, shows two endothermic peaks associated with the 154 K and 420 K phase transitions, which agrees with previous report [2]. The 154 K transition is first order and the second one at 420 K corresponds to the AHS melting point with a change of enthalpy of -131,16 J/g (The DSC measurements did not resolved the reported second order phase transition of AHS at 270 K). The sample with x=0.1, shows the same two peaks, as those of pure AHS but the peak intensities are reduced and the change of enthalpy (ΔH) at the melting point was –65.07 J/g. The sample with x=0.2, shows two endothermic peaks at about 400 K with a total enthalpy of –21.43 J/g. The DSC curve for x=0.25 concentration shows that the two peaks at higher temperatures are well separate and they appear at about 390 K and 398 K (ΔH= -11.76 J/g), respectively. The DSC results for the higher concentrations, $x \geq 0.3$, show that all phase transitions disappear. Thus, since the alumina is considered to be inert, the DSC results indicates that the crystalline phases of pure AHS are reduced with increasing Al_2O_3 concentrations and disappear for $0.7AHS-0.3Al_2O_3$ composite. The composites with x≥0.3 appears to be totally amorphous since no melting point is observed for these compositions.

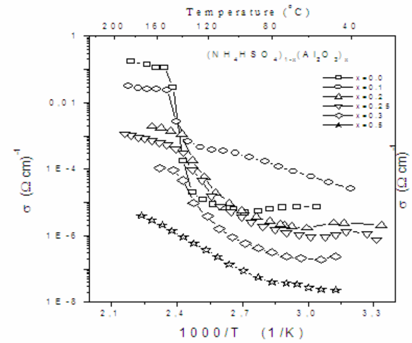

Fig. 3 *dc*-conductivity plots (σ vs. 1/T) of $(1-x)NH_4HSO_4-xAl_2O_3$ (x=0.0 - 0.5)

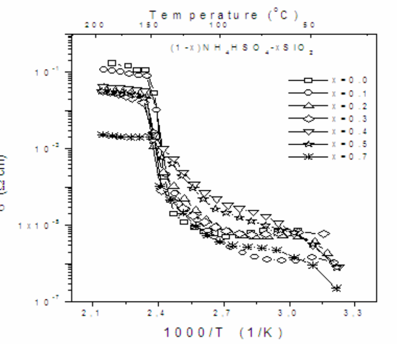

Fig. 4 *dc*-conductivity plots (σ vs. 1/T) of $(1-x)NH_4HSO_4-xSiO_2$ (x=0.0 - 0.7)

Fig. 2 shows representative DSC curves for $(1-x)NH_4HSO_4-xSiO_2$ (x=0.0 - 0.7) composites from 135 K to 435 K using a heating rate of 5 K min^{-1} with a dry N_2 flux. The results show that the phase transitions of NH_4HSO_4 at 154 K and 420 K (melting point) were not affected by the silica doping.

Fig. 3 shows the dc-conductivity versus reciprocal temperature for seven different concentrations of $(1-x)NH_4HSO_4-xAl_2O_3$ (x=0.0 - 0.5). The high temperature (above 420 K) conductivity decreases (from 10^{-1} to 10^{-5} $(\Omega\ cm)^{-1}$) upon adding alumina. This behaviour have been attributed to the percolation effect of the "conductor-insulator" type [8]. The highest values of the low temperature (below 420 K) conductivity is obtained for x=0.1. Similar behaviour have been observed in other composites [8,9]. The reason of this kind of maxima in conductivity is the formation of paths, built by highly conducting interfaces, that can be described in terms of a percolation model, where the composites conductivity occurs via structural protons [10].

Fig. 4 shows the dc-conductivity versus reciprocal temperature for seven different concentrations of $(1-x)NH_4HSO_4-xSiO_2$ (x=0.0 - 0.7). The high temperature (above 420 K) conductivity decreases (10^{-1} to 10^{-3} $(\Omega\ cm)^{-1}$) upon adding silica and below the melting point the conductivity shows a maximum at x=0.4, showing a similar effect than that observed in the alumina samples. In order to compare the values of the conductivity for the alumina composites with those for the silica composites, we plot in Fig. 5, σ vs x for $(1-x)NH_4HSO_4-xAl_2O_3$ (x=0.0 - 0.5) and $(1-x)NH_4HSO_4-xSiO_2$ (x=0.0 - 0.7) at 398 K and 440 K, respectively. The curves at 398 K shows a maximum at x=0.1 for the alumina composites and at x=0.4 for the silica composites. This kind of maximum is typical for this type of samples doped with an inert isolator [8-9]. The curves at 440 K (above the melting point of pure AHS) show that the conductivity decreases upon adding alumina or silica (see fig. 5). For both, the alumina and silica samples, the step variation of σ at about 420 K is reduced as x increases.

The X ray diffraction data indicates that the alumina composites becomes more amorphous as x increases, reaching completation for x ≥0.3, (see Fig. 6).

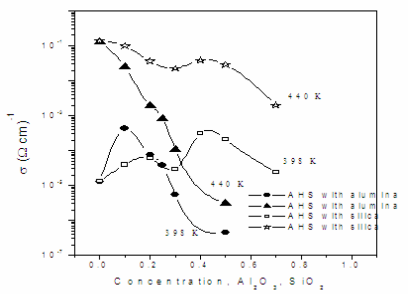

Fig. 5 Conductivity versus the concentration of AHS doped with alumina and silica.

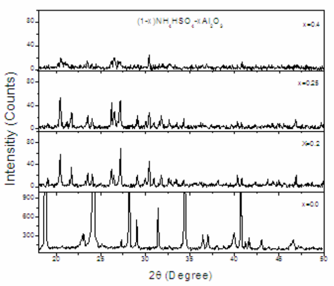

Fig. 6 X-ray diffraction patterns of a powdered (1-x)NH4HSO4-xAl2O3, x=0.0, 0.2, 0.25 and 0.4 room temperature and always in a dry helium atmosphere.

The conductivity results depend on x; below 420 K (the solid phase) the highest values of σ are obtained for samples with x=0.1 alumina and x=0.4 silica. However, the high-temperature (above 420 K) conductivity decreases upon adding alumina or silica and the step change of σ at 420 K is reduced on increasing x. The SiO_2 and Al_2O_3 have different effects on the NH_4HSO_4 thermal phase behaviour: the phase transitions of NH_4HSO_4 at 154 K and 420 K (melting point) were not affected by the silica doping, whereas in the $(1-x)NH_4HSO_4-xAl_2O_3$ composites, Al_2O_3 affects the enthalpy of both transitions such that the phase transitions at 154 K and at 420 K dessapeared for x ≥0.3. This effect may be attributed to a stronger interface interaction between NH_4HSO_4 and Al_2O_3 in comparison with that of the $(1-x)NH_4HSO_4-xSiO_2$ system. The DSC results show that new morphological state are formed by the Al_2O_3 doping because new phase boundaries are observed below the melting point of AHS in the composites. The DSC and X ray diffraction data indicate that the composites with alumina becomes more amorphous as x increases, reaching completion for x ≥0.3.

The authors would like to acknowledge the support of the Banco de la República de Colombia, and the International Program in the Physical Sciences, IPPS, of Uppsala, Sweden.

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