Effect of dispersed SiO_2 on the phase behaviour of NH_4HSO_4

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Phase equilibria and electrical conductivity of $(1-x)\text{NH}_4\text{HSO}_4\text{-}x\text{SiO}_2$ composites were studied by thermal and impedance measurements. Silica with particle size of 14 nm was used. The phase transitions of NH_4HSO_4 (AHS) at 154 K and 420 K (melting point) were not affected by the silica doping. No large changes in the low-temperature ($T < 420$ K) dc-conductivity and electrical relaxation of the composites were observed with the dispersed concentration. The corrected imaginary part of the relative permittivity (after subtracting the dc-conductivity contribution), $\epsilon''(\omega, T)$, as a function of frequency ($f = \omega / 2\pi$) and temperature (T) shows a dispersion peak at around 1 MHz for the lower silica concentrations, whose position (f_{max}) is also thermally activated. The dielectric results are discussed in terms of the effects of the lattice polarizability on the proton motion.

Key words: Composites; Solid electrolytes.

Efecto del SiO_2 disperso sobre el comportamiento de las fases del NH_4HSO_4

Estudiamos el equilibrio de fases y la conductividad eléctrica de las compositas $(1-x)\text{NH}_4\text{HSO}_4\text{-}x\text{SiO}_2$ por medidas térmicas y de impedancia. Se utilizaron partículas de silica de diametro 14 nm. Las transiciones de fase del NH_4HSO_4 (AHS) en 154 K y 420 K (punto de fusión) no fueron afectadas con el dopaje de silica. No se observaron grandes cambios a bajas temperaturas ($T < 420$ K) en la conductividad dc y la relajación eléctrica de las compositas al ser dopadas con silica. La parte imaginaria de la conductividad corregida (después de haber substraído la contribución de la conductividad dc), $\epsilon''(\omega, T)$, como función de la frecuencia ($f = \omega / 2\pi$) y la temperatura muestra un pico de dispersión alrededor de 1 MHz para pequeñas concentraciones de silica, cuya posición (f_{max}) esta también termicamente activada. Los resultados dieléctricos se discuten en terminos del efecto de la polarización de las celdas sobre el movimiento de los protones.

Palabras claves: Composites; Electrolitos sólidos

1. INTRODUCTION

Ammonium hydrogen sulphate (AHS) belongs to the hydrosulphate of alkali metals that show proton behaviour in the solid state. This family forms a interesting group of materials characterised by the presence of hydrogen bonding patterns between the tetrahedral ions (1). These bonds are also responsible for the ferroelectric phase transitions found in ammonium and rubidium hydrogen sulphates (2,3). From the earlier dielectric measurements, 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, below the melting point ($270\text{K} < T < 420\text{K}$) it has been claimed that some proton transport takes place in AHS (6).

Badot and Colomban (7), plotting the real versus imaginary parts of the dielectric constant observed different relaxation modes for CsHSO_4 and AHSe . In particular the

substitution of Cs^+ ions by ones introduces a new very low relaxation in the 3 - 10 MHz range. They claimed that this kind of relaxation might correspond to a reorientation of ions. Regular ions do not have a permanent dipole, but distortion can induce a dipole.

On the other hand, heterogeneous doping has been widely used as a route to improve the physical properties in solid ionic conductors. Two phase mixtures or composites are usually obtained by doping an ionic conductor and a highly dispersed inert isolator, such as Al_2O_3 , Fe_2O_3 , SiO_2 , TiO_2 , ZrO_2 , MgO , etc (8-11). In some cases, an enhancement of the conductivity have been observed, as in CsHSO_4 when doped with SiO_2 (10).

In this work we used a mechanical mixing technique to obtain composites with various silica (particle size of 14 nm) concentrations in order to study the influence of inert silica on the physical properties of $(1-x)\text{NH}_4\text{HSO}_4\text{-}x\text{SiO}_2$ composites.

2. EXPERIMENTAL PROCEDURE

Powders of NH_4HSO_4 (Merck) and SiO_2 (Sigma-Aldrich), particle size of 14 nm, were used as starting materials. The pure salt and the silica were weighed in stoichiometric amounts and then were mixed and ground in a mortar during 25 minutes, followed by heating at temperatures below the melting point (420 K) of NH_4HSO_4 during 60 minutes.

Differential scanning calorimetry (DSC) was performed with a Mettler-Toledo DSC 30 low-temperature cell. The measurements were done in the temperature range from 120 K to 473 K using a heating rate of 5 K min^{-1} . The samples were in all cases subjected to a dry N_2 flux.

The electrical conductivity of the samples was determined by complex impedance analysis using a two-electrodes configuration $\text{Ag}|\text{sample}|\text{Ag}$ in a dry atmosphere ($\leq 10\%$ relative humidity). Samples pressed at $1.5 \times 10^5 \text{ Pa}$ in to pellets of 13 mm diameter and 1-2 mm thickness were supported in a pyrex tube between two spring-loaded silver electrodes. The entire cell was inserted into a stainless steel block cylinder. The temperature control of the cell was achieved by a Eurotherm controller and using a noninductive heater wire wound around the stainless steel block and a type-K thermocouple attached to an electrode, close to the sample. The measurements were performed using a computer controlled Hewlett-Packard 4192A LCR meter over a frequency range of 5 Hz-13 GHz with an applied signal of 0.1 V. Possible non linear effect were checked at amplitudes up to 0.5 V over the entire frequency range for a typical cell. The dc -conductivity, σ_0 , was calculated as usual, from the extracted R_{bulk} values obtained from impedance plots at various temperatures.

3. RESULTS AND DISCUSSION

Fig. 1 shows representative DSC curves for $(1-x)\text{NH}_4\text{HSO}_4$ - $x\text{SiO}_2$ ($x=0.0, 0.2, 0.4$, and 0.7) composites from 120 K to 473 K using a heating rate of 5 K min^{-1} under a dry N_2 flux. For pure AHS ($x=0.0$), two endothermic peaks are observed at 154 K and 420 K, respectively, which are associated with previously reported first-order phase transitions in AHS. The 154 K phase transition is a solid-solid transformation and the second one at 420 K corresponds to the melting point of AHS with a latent heat of -131.16 J/g . For the concentrations ($x=0.1, 0.2, 0.3, 0.4, 0.5$ and 0.7 , respectively), the DSC curves show the same two endothermic effects as those observed for pure AHS, thus indicating that, for all silica concentrations, the two phases AHS and SiO_2 are separated in the composites.

Fig. 2 shows the dc -conductivity plots ($\ln \sigma$ vs. $1/T$) for several concentrations ($x=0.0, 0.1, 0.2, 0.3, 0.4, 0.5$ and 0.7) of $(1-x)\text{NH}_4\text{HSO}_4$ - $x\text{SiO}_2$. The room temperature dc -conductivity of the composites are in the range between 10^{-5} and $10^{-7} (\Omega\text{cm})^{-1}$. The high temperature ($T > 420 \text{ K}$, the melting point of AHS)) dc -conductivity of the composites are in the range $10^{-1} - 10^{-3} (\Omega\text{cm})^{-1}$ and decreases when the silica concentration increases. This behaviour of the dc -conductivity with silica content is very similar to that observed by Ponomareva et al (10) in the $\text{CsHSO}_4 - \text{SiO}_2$ system.

Fig. 3 shows typical plots of the corrected imaginary part of the relative permittivity (after subtracting the dc -conductivity contribution), $\epsilon''(\omega, T)$, as a function of frequency ($f = \omega / 2\pi$) at several isotherms ($T < 420 \text{ K}$) for the composite with $x=0.4$. A dielectric loss peak at around $f_{\text{max}} = 1 \text{ MHz}$ is observed, which shifts to higher frequencies as the temperature increases.

Fig. 1. Typical DSC curves for $(1-x)\text{NH}_4\text{HSO}_4$ - $x\text{SiO}_2$ ($x=0.0, 0.2, 0.4$ and 0.7) composites from 120 K to 473 K using a heating rate of 5 K min^{-1} under a dry N_2 flux.

Fig. 2. dc -conductivity plots ($\ln \sigma$ vs. $1/T$) for several concentrations ($x=0.0, 0.1, 0.2, 0.3, 0.4, 0.5$ and 0.7) of $(1-x)\text{NH}_4\text{HSO}_4$ - $x\text{SiO}_2$.

Fig. 3. Typical plots of the corrected imaginary part of the relative permittivity (after subtracting the dc -conductivity contribution), $\epsilon''(\omega, T)$, as a function of frequency ($f = \omega / 2\pi$) at several isotherms ($T < 420 \text{ K}$) for the composite with $x=0.4$.

Fig 4 shows the temperature dependence of $f_{\max}$, plotted as $\ln f_{\max}$ vs. $1/T$, for the same composition ($x = 0.4$). Two activated relaxation processes are clearly evidenced from Fig 4: one from 300 to 330 K with activation energy $E_a = 1.12$ eV and the second one from 330 to 380 K with $E_a = 0.28$ eV. In fact, the characteristic frequency $f_{\max}$ is usually related to the inverse of the relaxation time for conductive motion of the ions.

The dielectric loss peak observed in AHS-silica composites at around $f_{\max} = 1$ MHz is in the same range of frequency as that observed by Badot and Colombari (7) in NH_4HSeO_4 (AHSe), and which was assigned to a reorientation of ions. These ammonium reorientations and the proton displacement might change the local lattice polarizability. A proton, while sitting in a site, will either attract or repel its ions neighbours, thus creating a local polarisation cloud about the central proton that affects its motion. In this picture the activation energy for ionic migration is also caused by the dynamic processes of polarization, rather than fully determined by the static part of a simple barrier.

4. CONCLUSIONS

Thermal measurements on $(1-x)\text{NH}_4\text{HSO}_4-x\text{SiO}_2$ composites show that they are two-phase mixtures of AHS and SiO_2 . However, the dc -conductivity of the composite show similar behaviour at low and high temperatures (below and above the melting point of AHS at 420 K) as that observed in the $(1-x)\text{CsHSO}_4-x\text{SiO}_2$ system (10). A very slow dielectric relaxation is observed in composites with low silica concentrations in the same range of frequency (around 1 MHz) as that observed in AHSe (7), thus attributed to a reorientation of ions. The dielectric loss peak position ($f_{\max}$), which is related to the inverse of the relaxation time for this polarisation process, is thermally activated

that might be related to proton displacement. In other words, the proton displacement and the ion reorientation would induce polarization.

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Fig. 4. Temperature dependence of $f_{\max}$ plotted as $\ln f_{\max}$ vs. $1/T$, for the composition ($x = 0.4$).

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