Dielectric and electric investigations on $Rb_{1-x}(NH_4)_xHSO_4$ solid solution

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Abstract

Dielectric investigations in the temperature and frequency ranges 150 - 450K and 10^2 - 10^5Hz respectively show that the compositions x = 0.2 and x = 0.4 of the solid solution $Rb_{1-x}(NH_4)_xHSO_4$ are ferroelectric below T_c = 285K and T_c = 295K respectively. The symmetry of room temperature phase is $P_{2_{1/C}}$ for both investigated compositions.

Alternative current complex impedance measurements were performed on this ferroelectric and superconductor material at high temperatures. An impedance relaxation was observed. In addition, to the ferroelectric properties, a modest level of conductivity at high temperatures, which was attributed to the motion of H^+ proton, was observed for both compositions but this conductivity is more pronounced at low and high temperatures for the composition x = 0.2.

1. Introduction

The appearance of ferroelectricity in a good number of sulphates [1] and especially in NH_4HSO_4 and $RbHSO_4$ [2, 3] renders advisable the dielectric examination of the solid solution of $Rb_{1-x}(NH_4)_xHSO_4$. NH_4HSO_4 and $RbHSO_4$ are ferroelectrics below 270 and 258K respectively. They present a superionic phase transition [4, 5] at 370 and 404K for NH_4HSO_4 and $RbHSO_4$ respectively. At the ferroelectric phase the structure of NH_4HSO_4 is monoclinic, with space group Pc and the lowest temperature piezoelectric phase (below 154K) has triclinic symmetry P1 [2]. The symmetry of $RbHSO_4$ at the ferroelectric phase is monoclinic, with space group Pc [3] and its symmetry of the room-temperature phase is monoclinic, with space group $P_{2_{1/C}}$.

The aim of the present work was to study dielectric and electric properties in the solid solution $Rb_{1-x}(NH_4)_xHSO_4$. The presence of the proton H^+ between two SO_4^{2-} renders possible the superionic conduction in these materials at high temperature. Thus, this property leads to make electric conductivity measurements. A comparative study of the level

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of conductivity in the two compositions x = 0.2 and x = 0.4 of the solid solution was investigated.

2. Experimental

The synthesis of two compositions x = 0.2 and x = 0.4 single crystals by slow evaporation of H_2SO_4, Rb_2SO_4 and $(NH_4)_2SO_4$ aqueous solutions was described previously [6,7,8]. Rubidium ammonium sulphate contents were checked by chemical analysis and confirmed the sample composition. Complex permittivity $\varepsilon*(\omega) = \varepsilon'_r - i\varepsilon''_r$ was performed between 10^2 and $2\ 10^5$Hz and temperature range from 150K to 450K using a Wayne-Kerr capacitance bridge (model 6425). The single crystals were electroded on the two faces perpendicular to the polar axis. An a.c. frequency range 5 - $1.3\ 10^7$ Hz was covered by a HP 4192A analyzer in temperature range 250 - 550K. Both single crystals were heated at 150°C for 4h under vacuum to eliminate as much as possible the water deposited on the crystal faces.

3. Results and discussion
3(a) Dielectric measurements

The dispersion in the evolution of dielectric permittivity was studied previously in our last work and shows an important dispersion due to proton conductivity in this solid solution [9, 10].
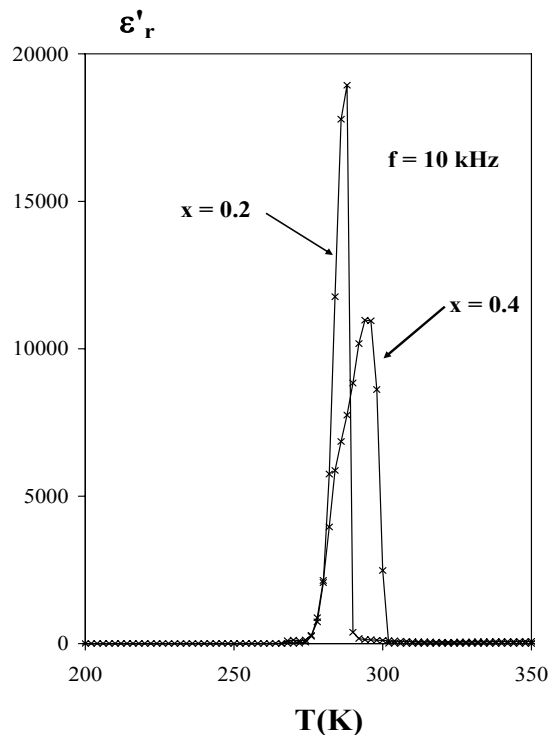

Fig. 1: Thermal evolution of dielectric constant ε'_r at the frequency 10 kHz for both compositions x = 0.2 and x = 0.4.

In fig. 1, we present the evolution of real part of dielectric permittivity with the electric field along the c axis which represents the polar axis in the temperature range 150 - 450K The ferroelectric phase transition is indicated by a pronounced dielectric anomaly

respectively at 285K and 295K for both x = 0.2 and x 0.4 compositions. The variation of ε'_r vs temperature exhibits the familiar characteristics of a second-order phase transition. The dielectric anomalies are very pronounced (the value of ε'_c rises to a peak values of 18000 for x = 0.2 and 11000 for x = 0.4 at 10^4 Hz). This evolution of the values of ε'_r from x = 0.2 to x = 0.4 is interpreted as follow: when the percent of ammonium is small it induces more conductivity in the structure because it causes an important disorder in the structure which facilitates the breaking of hydrogen bonds. Because that the part of dielectric permittivity which is attributed to conductivity is more pronounced at low frequency, the maximum of dielectric permittivity is more important for x = 0.2. The second observation is the small evolution of the Curie temperature which goes from 285 to 295K when we go from x = 0.2 to 0.4. This evolution can be due to the fact that the small percent of ammonium induces more disorder which facilitates the displacement from polar ferroelectric phase to no polar paraelectric phase than great percent of ammonium [11].

3(b) A.C. impedance measurements

The opposite faces of the crystals were carefully polished. Ag paste electrodes were deposited on the two sample faces. It was found by a.c. impedance measurements that no electrode effect was present in the frequency and temperature ranges considered. Before the measurements, the samples were heated for 4 h at 150°C to eliminate the organic species. The sample was put into a quartz tube shielded by a Faraday cage. The measurements were carried out in air at 20°C or 10°C intervals on both heating and cooling processes. At each measurement temperature T, the sample was maintained at T $\pm$ 0.5°C for 30min before collecting the data. A preliminary heating and cooling cycle was necessary to ensure reproducibility. An a.c. frequency range 5 - 1.310^7Hz was covered by a HP 4192A precession component analyzer controlled by a computer program. Fig. 2, shows the evolution of the conductivity versus inverse temperature $\log_{10}(\sigma T) = f(1000/T)$ for both compositions x = 0.2 and x = 0.4. This conductivity was determined by complex impedance method.
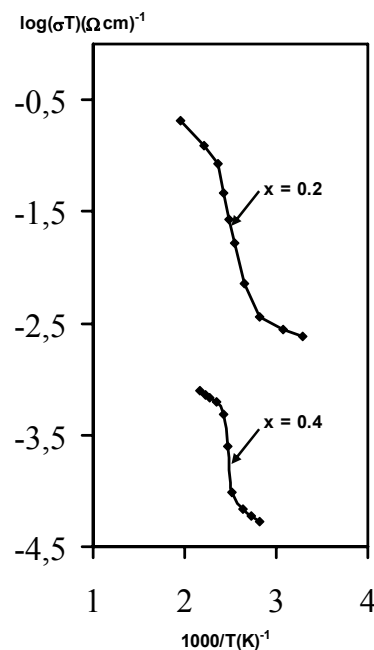

Fig. 2: Temperature dependence of log (σT) en fonction de 1000/T for both compositions x = 0.2 and x = 0.4.

This conductivity evolution presents a drastically jump at 410 and 420 K respectively for the compositions x = 0.2 and 0.4. In the low temperature phase which exists at the temperature lower than 410K and 420K respectively for both compositions x = 0.2 and x = 0.4, the values of conductivities are 210^{-5} $(\Omega cm)^{-1}$ and 210^{-7} $(\Omega cm)^{-1}$ respectively. For high temperatures higher than 410 and 420K respectively for both compositions x = 0.2 and x = 0.4, values of conductivities are respectively 2.310^{-4} and 2.410^{-6}. From these values of conductivity at low and high temperatures we can deduce that there is an important increasing of conductivity from the composition x = 0.4 to x = 0.2. These results at low temperature are in agreement with our interpretation from dielectric measurements. However, the important evolution of conductivity at high temperature from x = 0.4 to x = 0.2 confirm the great orientation disorder introduced by ammonium groups NH_4^+ when it is with small quantity. This disorder facilitates the braking of hydrogen bonds and increasing conductivity in the material. The fact that the temperature of transition from conductor to superconductor phase increases from x = 0.2 to x = 0.4 can be a second confirmation of our interpretation.

The f_p frequency relative to the imaginary part of the modulus M''_{max}(f_p = $1/2\pi\tau_\sigma$) measured in our last works [9, 10] and which is defined by the condition $\omega\tau_\sigma = 1$, where τ_σ is the most probable ion relaxation time; f_p increases with increasing temperature and the temperature dependence of f_p is of Arrhenius type $f_p = f_{p0}exp(-\Delta E_p/kT)$.
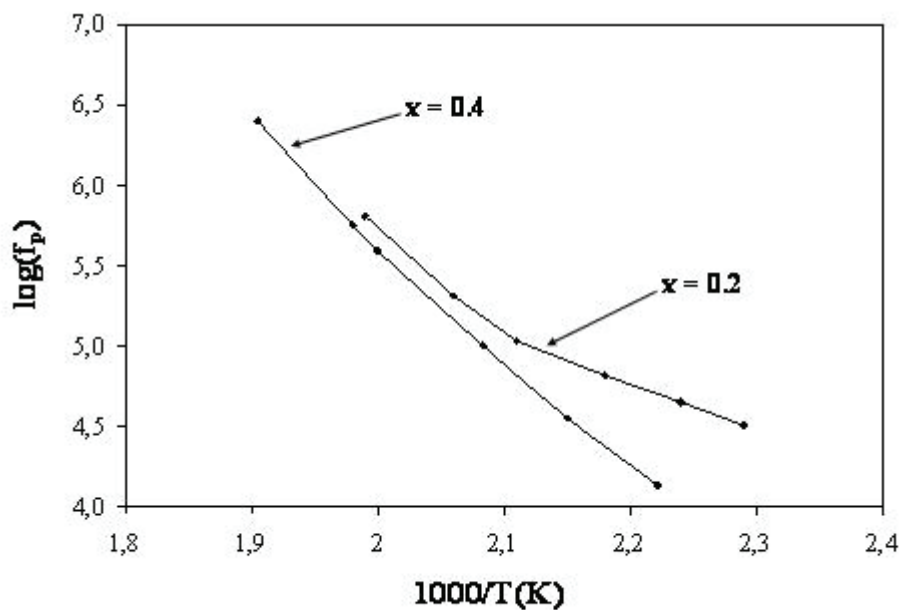

Fig 3: Thermal evolution of log f_p where f_p is the maximum of the imaginary part M''_{max} of the modulus for the both compositions x = 0.2 and x = 0.4.

Fig. 3 shows the evolution of Log(f_p) versus 1000/T for both compositions x = 0.2 and 0.4. Only for the composition x = 0.2 we observe an anomaly at 470K, which can be attributed to the fact that the proton go from the non conductor state to the super-conductor state. This result confirms that the proton conduction is more pronounced in the composition

$x = 0.2$. So the orientation disorder of the NH_4^+ group is more important when it is in small quantity.

3(c) IR measurements

We have used the infrared measurements to study the evolutions of bonds linked to the proton in both compositions.
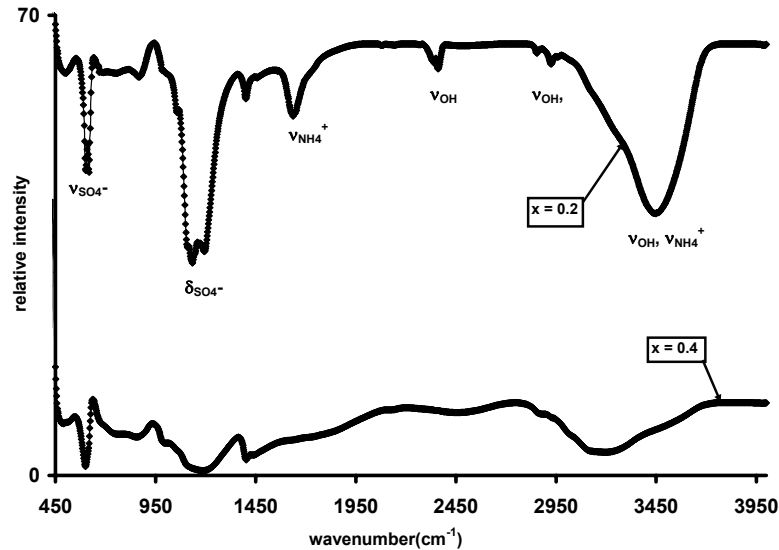

Fig. 4: IR spectrums at room temperature for the both compositions $x = 0.2$ and $x = 0.4$.

Fig. 4 shows the both IR spectrums for the two compositions $x = 0.2$ and $x = 0.4$ at the room temperature. From this evolution and after attribution of all bonds, we can remark that those attributed to hydrogen bands are less intense and more diffused for the composition $x = 0.2$ than for $x = 0.4$. This behaviour confirms our last interpretation that the disorder of the ammonium NH_4^+ group when it is in small quantity is more important. So the hydrogen bonds became less strong and its bricking is easier.

4. Conclusion.

This study confirms the roll of the small percent of ammonium NH_4^+ in the structure because of its important disorder. The first roll observed by dielectric study is:
1- The decreasing of the temperature of the ferroelectric-paraelectric phase transition which shows that this group facilitates the disappearance of the polar phase.
2- The great evolution of the maximum of dielectric permittivity at Tc from the composition $x = 0.4$ to $x = 0.2$, shows that the part of permittivity related to conductivity is more pronounced for $x = 0.2$ so when we have the small amount of ammonium. This observation was confirmed by conductivity measurements which when conductivity presents an increasing at low and high temperature from $x = 0.4$ to $x = 0.2$ and this presents the second roll of NH_4^+ groups in the structure.

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