Solid State Ionics 252 (2013) 116–120

Contents lists available at ScienceDirect

Solid State Ionics

journal homepage: www.elsevier.com/locate/ssi

Superprotonic conductivity of $(NH_4)_3H(SO_4)_2$ in the high-temperature phase

Y.J. Sohn [a,*], K.M. Sparta [a], M. Meven [a,b], G. Roth [a], G. Heger [a]

[a] RWTH Aachen, Institut für Kristallographie, Jägerstr. 17-19, 52066 Aachen, Germany
[b] FZ Jülich, JCNS Outstation at FRM II, Lichtenbergstr. 1, 85747 Garching, Germany

ARTICLE INFO

Article history:
Received 15 January 2013
Received in revised form 24 June 2013
Accepted 26 June 2013
Available online 25 July 2013

Keywords:
$(NH_4)_3H(SO_4)_2$
Impedance measurements
Superprotonic conductivity
Crystal structure analysis
Single-crystal neutron diffraction

ABSTRACT

Impedance measurements were performed on single crystals of $(NH_4)_3H(SO_4)_2$ in the temperature range of 295–441 K. Anisotropy of protonic conductivity was found in the monoclinic room-temperature phase (space group $C2/c$) as well as in the rhombohedral high-temperature phase (space group $R\bar{3}m$). Above the high-temperature phase transition at 413 K, conductivity in the hexagonal (001) plane yields a value of $\sim 10^{-2}$ S cm^{-1}, which is typical for superionic conductors. A verification of a sample quality after the impedance measurements, using X-ray powder diffraction, showed minor additional peaks of $(NH_4)_2(SO_4)$. This suggests a beginning of thermal decomposition at high temperature. The possible pathways of proton conduction were discussed according to crystal structure analyses by single-crystal neutron diffraction method.

1. Introduction

$(NH_4)_3H(SO_4)_2$ (TAHS) is well known for its superprotonic conductivity ($10^{-2} \leq \sigma_{(001)} \leq 10^{-1}$ S cm^{-1}) in the high-temperature phase above 413 K [1,2]. The charge carrier of conductivity in TAHS was reported to be entirely protons by coulometric studies [3]. Whereas isolated hydrogen-bonded $(SO_4)H(SO_4)$ dimers are characteristic of the monoclinic crystal structure ($C2/c$) of TAHS at room temperature, two-dimensional pseudo-hexagonal networks of hydrogen bonds are formed between the SO_4 groups in the rhombohedral high-temperature phase $\left(R\bar{3}m\right)$. The O1 atom involved in the hydrogen bond between SO_4 groups is disordered [4]. It is slightly shifted from the threefold axis and split in three symmetry-equivalent positions. This splitting allows a shorter, hence stronger O1 – H1 – O1 hydrogen bond. With respect to hydrogen disorder in the high-temperature phase of TAHS, a detailed crystal structure analysis was carried out by single-crystal neutron diffraction [5]. There was a clear indication of a splitting of H-atom positions in the O – H – O hydrogen bonds. Hence, a split H-atom model was used in the crystal structure refinement. For this, the H-atom position was moved from the 9*e* Wyckoff position with a site occupancy factor of 1/3 to the 18*h* Wyckoff position with a site occupancy factor of 1/6. Proton diffusion takes place between these partly occupied split H-atom positions in two steps. One occurs between the two potential minima of the split H-atom positions, and the other one between the neighboring O – H – O hydrogen bonds. In the latter case, an existing hydrogen bond is broken and the proton jumps to a neighboring site, forming a new hydrogen bond. The corresponding H – H distance between two adjacent hydrogen bonds observed by single-crystal neutron diffraction was 2.27 (2) Å. Besides, the NH_4 groups are also disordered in this high-temperature phase of TAHS. There are two symmetrically independent NH_4 groups in the unit cell. Protons of these ammonium groups showed strongly enlarged anisotropic mean-square displacements by the crystal structure refinement. Therefore, a split H-atom model was also applied for these ammonium groups. Since they are both located on a special position with a high-site symmetry, altogether 12 and 9 split H-atom positions are formed around the N1 and N2 atoms, respectively. To build a NH_4 tetrahedron, six different orientations, in other words, combinations of split H-atom positions are possible for each ammonium group. Previous single-crystal neutron diffraction studies revealed very well localized N atoms (almost spherical anisotropic mean-square displacements) and large thermal ellipsoids of protons attached to it, which explains the librational motion of these ammonium groups. The role of ammonium groups in conduction was already reported by Reddy et al. [3], comparing the results of similar coulometric experiments on a reference system $Na_3H(SO_4)_2$. There was no evolution of gas observed in the system of $Na_3H(SO_4)_2$ and hence, a confirmation was made that the ammonium groups contribute to the conduction in TAHS. Supplementary proton conduction through the ammonium groups was also suggested by other groups [6,7]. This idea was also supported by the single-crystal neutron diffraction studies, in which the proton distribution of the ammonium group located in the pseudo-hexagonal network of hydrogen bonds in the (001) plane was illustrated according to the observed nuclear density maps. A clear correlation between the protons of the O – H – O hydrogen bonds and the ones of this particular ammonium group was observed and moreover, the distance between these

* Corresponding author. Tel.: +49 2418096906.
E-mail address: sohn@xtal.rwth-aachen.de (Y.J. Sohn).

0167-2738/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.ssi.2013.06.011

two protons was 2.26 (1) Å, that is almost the same H – H distance between the adjacent hydrogen bonds mentioned above.

Corresponding to our previous crystal structure analysis using single-crystal neutron diffraction, we measured the conductivity of TAHS both in the room- and high-temperature phases in the different crystallographic directions to study anisotropy of conductivity. The results of the conductivity measurements in the different crystallographic directions are discussed with respect to crystal structures. Moreover, a verification of the sample quality was made to make sure that the conductivity measured at high temperature corresponds to the high-temperature phase of TAHS, and not to a phase of a possible thermal decomposition. Proton conduction is also discussed in connection with the monoclinic and rhombohedral crystal structure in each phase of TAHS.

2. Experimental

Large TAHS single crystals of optical quality were grown from aqueous solution by the cooling method. The platelet-like crystals had a pseudo-hexagonal habitus. X-ray Laue photographs were taken from some of the well grown faces to check the precise orientation of the crystals. The back-scattering method of X-ray Laue measurements allows taking the diffracted reflections on a thin film. With the help of the analyzing program, OrientExpress Ver. 3.4 [8], the scanned film could be further interpreted. The program gives information on how the perpendicular direction of the measured crystal face is oriented, and can also calculate a new orientation of the crystal face from the orienting matrix, how to reorient the crystal to have desired orientation. Since the angle is given in real space relating to the coordinate system of the beam direction, the desired directions (cutting lines) were marked on the crystal. Thin plates of TAHS single crystals (~3 mm × 3 mm × 0.5 mm) were then cut perpendicular to the different crystallographic axes to measure anisotropy of conductivity. For this, the crystal was fixed on a holder, and was cut through by a tungsten carbide wire saw using distilled water. After cutting, the orientation of each crystal was checked again by X-ray Laue measurements. Silver paste was applied to the sample surface and served as contact for the electrodes. For conductivity measurements an impedance spectrometer Solartron 1174 was used in the temperature range of 295–441 K and frequencies in between 1 and 500 kHz. Following the impedance measurements, X-ray powder diffraction was used to verify the sample quality with respect to possible decomposition effects.

3. Results and discussion

3.1. Impedance measurements

Single-crystal platelets of TAHS were prepared with different orientations (perpendicular to monoclinic **a**, **b**, **c**) for the conductivity measurements. From the experimental Cole–Cole plots of the impedance measurements (see Fig. 1) the real part of the impedance at the minimum of the impedance curve was taken as an approximation to the electrolyte resistance, R (Ω) of the sample. The conductivity, σ is then calculated according to the following equation:

$$\sigma\left(\Omega^{-1}\mathrm{cm}^{-1}\right) = \mathrm{L(cm)/R}\ (\Omega) \times \mathrm{area}\left(\mathrm{cm}^2\right),$$

where L indicates the distance between two electrodes that is the thickness of the sample and the area is that of the electrode. The following Arrhenius equation expresses the conductivity as a function of temperature:

$$\sigma T = A\exp(-H/k_B T)$$

where A is the pre-exponential factor that corresponds to the y-axis intercept on the logarithmic Arrhenius plot shown in Fig. 2. H is the activation enthalpy which can be calculated from the slope of the Arrhenius plot and k_B is the Boltzmann constant. A few data points that slightly deviate from the linear behavior were excluded for the calculation of H and A. The values are given in Table 1 parallel to the different crystallographic directions and for the temperature ranges below and above the high-temperature phase transition at 413 K. The results show anisotropy of proton conduction in the monoclinic as well as rhombohedral phases. The geometrical relationship between the monoclinic and rhombohedral axes (hexagonal setting) is illustrated in Fig. 3. Above 413 K, protonic conductivity is high parallel to the monoclinic **b** and **c**-axes, corresponding to the (001) plane of the high-temperature phase of TAHS, and the activation energy for these two directions is the same. This indicates that there is a two-dimensional high proton conduction above 413 K. The conductivity value in the (001) plane yields ~10^{-2} S cm^{-1}, which is typical for superionic conductors. Along the monoclinic **a**-axis, that is inclined to this (001) plane of high-temperature phase with the monoclinic angle, $\beta = 101.83\ (5)°$ [9], a lower conduction was observed. The conductivity measured in the room-temperature phase of TAHS indicates anisotropy along the different crystallographic directions. Monoclinic TAHS shows the highest conductivity along the **c** direction and the lowest along the **a** direction. Furthermore, the changes in the slope of Arrhenius plot in the vicinity of the structural phase transition at 413 K are observed. This corresponds well to the observation made by NMR measurements, where the significant change of the dynamics related to ammonium groups was observed at ~397 K and the signal related to the free protons (involved in the O – H – O hydrogen bonds) of the high-temperature phase firstly appeared at 390 K [10].

In addition, a verification of the sample quality after the impedance measurements was carried out. The main purpose was, first of

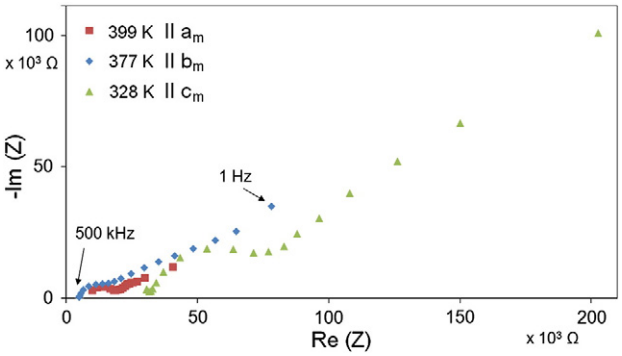

Fig. 1. Cole–Cole plots of the frequency-dependent impedance measurements along the different crystallographic axes of TAHS at different temperatures.

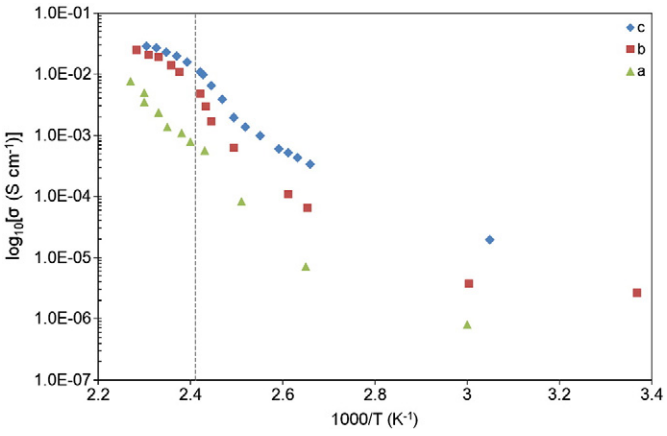

Fig. 2. Temperature-dependent Arrhenius plot of σ in different crystallographic directions. The high-temperature phase transition of TAHS is marked with a vertical dashed line at 413 K.