Proton dynamics in superprotonic Rb₃H(SeO₄)₂ crystal by broadband dielectric spectroscopy

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Abstract
Broadband dielectric and AC conductivity spectra (1 Hz to 1 THz) of the superprotonic single crystal Rb₃H(SeO₄)₂ (RHSe) along the c axis were studied in a wide temperature range 10 K < T < 475 K that covers the ferroelastic (T < 453 K) and superprotonic (T > 453 K) phases. A contribution of the interfacial electrode polarization layers was separated from the bulk electrical properties and the bulk DC conductivity was evaluated above room temperature. The phase transition to the superprotonic phase was shown to be connected with the steep but almost continuous increase in bulk DC conductivity, and with giant permittivity effects due to the enhanced bulk proton hopping and interfacial electrode polarization layers. The AC conductivity scaling analysis confirms validity of the first universality above room temperature. At low temperatures, although the conductivity was low, the frequency dependence of dielectric loss indicates no clear evidence of the nearly constant loss effect, so-called second universality. The bulk (intrinsic) dielectric properties, AC and DC conductivity of the RHSe crystal at frequencies up to 1 GHz are shown to be caused by the thermally activated proton hopping. The increase of the AC conductivity above 100 GHz could be assigned to the low-frequency wing of proton vibrational modes.

Keywords: proton conductor, phase transition, broadband spectroscopy

(Some figures may appear in colour only in the online journal)

1. Introduction
Dynamics of ionic charge carriers usually follows some universal rules. The universal frequency response of electrical conductivity has been studied and observed in many ion conducting and disordered solids [1–9]. This feature has been found to exist in different materials regardless of significant differences in the structure or type of charged ionic carriers. The first universality applies to high temperatures and has been studied since Jonscher [10]. He introduced the term UDR for ‘Universal Dielectric Response’ or ‘Universal Dynamic Response’. It was based on the observation that conductivity, caused by the hopping motion of mobile ions, consists of two parts: one due to the long-range motion (diffusion) of ions which contributes to the DC conductivity and the second one as the characteristic dispersive AC part due to the localized motion of the ions. The latter conductivity part increases continuously with frequency obeying a power law with expo-
nent never exceeding unity, until reaching a high-frequency (HF) plateau [11]. Both DC and AC conductivities are thermally activated obeying the Arrhenius law. The first universality is regarded as a "fingerprint" of the thermally activated ion hopping among the interconnected sites [4].

In the same frequency window in which the first universality can be detected, at low temperatures the nearly constant loss (NCL) effect is usually observed, as first revealed in 1991 [12]. This term applies for conducting materials, where the dielectric loss function, $\varepsilon''$, is virtually independent of frequency [13, 14]. At cryogenic temperatures, none of the thermally activated motion related to the ion transport is detectable, while the NCL effect is still present, termed as the second universality by Funke [15]. This effect is present in various ionic conductors regardless of their structure, such as glass, polymer [7], or crystalline [16] but also in insulators and semiconductors [17].

Large interest in studying electric properties of proton conductors, including superprotonic, can be explained by their huge application potential. Hydrogen conducting materials can be used in e.g. proton exchange membrane fuel cells, gas separators or electrochemical sensors [18–24]. Proton can be considered as a special type of charge carrier in solids due to its small size and lack of electron shell. These features are the cause for creating special environment for the existing protons in solids: hydrogen bond network. Translational motion of protons in solids usually consists of hopping between two existing available position (potential well cages) and reorientation of the nearest atoms in the neighbourhood. The open question was whether this complex behaviour of proton migration in the solid electrolyte affects the macroscopic behaviour. To answer this question, we have studied the electric properties of several proton conductors considering the universal conductivity spectra approach.

In the previous papers we have shown that both universalities of conductivity spectra can be observed in ordinary organic proton conductors, such as benzimidazolium azelate [25, 26] and imidazolium malonate [27]. Recently, we have shown that the universal conductivity spectra behaviour is also similar for the superprotonic (NH$_4$)$_3$H(SO$_4$)$_2$ single crystal, even when dielectric contribution from polar ammonia group influences the conductivity response [28].

However, the question whether both universalities also apply to proton conductors that exhibit phase transitions into a superprotonic phase is still open. To challenge this question, here we present the broadband dielectric studies of the Rb$_2$H(SeO$_4$)$_2$ (RHSe) single crystal. The RHSe crystal belongs to the family of well-known solid acids of general formula Me$_3$A(XO$_4$)$_2$ where Me = K, Rb, NH$_4$, Cs; A = H, D and X = S, Se. At room temperature, the crystal is ferroelastic and has a monoclinic unit cell that belongs to the space group C2/c with lattice parameters $a = 10.475(1)$ Å, $b = 6.090(1)$ Å, $c = 15.418(3)$ Å, and $\beta = 102.91(1)^\circ$ [29]. The structure of RHSe is built up of hydrogen-bonded SeO$_4$ dimers and Rb cations. Dimer of SeO$_4$–H–SeO$_4$ consists of two slightly distorted SeO$_4$ tetrahedra connected by the hydrogen bond. The ferroelastic domain structure at low temperature phase was reported by Chen [30]. In the high-temperature superprotonic (paraelastic) phase, the structure of RHSe belongs to the rhombohedral space group R3m with lattice parameters $a = 6.1181(5)$ Å, $c = 22.674(7)$ Å and hexagonal unit cell [31]. The previous conductivity measurements of RHSe by the low-frequency impendence spectroscopy have shown that the phase transition temperature $T_s$ ranges from 449 K to 456 K [32, 33]. Activation energies of the DC conductivity in the high-conducting phase are $E_a = E_b \approx 0.26$ eV and $E_c \approx 0.48$ eV along a, b, and c crystallographic axes, respectively [34]. Differences in the values of activation energy reflect the anisotropy of the RHSe crystal.

In this work we present our studies of the electric properties of the RHSe single crystal in a broad temperature and frequency range. Broad frequency range was required to receive precise information about the values of bulk DC conductivity at the highest temperatures, where the standard methods used to evaluate the electric properties of the sample are insufficient. The experiments were performed on a crystal with the electric field $E$ along the c axis. The study aimed to examine whether the first and second universalities of the conductivity spectra holds true in a crystallographically ordered proton conductor with a structural phase transition. The paper is organized as follows: in the next section we describe the experimental details, in the section 3 the results and discussion of dielectric and conductivity studies in a wide frequency range are presented, and we end with a short summary.

2. Experimental

Single crystals of RHSe were grown by a slow evaporation from stoichiometric aqueous solution at room temperature. The as-grown crystals were of plate-form with the predominant hexagonal (001) face [35]. Several experimental techniques were used to obtain the broadband dielectric and AC conductivity spectra of the RHSe crystal. At low frequencies, 1–10$^6$ Hz, impedance measurements were performed using a Novocontrol Alpha AN high-performance frequency analyzer. Temperature dependences were measured in a He-flow cryostat between 10 and 475 K. The appropriate surfaces of the crystals were covered with a silver paste (Hans Wolbring) to form electrodes. In the HF region (10$^6$–10$^9$ Hz), complex impedance of the rod-shaped cylindrical sample with gold electrodes evaporated on its flat surfaces was measured in the temperature range 300–473 K using a computer-controlled dielectric spectrometer with a Novocontrol BDS 2100 coaxial sample cell and an Agilent 4291B impedance analyzer. The complex dielectric permittivity was calculated taking into the account the electromagnetic field distribution in the sample. In the THz range (0.2–1 THz), time-domain transmission spectroscopy, employing custom made spectrometer based on an amplified Ti:sapphire femtosecond laser system [36], was applied to ~0.5 mm thick plane-parallel plate. THz measurements were performed in the temperature range 300–5 K during cooling. The HF data were slightly renormalised to adjust them to the low-frequency and THz data. To keep the physically important Kramers–Kronig relations, the HF permittivity and loss data were normalized in the same way, with the same parameters at all temperatures and frequencies. In
Figure 1. Frequency dependences of the electric parameters for selected temperatures: (a) dielectric permittivity, (b) dielectric loss, and (c) AC conductivity of RHSe for \(E \parallel c\).

Figure 2. Temperature dependence of electric parameters for selected frequencies: (a) dielectric permittivity, (b) dielectric loss and (c) AC conductivity of RHSe for \(E \parallel c\).

3. Results and discussion

3.1. Dielectric properties and AC conductivity

In order to discuss the ion dynamics and its temperature evolution, we have studied the RHSe crystal in a wide temperature and frequency range. Figure 1 presents the frequency dependences (\(\varepsilon'\) and \(\varepsilon''\) — real and imaginary part of the complex dielectric permittivity, and \(\sigma'\) — real part of the AC conductivity) for selected temperatures.

The same set of experimental data is shown in figure 2 as the temperature dependences at selected frequencies. Significant dielectric dispersion is observed in the whole studied frequency range at temperatures above 200 K. Two dispersion regions can be well separated and indicate two relaxation contributions to the dielectric properties and AC conductivity. The higher-frequency contribution to permittivity achieves \(\sim 10^4\) at 300 K, the lower-frequency one \(\sim 10^6\) above 450 K. We attribute the lower-frequency dielectric contribution providing colossal permittivity values to the electrode polarization effect [37]. The higher-frequency dielectric contribution is then considered to be caused by the ion dynamics in the RHSe bulk, i.e. it is attributed to the intrinsic polarization and conductivity mechanism. Additionally, the DC conductivity is observed as a low-frequency plateau at high temperatures in figure 1(c). Both relaxation contributions dramatically reduce on cooling and vanish in the permittivity below 200 K (figure 2(a)), but their contributions to dielectric loss (figure 2(b)) remain non-zero and frequency dependent down to 10 K. The frequency dependence of dielectric loss indicates no NCL effect (second universality) down to 10 K. Although the AC conductivity dependences at lowest temperatures almost overlap each other, the AC conductivity neither reach slope 1 nor \(\varepsilon''\) meets the criteria given by Ngai [38].

As seen in figures 1(c) and 2(c), AC conductivity at low temperatures is low. On increasing temperature the AC conductivity increases, indicating a thermally activated process due to proton migration and hopping. As seen in figure 2(a), the permittivity monotonically decreases on decreasing temperature, without showing any traces of a ferroelectric phase transition down to helium temperatures, suggested by Gesi [35]. This behaviour indicates that the RHSe is non-ferroelectric, but may show disorder related to random site occupation of the hydrogen atoms [39]. The THz measurements show an increase of the AC conductivity with increasing frequency (see figure 1(c)) which could be assigned to the low-frequency wing of proton vibrational modes [40, 41].

3.2. Bulk DC conductivity

The complex impedance spectra analysis is used to distinguish the intrinsic (bulk) properties from the extrinsic contributions
Figure 3. Nyquist plots of RHSe single crystal at different temperatures (463, 403 and 353 K). Open circles represent the data collected at low frequencies (10–106 Hz), whereas the diamonds show the values obtained from the HF experiment (106–109 Hz). The data were measured during cooling. Crosses represent characteristic data points, one per each decade. The lines, obtained using equation (1), show the impedance of the sample neglecting any additional components, e.g. from the electrode-sample interface. Notice that for higher temperatures (463 and 403 K) the breaks were used to show the whole response of the studied crystal.

such as the electrode polarization effect. Figure 3 presents typical Nyquist (\(-Z'' (Z')\)) dependence (\(Z'\) and \(Z''\) denotes the real and imaginary parts of the complex impedance \(Z^*\)) of the RHSe sample at three temperatures for two different phases: \(T = 463\) K (superprotonic phase I) and 403 K and 353 K (ferroelastic phase II).

The data points presented in the graphs were collected upon cooling the sample. The characteristic points, one per each decade, are presented to show the evolution of the semicircle. Although the shape of the semicircle, related to the bulk response of the sample, is roughly the same for the presented temperatures, the frequencies, where the bulk response can be measured, moves towards lower values on decreasing temperature. Please notice that in case of the higher temperatures (463 and 403 K) the break of the scale was used to show also the response related with the electrode polarization.

Figure 4. Arrhenius plot of the crystalline DC conductivity of RHSe. The data were measured during heating (up triangles) and cooling (down triangles). Inset shows the data near the phase transition.

The obtained complex impedance \(Z^*\) can be described using an equivalent circuit model of one parallel RC term by the following expression:

\[
Z^*(\omega) = \frac{R}{1 + (i\omega RC)^{1-\alpha}}, \tag{1}
\]

where \(R\) denotes the resistance of the bulk material (crystal), \(C\) denotes the capacity of the circuit, \(\alpha\) is the fitting parameter which describes the distribution of relaxation times, and \(\omega = 2\pi\nu\) is the angular frequency of the measuring E-field. The values of \(\alpha\) increase slightly with cooling from 0.008 at \(T = 473\) K (superprotonic phase) to 0.022 at \(T = 333\) K. Such small values are typical for Debye-type behaviour with only single relaxation process. Fitted lines, corresponding to the intrinsic impedance of the crystal, are presented in figures 3 and 4. Calculated \(R\) was used to determine the DC conductivity of the bulk material \(\sigma_{\text{bulk}}\) using the known sample geometry:

\[
\sigma_{\text{bulk}} = \frac{1}{R S d}, \tag{2}
\]

where \(d\) denotes the thickness and \(S\) is the surface area of the plane-parallel sample. The Arrhenius plot of the bulk conductivity, measured during heating and cooling cycle, is presented in figure 4. Calculated values of the bulk conductivity are in good agreement with the literature [42, 43]. Similarly, activation energy of the proton hopping in the superprotonic phase \(E_A = 0.49\) eV is in a good agreement with that by Baranov [44].

Increase in the conductivity is caused by increasing number of sites available for protons that occur above the phase transition. At temperatures below the phase transition, centres of hydrogen bonds are ordered and form an ordered hydrogen-bond network [44]. In the high-temperature phase, hydrogen bonded apical O(2) atoms of the tetrahedra move into the disordered state which has six energetically equivalent positions, and in consequence, number of sites for protons increases [45]. The hydrogen bonds form dynamically disordered network [44]. The important role of vertex oxygens and their displacements on creating exceeding number of energetically equivalent sites for protons, which leads to low activation energy...
for proton transport, was also confirmed by DFT studies by Pavlenko [46].

The characteristic conductivity change on heating due to the superionic phase transition appears at slightly higher temperature than on cooling. The small thermal hysteresis (~2 K) points to the first order of the phase transition [33]. X-ray diffraction studies indicate that the symmetry of the intermediate phase, existing in the narrow temperature range, is $C2/m$. Its structural characteristic differs from the ferroelastic phase (symmetry $C2/c$) due to the arrangement of H bonds and orientation of the $\text{SeO}_3$ groups [47]. One can see that the conductivity after cooling from the superionic phase is the same as during the heating.

3.3. Scaling of the frequency dependent conductivity

To better understand the mechanism of proton migration, it is useful to scale the frequency dependence of the conductivity [48, 49]. The conductivity spectra of disordered solids at different temperatures can be superimposed into a single master curve by choosing a suitable scaling parameter [48]. One of the possible ways is the Summerfield scaling [50]:

$$\frac{\sigma'_{ac}}{\sigma_{bulk}} = F \left( \frac{\nu}{\sigma_{bulk} T} \right),$$

where $\sigma'_{ac}$ denotes the AC conductivity, $\sigma_{bulk}$ the bulk DC conductivity and $T$ the temperature. The advantage of such scaling method is using only parameters obtained directly from the experiment. The scaled conductivity–frequency dependencies are presented in figure 5. The AC conductivity axis is scaled by the respective bulk DC conductivities, while the frequency axis is scaled by the product of temperature and bulk DC conductivity. The scaled data superimpose into a single master curve in the temperature range 293–473 K and no changes in the shape of the isotherms below and above the phase-transition temperature are observed. It means that the conductivity obeys the time–temperature superposition principle, as the spectral shape is independent of temperature. However, in the measured AC conductivity spectra we can easily distinguish three parts of the scaled conductivity. At the highest temperatures, especially above the superionic phase transition, we observe deviation from the expected shape of the master curve. In the measured frequency window the AC conductivity in a wide frequency range is lower than the bulk conductivity of the RHSe crystal due to the polarization effect of electrodes (see figures 3 and 4). This characteristic feature of ion conducting materials [51] causes the scattered tail at the left end of the plot in figure 5.

Next, a wide frequency and temperature independent plateau is observed on the master plot, where the measured AC conductivity is equal to the bulk DC conductivity. At the right end of the scaled spectra (at the highest frequencies), a crossover into the dispersive region occurs, in which the conductivity increases with frequency. This part of spectra is observed in the lowest temperature range where $\sigma_{bulk}$ can still be calculated. Scaling procedure was performed for the data at $T > 293$ K. For lower temperatures calculations were not possible as the DC conductivity could not be estimated due to the too high resistivity of the RHSe crystal.

The created curve in figure 5 indicates superposition of the frequency characteristics of conductivity and suggests a temperature independent conductivity (relaxation) mechanism [52, 53], i.e. proton migration in the whole temperature range. This mechanism can be explained by the linear response theory [49, 54, 55]. Within the framework of this theory, the frequency-dependent electrical conductivity can be directly related to the time-dependent displacements of the mobile ions in the thermal equilibrium and absence of the electric field [55]. The Summerfield scaling transforms directly into the following law [55]:

$$\langle r^2(t) \rangle = G(\sigma_{dc}, T, t),$$

where $G$ is the temperature independent scaling function, and $\langle r^2(t) \rangle$ is the time-dependent mean-square displacement of the mobile ions. The characteristic time window, in which the transition from a long range diffusion of ions to the fast but localized motion takes place, is temperature dependent. Temperature changes of the AC conductivity spectra are responsible only for the shift in the time scale (frequency). The frequency, at which the crossover between the diffusive, long-range motion of the charge carrier and the localized behaviour takes place, is temperature dependent.

Our recent studies have revealed the similar universal conductivity behaviour also in organic proton conductors that do not undergo structural phase transitions [25, 27]. The proton hopping process in these conductors is strictly caused by the thermal activation of charge carriers. Mechanism of the proton transfer through the sample in both phases can be well described within the Grotthuss model [27]. Shape of the calculated master curve of benzimidazolium azelate [25] and imidazolium malonate [27] is the same as for the RHSe crystal. Even though the hydrogen bond network changes from the ordered to disordered one [44], no changes in the shape of the master curve are observed. The small difference between the normal proton conductors and RHSe is observed only at the highest temperatures, where in the case of superprotonic conductors the measured low-frequency conductivity is not equal to the bulk DC conductivity.

Figure 5. Scaled frequency dependences of the RHSe AC conductivity obtained using Summerfield scaling (first universality). Data were collected during cooling for both the ferroelastic phase II ($T < 453$ K) and superionic phase I ($T > 453$ K).

\[\text{ Diagram of conductivity spectra }\]
Similar universal response was also observed in another superprotonic conductor (NH$_4$)$_3$H(SO$_4$)$_2$ [28] that also undergoes a superionic phase transition. It shows that despite the existing differences in the structures, the scaling procedure and the universal frequency behaviour of the conductivity spectra is well applicable to the case of superprotonic conductors. It is worth to notice that in the RHSe single crystal at higher frequencies, no additional contribution has been observed than that from the mobile protons. Additional conductivity contribution was, however, observed in (NH$_4$)$_3$H(SO$_4$)$_2$, caused by the polar ammonia groups [28]. However, in (NH$_4$)$_3$H(SeO$_4$)$_2$ superprotonic conductor first universality of conductivity was not observed, due to existence of unique low conducting, ferroelastic phase III of symmetry (P1) [56]. This phase is unstable and under sufficient high pressure disappears [56].

At lower temperatures, $T < 280$ K, the conductivity contribution of the thermally activated proton dynamics is rather low so that the DC conductivity cannot be estimated within the studied frequency window.

4. Conclusions

The detailed studies of superprotonic conductor RHSe has been carried out using broadband dielectric/impedance spectroscopy. Study of the electrical properties of the superprotonic RHSe crystal along the c axis enabled us a separation of the contribution of the interfacial electrode polarization layers from the bulk electrical properties. The bulk DC conductivity was evaluated above room temperature. The phase transition to the superprotonic phase, which occurs at $T_S \sim 453$ K, was shown to be connected with the steep but almost continuous increase in the bulk DC conductivity and giant permittivity effects due to enhanced proton hopping and interfacial electrode polarization layers. The phase transition is caused by structural reorientation from monoclinic unit cell with space group $C2/c$, characteristic for low temperature ferroelastic phase, to rhombohedral space group $R3m$. The latter belongs to high-temperature superprotonic (paraelastic) phase.

The AC conductivity scaling analysis, performed using Summerfield scaling method, has shown that the master curve is not disturbed by the structural phase transition ($T_S \sim 453$ K) and the first universality criteria are satisfied. The same shape of master curve is observed for scaled data measured at wide temperature range, from 473 K down to 280 K, that covers superionic and ferroelastic phases. Below 280 K the DC conductivity cannot be estimated within the measured frequency window. On the other hand, at low temperatures, although AC conductivity decreases drastically with temperature, the dielectric loss is still weakly frequency dependent, therefore the NCL effect (second universality) is not obeyed. We conclude that the bulk (intrinsic) dielectric properties, AC and DC conductivity of the RHSe crystal are caused by the thermally activated proton hopping (up to 1 GHz at least). The observed increase in the AC conductivity above 100 GHz could be assigned to the low-frequency wing of the proton vibrational modes.

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