# Dielectric relaxation of CsHSeO$_4$ above room temperature

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## ARTICLE INFO

## ABSTRACT

Dielectric measurements of CsHSeO$_4$ show a distinct relaxation at low frequencies at several isotherms ($T<363$ K). For example, the relaxation frequency is around 4 kHz at 323 K and increases to higher frequencies (~100 kHz) as the temperature increases. The relaxation has an activation energy of 0.8 eV, which is in close agreement with that associated with transport of charge carriers. We suggest that the observed dielectric relaxation could be produced by the H$^+$ jump and SeO$_4^{-2}$ reorientation that cause distortion and change the local lattice polarizability, inducing dipoles like HSeO$_4^-$.

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## 1. Introduction

Cesium hydrogen selenate (CsHSeO$_4$) belongs to the family of hydrogen bonded compounds with a general formula MHXO$_4$, where M = NH$_4^+$, Rb$^+$, Cs$^+$, K$^+$ and X = S, Se. These compounds show high temperature phase transition phenomena that have been investigated by several researchers. This family forms an interesting group of materials characterized by the presence pattern of hydrogen bonding between the HXO$_4^-$ tetrahedral ions [1]. These bonds are also responsible for the ferroelectric phase transition found in ammonium and rubidium hydrogen sulphates [2,3]. They offer the possibility of studying proton behavior. The CsHSeO$_4$ is a solid electrolyte that exhibits a superionic protonic conduction behavior above $T_c = 401$ K [4–7]. The first order phase transition is accompanied by a strong conductivity increase, by four orders of magnitude, which essentially originates from proton diffusion [8–11].

Research has been devoted to understand the dynamics of ionic transport in ionically conducting materials. Most research activity in this field has focused on the origin and properties of the ion motions, and electrical relaxation is the most commonly used experimental tool to access the ion dynamics.

Experimentally, complex impedance methods have successfully been used to measure the ac conductivity of liquid and solid electrolytes in the low frequency range, typically from 0.1 Hz to 1 MHz, in which the conductivity spectra is frequently dominated by "long range" charge motions depending on temperature which is a determining parameter in conduction phenomena. Measurements of

the dielectric properties up to the GHz range [12–14] can reveal dielectric relaxations associated with local motions (reorientations, ion jumps). Badot and Colomban [14] have investigated relaxation phenomena in acid sulphates and selenates (CsHSO$_4$, CsHSeO$_4$, CDSeO$_4$ and NH$_4$HSeO$_4$) using broad band dielectric measurements. As one of their main results, they found relaxations at about 50–100 MHz and 20 GHz at 300 K in all samples. They assigned these relaxations to proton transfer and to HSeO$_4^-$ reorientation, respectively, in agreement with the Colomban–Novak classification [15]. They also observed that substitution of Cs$^+$ ions by NH$_4^+$ introduces a new very slow relaxation in the 3–10 MHz range. They argue that regular NH$_4^+$ ions do not have a permanent strong dipole moment, but distortion can induce a dipole and thus, this relaxation can correspond to a reorientation or local jump.

Our research team [16–19] observed that the dielectric response of MH$_2$PO$_4$ (M = K$^+$, NH$_4^+$) and L$_2$SO$_4$ (L = K$^+$, Cs$^+$), reveals a dielectric relaxation at low frequency, for example for K$_2$SO$_4$ around $1.4 \times 10^4$ Hz at 403 K, which shifts to higher frequencies (~10$^6$ Hz) as the temperature increases. We have suggested that this dielectric relaxation could be due to the proton jump and phosphate or sulphate reorientation that causes distortion and changes the local lattice polarizability inducing dipoles like H$_2$PO$_4^-$ in MH$_2$PO$_4$ (M = K$^+$, NH$_4^+$) and like LSO$_4^-$ in L$_2$SO$_4$ (L = K$^+$, Cs$^+$, respectively). Also, we observed that the substitution of NH$_4^+$ instead of K$^+$ only shifts the characteristic relaxation frequency, $f_{max}$, to slightly higher values.

The aim of our work is to obtain more insight into the low frequency dielectric behavior of CsHSeO$_4$, in which the rotation of the HSeO$_4^-$ radicals has been claimed to be important. If the complex permittivity representation of measured dielectric data is used, the real and imaginary parts ($\varepsilon'$ and $\varepsilon''$) are dependent on each other as inferred from the Kramers–Kronig relations [20]. Such relations

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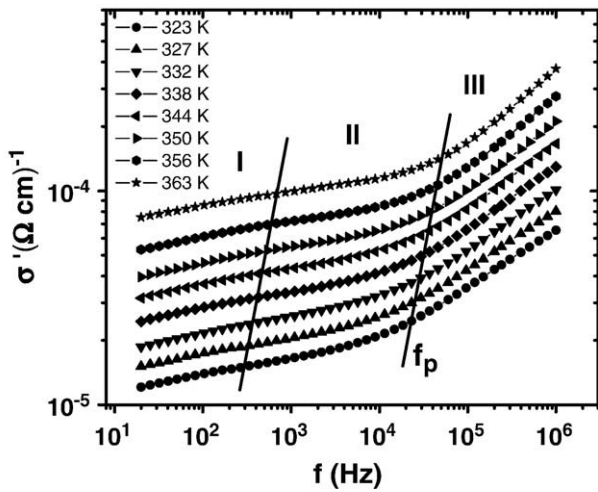 *E-mail address:* oscarche@univalle.edu.co (O. Checa).

**Fig. 1.** Frequency dependence of the real part of the conductivity for CsHSeO$_4$ at several temperatures.

evidence the correlations between dispersion (variation of $\varepsilon'$ as a function of frequency) and absorption (non-zero value of $\varepsilon''$): any dielectric dispersion is accompanied by an absorption peak. The real and imaginary part of the complex permittivity, $\varepsilon^*$, can be determined from measured impedance data since

$$\varepsilon' = -\frac{Z''}{\omega C_0 (Z'^2 + Z''^2)} \tag{1}$$

$$\varepsilon'' = \frac{Z'}{\omega C_0 (Z'^2 + Z''^2)} - \frac{\sigma_0}{\omega \varepsilon_0} \tag{2}$$

where $\omega = 2\pi f$ (Hz) is the angular frequency, $C_0$ is the capacitance of the empty sample cell, $\sigma_0$ is the dc-conductivity while $Z'$ and $Z''$ are the real and imaginary part of the impedance. The last term in Eq. (2) results from the definition of the complex conductivity by the relation $\sigma^*(\omega) = \sigma'(\omega) + \sigma_0 + i\sigma''(\omega) = i\omega\varepsilon_0\varepsilon^*(\omega)$, where the real component includes the "true dc" conductivity, then, the "dielectric" components are given by $\sigma'(\omega) = \omega\varepsilon_0\varepsilon''(\omega)$ and $\sigma''(\omega) = \omega\varepsilon_0\varepsilon'(\omega)$. Since $\varepsilon'(\omega)$ is correlated with polarization and $\varepsilon''(\omega)$ with energy losses, then, the dielectric loss contribution due to displacement of charge (last term in Eq. (2)) makes it difficult to detect dielectric relaxations due to dipolar processes in ionic conductors at low frequency. Even if the corrective term in Eq. (2) is properly used, this becomes particularly evident in the present situation in which both terms in Eq. (2) become large at
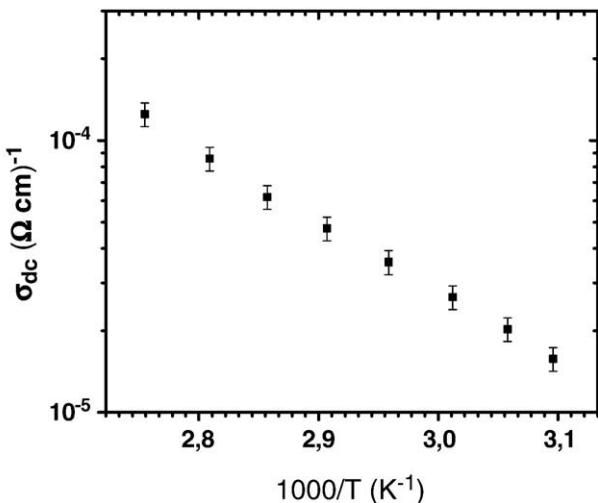
low frequency since $\varepsilon''(\omega)$ is determined by subtracting the two. We report here the results of dielectric relaxation measurements for polycrystalline CsHSeO$_4$ in the 1 Hz to 1 MHz frequency range.

## 2. Experimental

The electrical measurements were performed using a two-electrode configuration. The polycrystalline CsHSeO$_4$ samples were grown from an aqueous solution of Cs$_2$CO$_3$ and HSeO$_4^-$ by slow evaporation. Cylindrical pellets 0.5 mm thick were prepared for electrical measurements. Platinum electrodes (with diameter 5 mm) were painted at both faces. Impedance spectroscopy measurements were performed by using a LCR meter HP 4284A, in the frequency range 100 Hz–1 MHz, and varying temperature between 320 K and 400 K.

## 3. Results and discussion

Fig. 1 shows the frequency dependence of the real part of the ac conductivity, $\sigma'(\omega)$, at several temperatures for the samples under study. As is expected, we observe an increase of the conductivity as the temperature increases. We distinguish three dispersive regions with
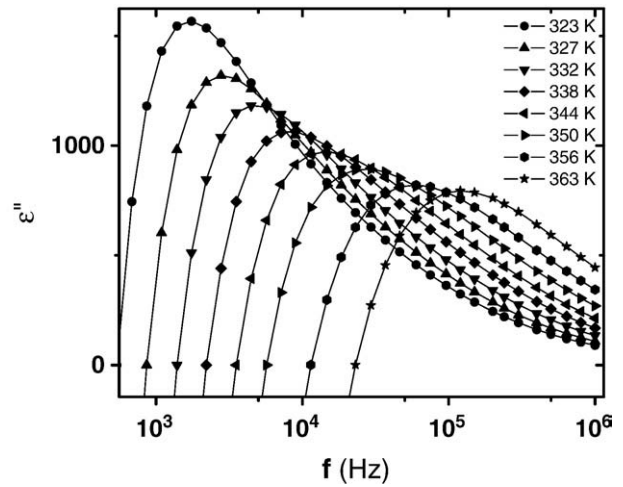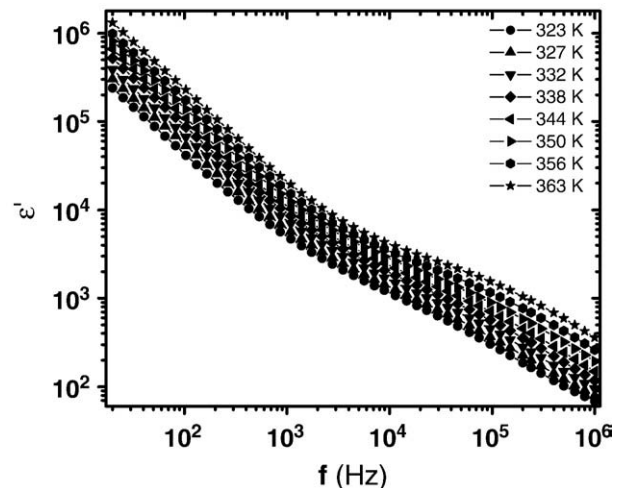


**Fig. 3.** Corrected imaginary part of the relative permittivity (after subtracting the dc-conductivity contribution), $\varepsilon''(\omega, T)$, as a function of frequency at several isotherms.



**Fig. 2.** Arrhenius plot of "near dc" conductivity for the sample CsHSeO$_4$, between 320 K and 363 K, during a heating run. $\sigma_{dc}$ was calculated as discussed in the text.



**Fig. 4.** Real part of the permittivity $\varepsilon'(\omega, T)$ as a function of frequency at several isotherms (323 K<$T$<363 K) for CsHSeO$_4$.
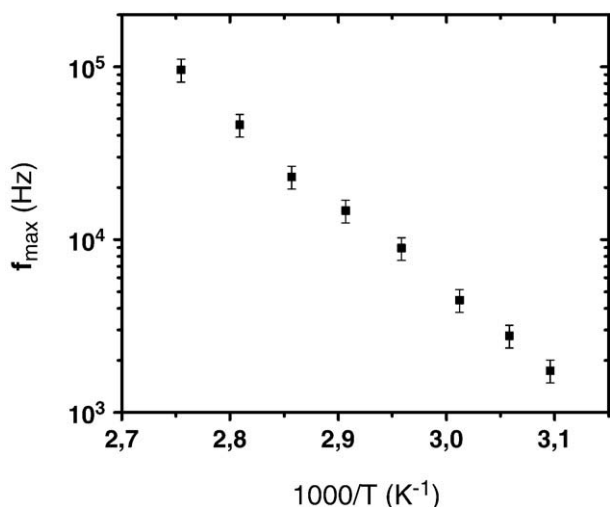
**Fig. 5.** Temperature dependence of $f_{max}$ (taken from $\varepsilon''$ representation), plotted as $f_{max}$ vs. $1/T$ for CsHSeO$_4$.

increasing frequency: a low-frequency region I, which corresponds to the electrode blocking effects as a consequence of transfer of charge across the electrode/sample interface. An intermediate-frequency region II, where the conductivity increases less gradually with increasing frequency, i.e., it is not quite direct current (dc) conductivity, as it is frequently seen in other ion-conducting materials [21], that may correspond to volume low frequency dispersion (LFD) processes [22]. In general, LFD behavior is seen in dielectric systems at low frequencies, in which the ionic carrier responses predominate over the more conventional dipolar effects which ultimately dominate at high-frequency processes. This brings us to the question of the "true dc" component $\sigma_0$ to be used in Eq. (2), which, in principle, is dominant at sufficiently low frequencies. The question whether this dc component is experimentally separable from any LFD component is open to debate [22], however, being the "long range" ionic hop the principal transport element in LFD, it is expected that the conductivity data in this region is very similar to "true dc" in its activation energy and the magnitude of conductivity associated with it. The high-frequency region III is a more rapidly rising branch which begins at a characteristic frequency $f_p$ that increases with increasing temperature.

The temperature dependence of the "near dc" conductivity data calculated at the starting point of region II (see Fig. 1) is plotted in Fig. 2 as a function of reciprocal temperature of the sample CsHSeO$_4$. An Arrhenius-type activation process is clearly seen and the activation energy was calculated as 0.6 eV.

The imaginary part of the relative permittivity after subtracting the "near dc" conductivity contribution, $\varepsilon''(\omega)$, is shown in Fig. 3 as a function of frequency at several isotherms. A broad peak is observed at low frequencies, for example, at 323 K the peak frequency is $1.7 * 10^3$ Hz. The peak shifts to higher frequencies and the peak height decreases as the temperature increases as expected for a dipolar relaxation.

Fig. 4 shows the frequency dependence of the real part of the permittivity $\varepsilon'(\omega)$ plotted in log–log plots at various isotherms. It is clear the correlation between the absorption peak observed in the imaginary part of the permittivity data, $\varepsilon''(\omega, T)$ (Fig. 3), and dispersion (step change) in its real part $\varepsilon'(\omega, T)$. Thus, this observation in the dielectric response of CsHSeO$_4$ in the operating frequency and temperature ranges can be interpreted in terms of polarizing processes as discussed below.

The peak frequency, $f_{max}$, for CsHSeO$_4$ sample (taken from $\varepsilon''$ representation) as a function of inverse temperature is shown in Fig. 5. The figure shows that for the sample there is an activated relaxation process (Arrhenius-type) in the temperature range 323–363 K with an

activation energy, $E_a = 0.8$ eV, close to the value obtained from the ionic conductivity for the same temperature range (see Fig. 2). This type of low frequency relaxations has to our knowledge not been studied in detail earlier for the CsHSeO$_4$ compound. The relaxation frequencies that we have measured are even lower than that reported for the low frequency relaxation observed by Badot and Colomban [14] in NH$_4$HSeO$_4$. In that case the relaxation was assigned to a reorientation of NH$_4^+$ ions since the ammonium reorientations and the proton displacement may change the local lattice polarizability. According to the Colomban–Novak classification [15], the proton transfer and the HXO$_4^-$ reorientation take place for frequencies at around 50 MHz and 20 GHz respectively. However, proton dynamics at temperatures below the superprotonic transition (phase II) of CsHSO$_4$ [23,24] studied by proton NMR have revealed that the SO$_4^{-2}$ reorientation is in a time scale of $10^{-4}$ s around 300 K and that this correlation time is claimed to obey the Arrhenius relation. The inverse of this correlation time is of the same order as the relaxation frequencies that we have measured in phase II of CsHSeO$_4$.

Based on the above findings on acid selenates and sulphates and our results for MH$_2$PO$_4$ (M = K$^+$, NH$_4^+$) and L$_2$SO$_4$ (L = K$^+$, Cs$^+$), we suggest that, when the temperature of CsHSeO$_4$ is increased, the hydrogen bonds become progressively weaker allowing proton jumps between sites and selenates tetrahedra partial rotations causing distortion and changing of the local lattice polarizability inducing dipoles. Thus a configuration such as HSeO$_4^-$ may be formed and the observed relaxation can correspond to H$^+$ local jumps or SeO$_4^{-2}$ reorientation. As a result of lattice polarizability, we do believe that this kind of relaxation may occur in CsHSeO$_4$ at lower frequencies.

## 4. Conclusions

In summary, the permittivity data for CsHSeO$_4$ clearly show a very slow dielectric relaxation, at around $10^3$ Hz, and shifting to higher frequencies (~1 MHz) as the temperature increases. We suggest that, on increasing the temperature of CsHSeO$_4$ above 323 K, the hydrogen bonds become progressively weaker such that the protons start to jump from one site to another site and the selenate tetrahedra adopt new reorientations that cause distortion and change the local lattice polarizability inducing dipoles. Thus configurations such as HSeO$_4^-$ may be formed resulting in a dielectric relaxation at lower frequencies. The relaxation frequency is thermally activated with an activation energy $E_a = 0.8$ eV which is in close agreement with that associated with transport of charge carriers.

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