

Dielectric Response of Holmium Formate Crystallohydrate at 100mHz–10MHz

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The dielectric response of Holmium formate crystallohydrate was studied in the frequency range of 10^{-1} – 10^7 Hz at 20–70°C. Experimental data were analyzed within formalisms of dielectric permittivity, conductivity and dielectric modulus. Specific features of dielectric properties and conductivity which were detected are typical for crystallohydrates and ferroelectrics with hydrogen bonds. It is assumed that such anomalies are caused by changes in the dynamics of protons that participate in hydrogen bonds in the crystal structure.

Keywords Crystallohydrate; dielectric spectroscopy; hydrogen bonds

1 Introduction

The temperature and frequency dependencies of electrical parameters (dielectric permittivity ϵ' , dielectric loss ϵ'' , loss tangent $\tan\delta$, conductivity σ , dielectric modulus M'') have the same features in compounds with various chemical and structural organizations which have hydrogen bonds or hydrogen-containing groups. The relaxation behaviour of ϵ' , ϵ'' , and $\tan\delta$ of crystallohydrates, polymers, and hydrogels with OH...O hydrogen bonds that are 0.26–0.29 nm in length were discussed in our previous papers [1–4]. The same bond is in ice and water, which means that many materials, including biopolymers with water, can exhibit such an abnormal behavior of these parameters.

In the present work we investigated dielectric properties of Holmium formate crystallohydrate in frequency range of 10^{-1} – 10^7 Hz at 20–70°C. Measurements of ϵ' and $\tan\delta$ allow to get many other parameters: conductivity σ , dielectric modulus M'' , which make it possible to make assumptions about relaxation time spectrum, conductivity mechanism, nature of charge carriers, and allow to draw conclusions about nature of temperature anomalies (phase and relaxation transitions).

Relaxation transitions in crystals are associated with their structural disorder, and it is typical of them to have stochastic and probabilistic behavior and multifractal universality of dielectric properties.

Holmium formate $\text{Ho}(\text{HCOO})_3 \times 2\text{H}_2\text{O}$ has two hydrogen bonds (2.81–2.97 nm in length) per molecule [5]. The space group of formates is $P2_12_12_1$; there are 3 formula units in the unit cell. The hydrogen atom of the formate group does not form a hydrogen bond with any of the

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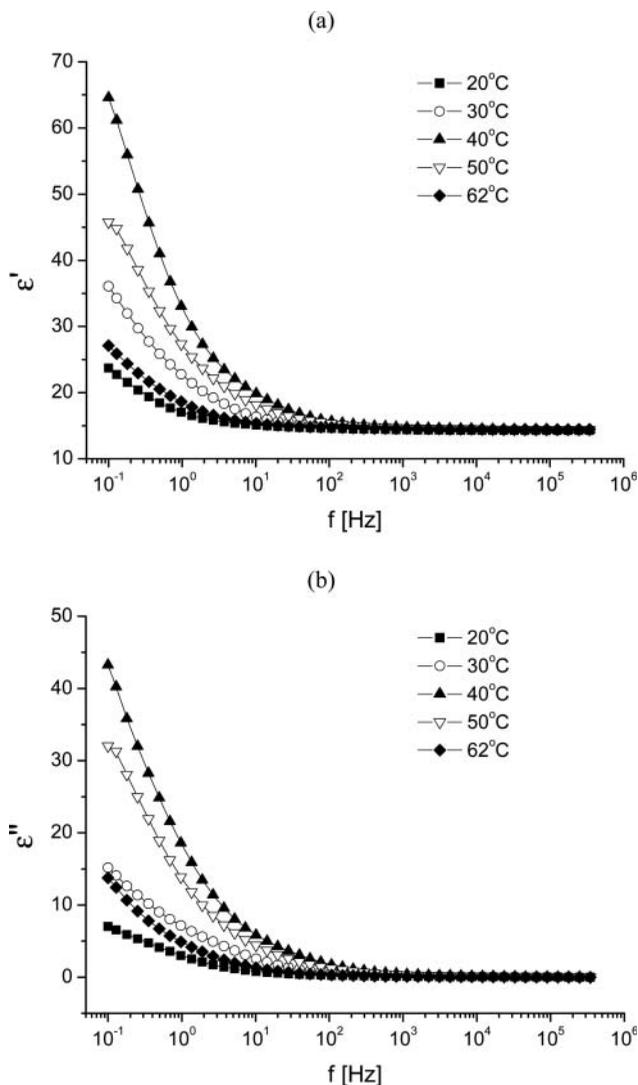


Figure 1. The measured real (a) and imaginary (b) parts of complex dielectric permittivity versus frequency for holmium formate at temperatures indicated on the plot.

crystal oxygens. The hydrogen atom of the water molecule is included in hydrogen bonds of water oxygens and the oxygens of formate ions. Water loss of formate crystallohydrates is observed at 140°C – 160°C [5]. Previous investigations of conductivity of Holmium formate showed that at heating from 20 to 70°C there is anomaly at 40 – 45°C on $\ln(\sigma T)(1/T)$ dependence [6]. In our previous papers we reported on dielectric properties of Yttrium [7] and Erbium [8, 9] formates. Formates are used in quantum electronic devices at 0.25 – $1.45\mu\text{m}$.

2 Experimental

Dielectric measurements were performed on a broadband Novocontrol Concept 40 spectrometer in frequency range of 10^{-1} – 10^7 Hz at 20 – 70°C . Temperature steps were 2 – 3° and temperature stabilization time was 10 min.

The sample was 0.5 mm thick and had 11 mm^2 silver paste electrodes.

3 Experimental Results and Discussion

Frequency dependencies of real ε' and imaginary ε'' parts of complex dielectric permittivity for Holmium formate are presented on Fig. 1. Frequency dependencies of ε'' at each temperature were approximated using the following expression:

$$\varepsilon^*(\omega) = \varepsilon' - i\varepsilon'' = i \frac{\sigma_0}{\varepsilon_v \omega^N} + \frac{\Delta\varepsilon}{[1 + (i\omega\tau)^\alpha]^\beta} + \varepsilon_\infty, \quad (1)$$

where the first term describes the relaxation of mobile charges, and the second term is the empirical Havriliak-Negami function [10] describing single relaxation process. Here $\Delta\varepsilon = \varepsilon_0 - \varepsilon_\infty$ is the relaxation strength (ε_0 and ε_∞ are the low- and high-frequency limits of the real part of dielectric permittivity ε'), $\omega = 2\pi f$ is the angular frequency of the electric field, α and β ($0 \leq \alpha, \beta \leq 1$) are parameters describing width and asymmetry of distribution of relaxation times respectively, τ is the relaxation time, σ_0 is dc conductivity, $0 \leq N \leq 1$ is the exponential factor, ε_v is the dielectric permittivity of vacuum.

The example of separation of dielectric spectra into relaxation process (curve 1) and conductivity (curve 2) according to (1) is showed on Fig. 2 for 30°C. We attribute the relaxation process to relaxation of OH...O bond in water molecules.

Figure 3 demonstrates several Cole-Cole plots for number of temperatures. One can see from the figure that the data at low frequencies show linear dependence. This means that we observe here the Universal Linear Low-Frequency Dispersion which is typical for wide class of dielectrics containing OH...O hydrogen bonds (2.6–2.9 nm in length) and many other isolators with ionic conductivity: Erbium and yttrium formates, ferroelectrics

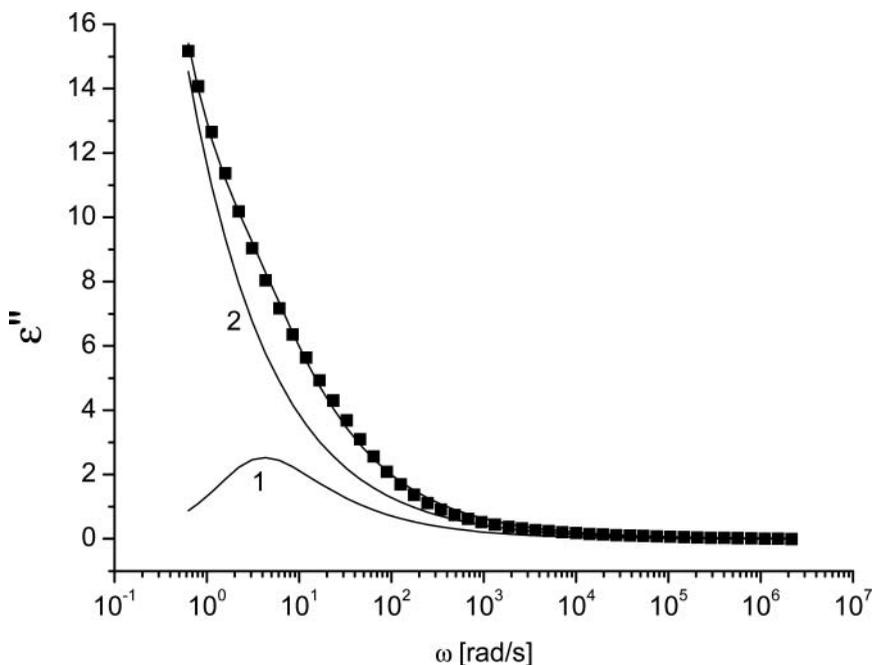


Figure 2. Example of fitting of dielectric loss of Holmium formate at 40°C. The lines marked 1 and 2 are Havriliak-Negami and conductivity terms (Eq. 1), respectively.

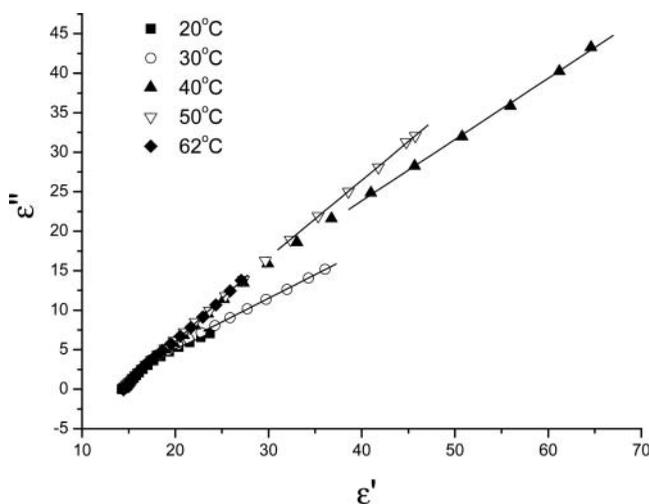


Figure 3. Cole-Cole plots for holmium formate at temperatures indicated on the plot. Solid lines indicate the region of Linear Low-frequency Dispersion.

triglycine sulphate, triglycine selenate, colemanite, VDF/TrFE copolymers, epoxy resin and other [6–9, 12].

Figure 4 shows double-logarithmic plot of frequency dependence of conductivity $\sigma(f)$ for several temperatures for Holmium formate under application of electric field 20V/cm. It is clearly seen that experimental curve at each temperature can be divided into 3 regions each of them showing linear behavior (I, II, III), as indicated in the plot for 40°C. Within each region the conductivity can be approximated by $\sigma \sim \omega^s$, where s is the power parameter. Value of s is around 0.6 in low- (I) and high-frequency (III) regions, and around 0.4 at moderate frequencies (II). Such values of s indicate that the proton could be a charge carrier [13]. This means that hopping of charge carriers is realized in

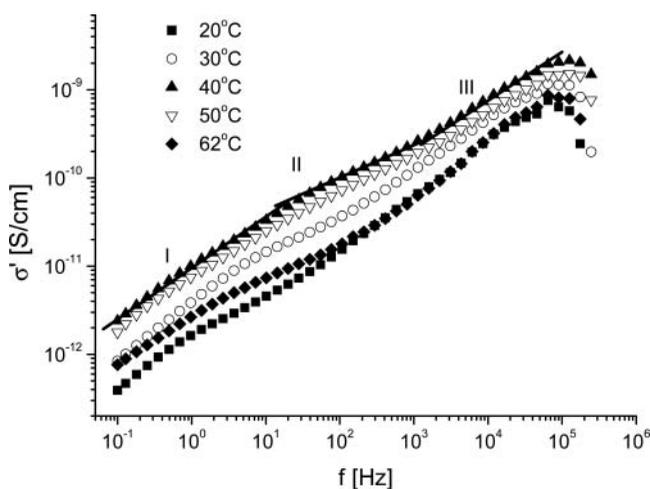


Figure 4. Frequency dependence of the conductivity for holmium formate at temperatures indicated on the plot.

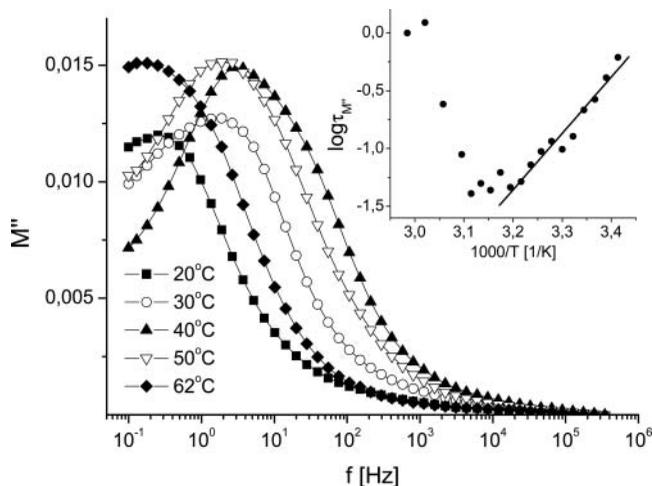


Figure 5. Frequency dependence of the imaginary part of electric modulus for holmium formate at temperatures indicated on the plot. At the insert: Arrhenius plot (semi-log scale versus the inverse temperature) of the characteristic relaxation time.

fractal space through cluster of localized sites, and the extension of this cluster is frequency dependent. When the frequency of the electric field increases, the cluster size becomes smaller and this increases the probability of charge carrier's scattering on defects.

In case of relaxation nature of conductivity it is convenient to use formalism of complex electric modulus: $M^* = 1/\varepsilon^*$. Imaginary part of electric modulus, M'' , “transforms” the ionic conductivity contribution, which leads to low-frequency increase of ε'' , into so-called “conduction” peak. The frequency position of this peak f_σ is related to the value

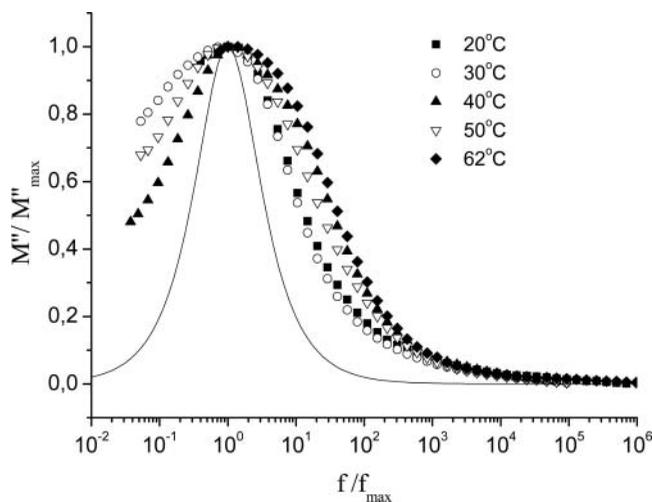


Figure 6. Peaks of imaginary part of electric modulus (data from fig. 4) for holmium formate normalized by frequency and amplitude for several temperatures indicated on the plot. The solid line is the Debye peak.

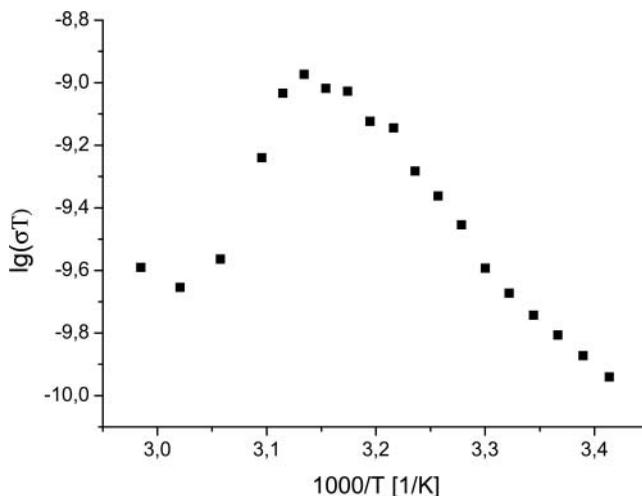


Figure 7. Dependence of $\lg(\sigma T)$ (for 0.1 Hz) on the inverse temperature for holmium formate.

of dc conductivity σ_{dc} according to Barton-Nakajima-Namikawa relationship $f_{\sigma} \sim \sigma_{\text{dc}}$ [14–17]. Fig. 5 shows several $M''(f)$ peaks for different temperatures for Holmium formate. Temperature dependence of the relaxation time (τ), calculated from the frequency position of $M''(f)$ peak, is shown in Arrhenius coordinates at the insert to Fig. 5. We see here that below $\sim 40^\circ\text{C}$ there is activation behaviour, which was analyzed using the Arrhenius relationship $\tau = \tau_0 \exp(E/kT)$, where E is the activation energy, k is the Boltzmann constant. The value obtained for E was 0.94 eV, which confirms the hypothesis about the proton hopping conduction.

Figure 6 demonstrates $M''(f)$ peaks normalized by frequency and amplitude for several temperatures. As seen, the peak is two–three times wider than the Debye peak, but its shape does not change with temperature.

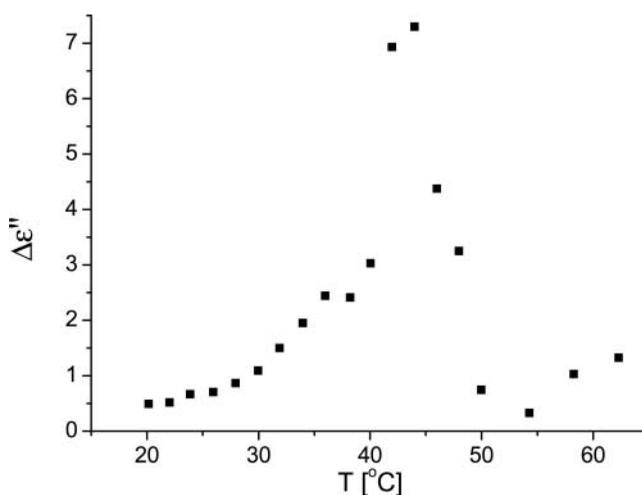


Figure 8. Temperature dependence of $\Delta\epsilon'' = \epsilon''_{0.1\text{Hz}} - \epsilon''_{0.13\text{Hz}}$ for holmium formate.

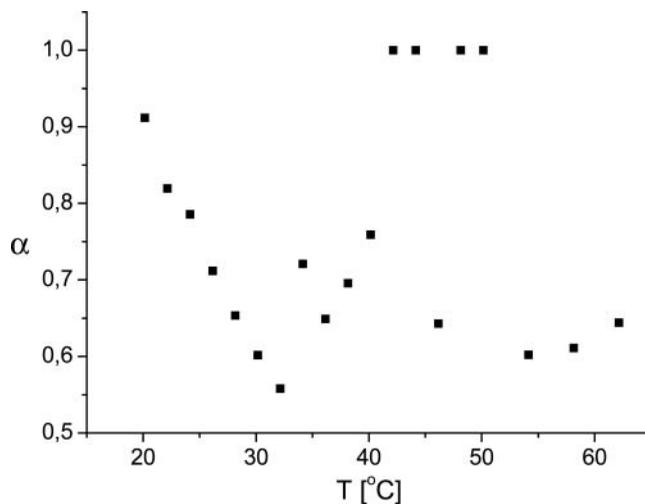


Figure 9. Temperature dependence of shape parameter α (Eq. 1) for holmium formate.

The shape of $M''(f)$ peak is often considered to be related with peculiarities of ionic conductivity [13–15]. Broadening of the peak in relation to the Debye peak may be due to the non-exponential processes, or to structure heterogeneities or nonequilibrium states of matter. The latter may cause spatial distribution of local heterogeneities and relaxation times [17], as well as potential barriers.

Using the experimental data shown on Figs. 2, 3, 6 we can obtain the following “universal” dependencies: $\ln(\sigma T)(1/T)$ (Fig. 7), temperature dependence of $\Delta\epsilon'' = \epsilon''_{0.1\text{Hz}} - \epsilon''_{0.13\text{Hz}}$ (Fig. 8) which describes so called “memory effect” – non-marcovian relaxation at very low frequencies, temperature dependence of shape parameter α from Eq. 1 (Fig. 9). These figures (7–9) demonstrate typical feature: there are anomalies on temperature dependences in the region of 40–50°C. Such anomalies have been previously detected on crystals upon heating after sharp (20°/min) cooling down to $-20\div-60^\circ\text{C}$: colemanite [1,2], diglycine nitrate [1], triglycine tellurate [3].

We suggest two possible mechanisms of this behavior. First is re-filling of proton levels, because our experiments showed broadening of relaxation time spectrum and change of potential barrier (Fig. 5). The second possible mechanism needs further investigations: it may be related to the phase transition in water and other compounds containing oxygen and hydrogen – ortho-para transition [18, 19].

4 Conclusion

As the result of investigations of dielectric dispersion of Holmium formate it was determined that the following “universal” dependencies hold: linear dispersion, hopping proton conductivity, non-Debye relaxation time spectra at frequencies 0.1–10⁷ Hz. The experimental data were analyzed with the help of complex electric modulus formalism. The anomalies on temperature dependencies of $\ln(\sigma T)$, $\Delta\epsilon''$ and α that were detected in the region of 40–50°C are related to broadening of relaxation time spectra or ortho-para transition in water molecules.

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