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Generalized Mittag-Leffler relaxation of $NH_4H_2PO_4$: Porous glass composite

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ABSTRACT

In this paper the dielectric spectroscopy data of ammonium dihydrogen phosphate $NH_4H_2PO_4$: porous glass composite was studied at various temperatures. It was found that the investigated material exhibits the two-power-law relaxation pattern with the low- (m) and high-frequency (n-1) exponents satisfying the relation $m<1-n$, where $0<m, n<1$. Such a relaxation behavior belongs to the class of less typical ones and cannot be fitted by any of the well-know empirical relaxation functions. In order to explain the relation between the power-law exponents of the studied sample we utilize a new relaxation function, recently derived (Stanislavsky et al. (2010) [1]) in the framework of the relaxation diffusion scenario.

1. Introduction

The potassium dihydrogen phosphate (KDP) family compounds are one of the most extensively studied hydrogen-bonded ferroelectric crystals. This is due to the fact that these materials can exhibit either ferroelectric or antiferroelectric properties [2].

Impedance spectroscopy measurements performed on the $K_2H_2PO_4$ crystals revealed the presence of a slow dielectric relaxation process at around 10^4 Hz at T = 403 K which shifts to higher frequencies with increasing temperature [2]. The relaxation behavior of $K_2H_2PO_4$ was explained assuming proton jumps and phosphate reorientation resulting in a change of the local lattice polarizability inducing HPO_4^- dipoles [3,4]. Measurements of the dielectric responses performed for acid sulfates and selenates ($CsHS0_4$, $CsHSeO_4$, $CsDSeO_4$ and $NH_4H_2SeO_4$) [5] showed maxima peaks at 50–100 MHz and 20 GHz for T = 296 K. Similarly, these relaxation processes were associated to proton transfer and HXO_4^- groups reorientation.

Ammonium dihydrogen phosphate $NH_4H_2PO_4$ (ADP) crystals, which are subject of this study, have a wide range of applications due to their non-linear optical, piezoelectric, antiferroelectric and electro-optical properties. In the paraelectric phase of ADP is isomorphous to $K_2H_2P0_4$ (KDP) but below the phase transition temperature (T_p = 148 K [6]) ADP, on the contrary to $K_2H_2PO_4$ crystals, is antiferroelectric and the structure below T_p differs from that of the ferroelectric crystals [7–9]. For ADP crystals dielectric relaxation was observed at frequencies $1*10^5$ Hz at 343 K and stated to be shifted to $3*10^5$ Hz with increasing temperature. The activation energy was reported to be E_a = 0.55 eV which is in agreement with that of proton transport [4]. The relaxation process in $NH_4H_2PO_4$ is almost identical with KH_2PO_4. The only difference is that substitution of K^+ with NH^{4+} ions results in a shift of the peak frequency to higher values [4]. Therefore similar microscopic dipolar structure of ADP may be assumed.

In this paper we analyze the dielectric spectroscopy data obtained for the ADP crystals embedded into porous silica glasses with 160 nm average sizes of pores. We have found that the frequency-domain response of the studied sample exhibits the two-power-law relaxation pattern. However, it cannot be properly described neither by the Havriliak-Negami, Cole-Davidson nor Cole-Cole relaxation function. Our studies, based on relaxation scenario of the correlated-cluster systems [10–12] leading to the generalized Mittag-Leffler relaxation response, give insight into the microscopic origins of the power laws found experimentally. According to our best knowledge this is the first attempt to fit the experimental data collected for ADP samples by means of the theoretical function [1] which is physically justified.

2. Experiment

Preparation of the porous silica glasses was reported in details elsewhere (see Ref. [13,14]). Porous matrix was obtained with 160 nm average sizes of pores labeled PG160 (heated at 933 K).

Porous wafers with pores of dimensions $10\times10\times1$ mm^3 were soaked in saturated water ADP solution at 363 K for 3 h. Then the glass samples were heated at 493 K for 3 h to remove the absorbed water. The soaking and heating processes were repeated three times to improve filling efficiency which was about 90%. At the end mechanical polishing was used to remove microscopic ADP crystals from the porous glasses surface. The samples were labeled ADP-PG160 for ADP embedded into glasses of mean pores size of 160 nm.

Dielectric permittivity measurements were performed using Novocontrol Alpha impedance analyzer at frequency range from 1

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to 10^6 Hz. The dielectric measurements were carried out during cooling processes with the temperature rate of 1 K/min. All the data were automatically transferred into the PC for analyses.

3. Results

In Fig. 1 sample complex permittivity $\varepsilon^*(\omega)=\varepsilon'(\omega)-i\varepsilon''(\omega)$ plot obtained for the ADP crystals embedded into glass is presented in the Cole-Cole representation. It is known that for dipolar materials, relaxing in a manner similar to the classical Debye behavior, the $\varepsilon''(\omega)$ versus $\varepsilon'(\omega)$ plot approximates a semi-circle [15]. However, for the investigated material the complex plane representation revealed an asymmetric peak suggesting the non-Debye relaxation pattern.

In Fig. 2 the imaginary term of the complex permittivity $\varepsilon^*(\omega)$ is presented for the investigated temperature range. In Fig. 3 the normalized data corresponding to these in Fig. 2 are depicted. The normalization results in a master curve exhibiting a single maxima peak. Such a peak observed in the dielectric response of a sample is characteristic for dipolar systems [15,16]. This observation confirms the preliminary assumption of the dipolar structure of the analyzed composite. Moreover, the value of slope coefficient of linear fit to the low-frequency data (m) is smaller than the high-frequency one ($1-n$). This implies that interpretation of relaxation data obtained for the ADP-PG160 nanocomposite would require application of a new theoretical approach. This is due to the fact that such a relaxation response cannot be explained by means of 'standard' relaxation approaches [15,16].

The loss peak frequency ω_p (frequency corresponding to maximum value of imaginary part of dielectric permittivity) for the investigated sample as a function of the inverse of temperature is presented in Fig. 4. The figure reveals that for the analyzed nanocomposite of $NH_4H_2PO_4$ crystals there exists thermally activated Arrhenius-type process which possesses similar origin to the one observed in single crystals of ADP [4]. However, the value of activation energy $E_a=0,4$ obtained for the ADP-PG160 sample is smaller than the one reported for ADP ($E_a=0.55$ eV) [4]. This indicates that introduction of $NH_4H_2PO_4$ crystals into porous glass matrices may affect the dielectric properties of this material.

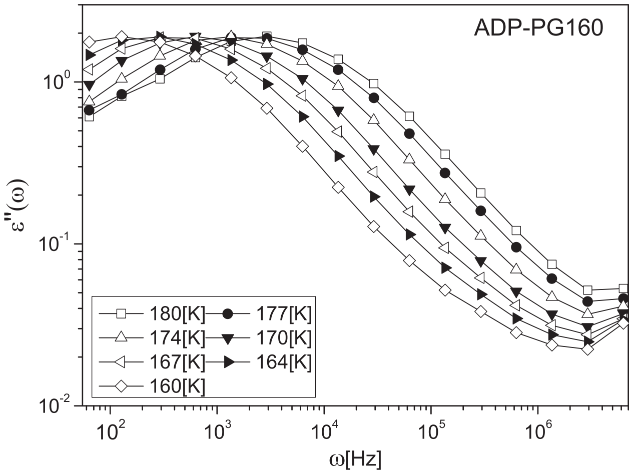

Fig. 2. Imaginary part of the dielectric permittivity of the ADP-PG160 measured at different temperatures (log-log scale).

4. Discussion

It is clear from the results presented above that the dielectric response of investigated ADP-PG160 is non-Debye one (cf. Fig. 1). Furthermore, it follows the anomalous relaxation mechanism [16] (cf. Fig. 3) represented by low- and high-frequency power-law dependence of the imaginary part of dielectric permittivity on frequency:

$$\begin{aligned}&\varepsilon''(\omega)\propto\left(\omega/\omega_p\right)^m \quad \text{for } \omega<\omega_p,\\&\varepsilon''(\omega)\propto\left(\omega/\omega_p\right)^{n-1} \quad \text{for } \omega>\omega_p,\end{aligned} \tag{1}$$

where ω_p denotes the loss peak frequency and $0<m,\ n<1$. It should be noted that for the investigated ADP-PG160 the power-law exponents satisfy the relation $m<1-n$. This property is a characteristic for the so called 'less typical' relaxation data which cannot be interpreted by means of the well-know Havriliak-Negami (HN) function [15,16]

$$\varphi^*_{HN}(\omega)=\frac{1}{\left[1+\left(i\omega/\omega_p\right)^{\alpha}\right]^{\gamma}},\quad 0<\alpha,\ \gamma<1 \tag{2}$$

yielding the opposite inequality $m\geq 1-n$. For a long time period to fit the less typical dielectric relaxation data $\varepsilon^*(\omega)=(\varepsilon_0-\varepsilon_\infty)\varphi^*(\omega)+\varepsilon_\infty$ (where ε_0 is the static permittivity and the constant ε_∞ represents the asymptotic value of dielectric permittivity at high frequencies), HN function with extended parameters range, i.e. $0<\alpha<1$ and $0<\alpha,\ \alpha\gamma<1$, was used. In this case, however, the HN formula can be used solely as a fitting function but none of the known relaxation models can justify the values $\gamma>1$ for the observed fractional two-power-law property [17,18]. Fortunately, progress in stochastic

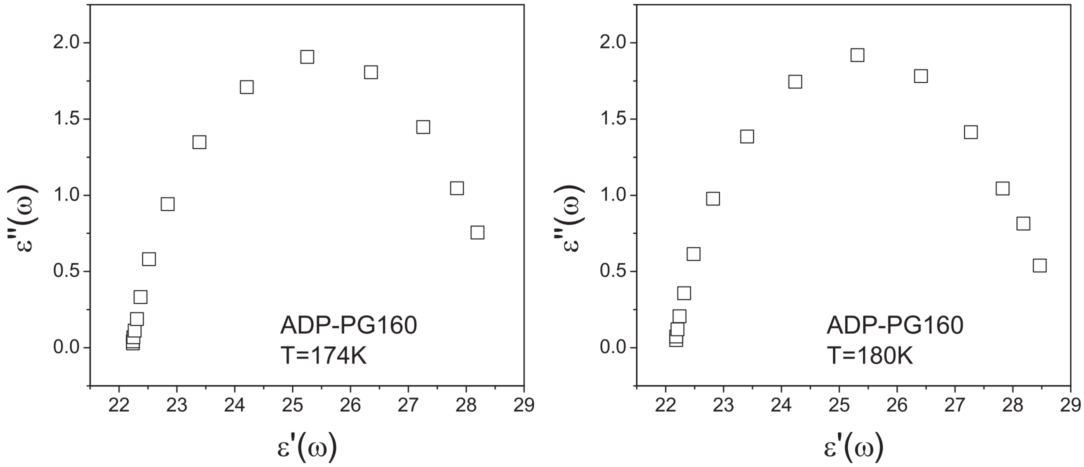

Fig. 1. The complex permittivity diagrams (Cole-Cole plots) for two different temperatures. The asymmetric peak is a fingerprint of the non-Debye relaxation response of the investigated sample.