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DIELECTRIC AND EPR MEASUREMENTS OF THE DEUTERATED
GLASS D-RADA $x = 0.46$

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Abstract The results of the complex dielectric permittivity measurements and the spin-lattice relaxation times of the deuterated glass D-RADA $x = 0.46$, by the dielectric and EPR techniques are reported. The transition from paraelectric to antiferroelectric phase is detected at $T_N = 162$ K. Below 90 K the dispersion of the complex dielectric permittivity was detected. The shape of the temperature dependence of the imaginary part of the dielectric permittivity was analyzed. This analysis shows the existence of two relaxation phases forming among the antiferroelectric domains, described by Arrhenius equation, and the glass state appears after the antiferroelectric ordering has been destroyed. The dielectric results are confirmed by the spin-lattice relaxation times data.

INTRODUCTION

The proton glass behavior in the mixed crystal of the formula $Rb_{1-x}(NH_4)_xH_2PO_4$ (RADP) was discovered by Courtens¹ in 1982. This captivating attention state of crystal in which the long-range order, characteristic for the ferroelectric (RbH_2PO_4) and antiferroelectric ($NH_4H_2PO_4$) crystals, disappears whereas a local short-range order within clusters start to arise, has also been discovered by Trybuła et al.² in 1986 in isomorphic mixed crystal $Rb_{1-x}(NH_4)_xD_2AsO_4$ (RADA). The dielectric measurements^{3,4} in RADA show an asymmetric phase diagram compared to that of RADP⁵, and the glass state in the RADA occurs for an ammonium concentration $0.13 \leq x \leq 0.49$. Deuteration leads to the narrowing of glass existence range to $0.2 \leq x \leq 0.35$ for $Rb_{1-x}(ND_4)_xD_2AsO_4$ (D-RADA)^{6,7}. Recent studies on proton and deuteron glass have revealed that the state of glass may coexist with the ferroelectric⁸⁻¹¹ or antiferroelectric¹¹⁻¹³ order. Our last paper¹³ has reported the first dielectric investigation of deuterated glass D-RADA

$x = 0.39$ in this interesting range between deuteron-glass and antiferroelectric order ("relaxor" range¹¹). We proved the existence of two phases of different mechanisms of relaxation, forming among the antiferroelectric domains.

To contribute to better understanding this coexistence range we present in this paper our dielectric and EPR investigation of the deuterated D-RADA $x = 0.46$.

EXPERIMENTAL METHODS

The D-RADA $x = 0.46$ crystal to be studied was grown from a solution of two components: $\text{ND}_4\text{D}_2\text{AsO}_4$ and RbD_2AsO_4 , taken at stoichiometric ratio in D_2O by the method of slow evaporation of D_2O in atmosphere of gas argon to eliminate the access of H_2O from the air. The concentration of ND_4 in the crystal, x , was ascertained from the number of rubidium ions determined by atomic absorption spectroscopy. The sample to be studied by the dielectrometric method, was cut out of the crystal along the a axis, its surfaces were polished and coated within silver paste electrodes. Dielectric measurements were carried out in a flow-through helium cryostat for temperature ranging from 4 to 300 K, by a GenRad RLC Digibridge model 1689M varying the electric measuring field frequency from 1 kHz to 20 kHz.

EPR measurements were carried out with a Varian X-band spectrometer operating with an Oxford liquid helium system in the temperature range from 4 to 300 K. To get the AsO_4^{4-} center the sample of D-RADA $x = 0.46$ to be EPR studied was irradiated by an x-ray source with a copper anode operating at 20 kV and 10 mA for 6 h.

RESULTS

Dielectric method

The temperature dependence of the real part of permittivity $\epsilon'_a(T, \nu)$ for the D-RADA $x = 0.46$ crystal is shown in Figure 1(a), where typical behavior attributed to the transition from paraelectric to antiferroelectric phase is clearly marked at $T_N = 162$ K. This antiferroelectric phase transition take place at the same temperature for different frequencies of the electric measuring field. The dispersion of the real $\epsilon'_a(T, \nu)$ (Figure 1(a)) and imaginary $\epsilon''_a(T, \nu)$ (Figure 1(b)) parts of electric permittivity above 170 K is related to electric conductivity σ of deuterons. The activation energy of this process was obtained to be $E_c = 1855$ K (0.16 eV). The solid lines on Figure 1(b) represent the best fit of the experimental data using equation:

$$\epsilon''_a(T, \nu) = (2\pi\sigma\epsilon'/\nu\epsilon_\infty) \exp(-E_c / T) . \quad (1)$$

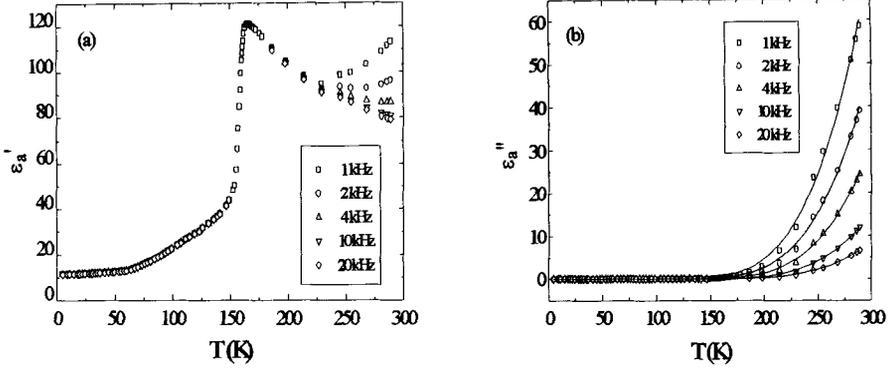


FIGURE 1 The temperature dependencies of the electric permittivity for D-RADA $x = 0.46$: (a) $\epsilon'_a(T, \nu)$; (b) $\epsilon''_a(T, \nu)$.

Precise dielectric measurements in temperatures below antiferroelectric phase transition show dispersion of the permittivity $\epsilon'_a(T, \nu)$ in the temperature below 90 K, which is illustrated in Figure 2. This fact suggest the presence of regions of ordering other than the antiferroelectric one, similar to the results¹³ of the D-RADA $x=0.39$. The temperature dependencies of $\epsilon''_a(T, \nu)$ below 90 K show dispersion too. Figure 3 presents temperature dependence of $\epsilon''_a(T)$ for frequency 4 kHz. The small values of ϵ''_a , which are by three orders of magnitude smaller than those characteristic for the "pure" deuteron glass⁷, prove that the regions in which the glass state originates are formed where long-range order disappears. Assuming a gaussian shape of the temperature dependence of $\epsilon''_a(T, \nu)$ and the involvement of two different mechanisms of relaxation, one can fit the experimental points to the equation:

$$\epsilon''_a(T) = A \{ \exp [-(T-T_{gI})^2 / 2\Delta I^2] \} + B \{ \exp [-(T-T_{gII})^2 / 2\Delta II^2] \}, \quad (2)$$

where T_{gI} and T_{gII} are the freezing points for two relaxation processes at which ϵ''_a reached the maximum values. This fit is marked on the Figure 3 by the solid line. The $\epsilon''_a(T)$ dependence decomposed into two gaussian-shape curves using Equation (2) (dotted and dashed lines) illustrates the presence of two relaxation regions with characteristic dispersion: 20 to 50 K and 50 to 90 K, obeys the Arrhenius Equation:

$$\nu_c = \nu_0 \exp (-E_c / T), \quad (3)$$

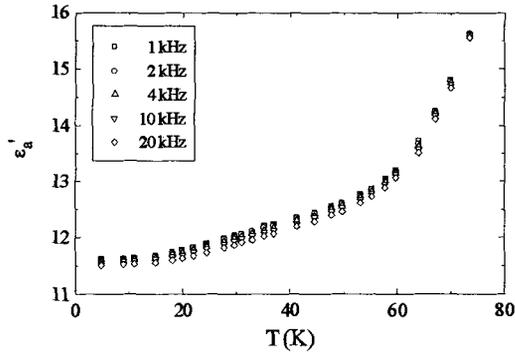


FIGURE 2 The low temperature dispersion of $\epsilon'_a(T, \nu)$ for D-RADA $x = 0.46$.

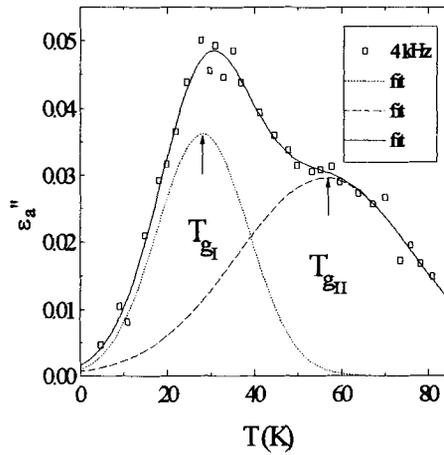


FIGURE 3 The fit, from Equation (2) of the experimentally obtained $\epsilon'_a(T)$ data at 4 kHz. The contribution of two different relaxation mechanisms is marked.

where E_c is the activation energy for reorientation of the electric dipoles. The best fit to these relaxation process was obtained for the following values of the parameters: $E_{cI} = 208.8$ K, $\nu_{cI} = 1.79 \cdot 10^{11}$ Hz in the temperature range from 20 to 50 K, and $E_{cII} = 327.0$ K, $\nu_{cII} = 2.94 \cdot 10^9$ Hz for the temperature range from 50 to 90 K.

EPR method

The temperature dependence of linewidth ΔH_{pp} for the highest-field AsO_4^{4-} hyperfine component in D-RADA $x = 0.46$ is shown in Figure 4. This linewidth ΔH_{pp} for an antiferroelectric crystals is temperature independent, but for the glass crystals (solid line on Figure 4 for the RADA $x = 0.35$ proton-glass) is temperature dependent and reflected the expected random distribution of local field (the order parameter $q \sim \Delta H_{pp}$). Unlike the "pure" glass state the temperature dependence of the linewidth ΔH_{pp} for the D-RADA $x = 0.46$ is complex.

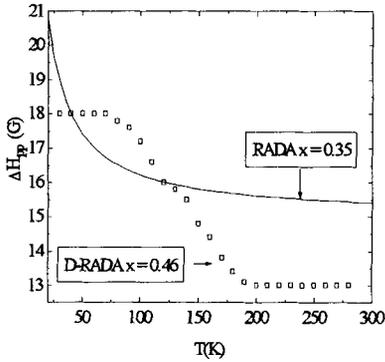


FIGURE 4 The linewidth ΔH_{pp} temperature evolution for the highest-field hyperfine component of AsO_4^{4-} in D-RADA $x = 0.46$ (experimental points) and in the proton glass RADA $x = 0.35$ (solid line).

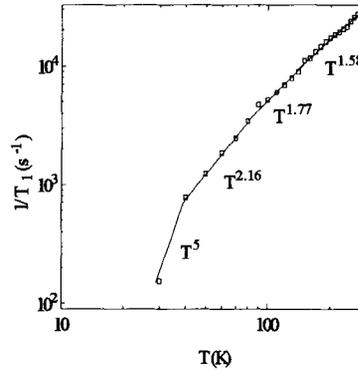


FIGURE 5 The temperature dependence of the inverse of the spin-lattice relaxation time $1/T_1$ for the D-RADA $x = 0.46$.

The temperature dependence of the spin-lattice relaxation time $1/T_1(T)$ (Figure 5) is different from the antiferroelectric and glass dependencies¹⁴. The spin-lattice relaxation time T_1 was measured by saturation method¹⁴, using Equation:

$$T_1 = 1.81 \cdot 10^{-4} \Delta H_{pp} / P_s, \quad (4)$$

where ΔH_{pp} in G is the linewidth for the highest-field hyperfine component of AsO_4^{4-} , and P_s is the microwave power level in mW which assures saturation at a given temperature. The relaxation time for the antiferroelectric ADA follow the law:

$$T_1^{-1} = A T^n \quad (5)$$

with $n = 5$ below T_N and $n = 2$ above T_N . In the case of proton glass RADA $x = 0.35$ the values are equal: $n = 1$ below $T = 15$ K, $n = 1.6$ between temperatures 15 and 50 K, and $n = 2.47$ above temperature 120 K, and relaxation processes were described in fracton model of relaxation¹⁴. For the D-RADA $x = 0.46$ the following n values were found: $n = 5$ below 40 K, $n = 2.16$ between 40 and 90 K, $n = 1.77$ between 90 and 160 K and $n = 1.58$ above 160 K. For now the model of relaxation for the D-RADA $x = 0.46$ is unknown. The future investigations are being prepared.

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