# Frequency Dependence and Anisotropy of the Glass Transition $T_g$ of $Rb_{0.52}(ND_4)_{0.48}D_2PO_4$

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# FREQUENCY DEPENDENCE AND ANISOTROPY OF THE GLASS TRANSITION $T_g$ OF $Rb_{0.52}(ND_4)_{0.48}D_2PO_4$

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Abstract The frequency dependence of the glass transition temperature $T_g$ has been calculed from the Vogel-Fulcher law using dielectric data obtained in the $10^2$ Hz to $10^{10}$Hz region. The best fit was obtained with $\ln f_o = 29$ and $T_o = 38$ K. The anisotropy of $T_g$ predicted recently by theory has been observed.

## EXPERIMENTAL RESULTS AND DISCUSION

Studies of the frequency-dependent dielectric properties of $Rb_{0.52}(ND_4)_{0.48}D_2PO_4$ at low frequency were done by Samara and Schmidt[1] and others[2,3]. In this paper we report the real $\varepsilon'$ and imaginary $\varepsilon''$ dielectric permittivity in the X-band microwave region for temperatures from 5 K to 180 K. Typical rounded cusp dependence for $\varepsilon'(T)$ and narrow rounded maximum for $\varepsilon''(T)$ were observed.Treating this maximum as the temperature $T_g$ of the glass "transition", $T_g$=86 K for f=9.3 GHz when the microwave electric field is parallel to the c-axis of the $Rb_{0.52}(ND_4)_{0.48}D_2PO_4$ mixed crystal (FIGURE 1).

According to cluster models of proton glass[4] , short range interactions form partly ordered clusters imbedded in the frustrated proton system. The clusters have a mean relaxation time $\tau$ strongly related to their volume and temperature, and $\tau$ decreases rapidly with increasing temperature. According to another viewpoint, to be explained in detail elsewhere[5], the $\tau$ distribution is governed by effective diffusion of $HPO_4$ and $H_3PO_4$ defects. In either case, the

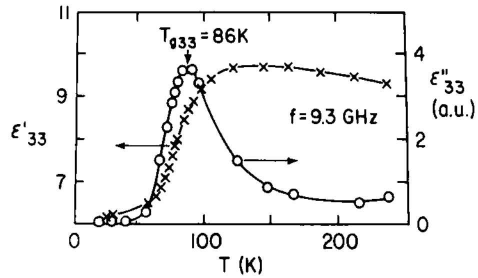


FIGURE 1 Temperature dependences of the real $\varepsilon'_{33}$ and imaginary $\varepsilon''_{33}$ parts of dielectric permittivity of 72% deuterated RADP.

mean $\tau$ is given by the Vogel-Fulcher law[6] :

$$\tau^{-1}=f_0\exp(-E/k(T-T_0)), \tag{1}$$

where $f_0$ and $T_0$ are scaling parameters and E is an activation energy. The frequency $f_0$ is the O-D...O deuteron intrabond transfer attempt frequency, and $T_0$ should be treated as the temperature below which the O-D...O deuteron system is "frozen". Courtens[2] proposed that Eq.(1) should be modified to the form:

$$\tau^{-1}=f_0\exp(-E/k(T-T_0)^{\alpha}) . \tag{2}$$

At the temperature giving maximum $\varepsilon''$ we can say that $\tau^{-1}=f$, where f is the measurement frequency and $T=T_g$ . Then Eq.(2) gives the formula :

$$(\ln f_0-\ln f)^{-1}= k(T_g-T_0)^{\alpha}/E . \tag{3}$$

Figure 2 shows the plot of Eq.(2) for $\alpha=2$, $\ln f_0=29$ and $T_0=38$ K, using our experimental point and low frequency measurements[1,3] for $\varepsilon''_{33}$ . The good agreement shows that the Eq.(2) form of the Vogel-Fulcher law describes the proton glass system in our crystal. The values of $\ln f_0$ and $T_0$ are practically the same as found by Courtens[2], $\ln f_0=28.5$ and $T_0=30$ K for $Rb_{0.38}(ND_4)_{0.62}D_2PO_4$ . In terms of physical parameters, these results illustrate the rapid slowing down of dynamic processes with decreasing temperature, and depending on the model adopted, the increase in cluster size[4] or the increase in defect diffusion path length between creatio and annihilation[5].

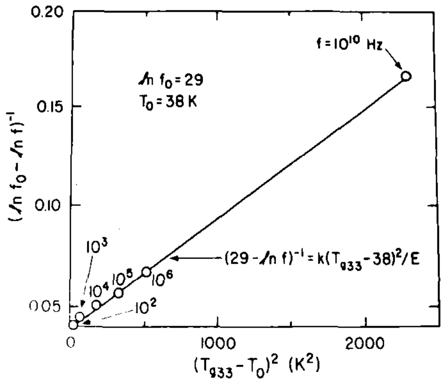


FIGURE 2 A plot of $(\ln f_0 - \ln f)^{-1}$ vs. $(T_{g33} - T_0)^2$ for $\ln f_0 = 29$ $T_0 = 38$ K and $\alpha = 2$.

Matsushita and Matsubara[7] (MM) using a cluster theory[4] predicted anisotropy of $T_g$- different values of $T_g$ for susceptibility along the c and a axes. They introduced two order parameters, $q_x$ and $q_z$, which give the temperatures $T_{g11}$ and $T_{g33}$. Figure 3 shows that for $Rb_{0.52}(ND_4)_{0.48}D_2PO_4$ the $\varepsilon''$ maxima occur at different temperatures for microwave electric field parallel to the a and c axes. Our data show $T_{g11} = 82$ K and $T_{g33} = 86$ K, in accord with MM theory which gives $T_{g33} > T_{g11}$ for concentration $x < 0.5$. Further experiments are planned.

## CONCLUSION

These experiments show that dielectric behavior for proton glasses obeys the Vogel-Fulcher law also when these is isotropic randomness (72 % deuteration ) as well as cation randomness (48 % $ND_4$). In addition, the anisotropy of $T_g$ predicted by Matsushita and Matsubara [7] was observed.

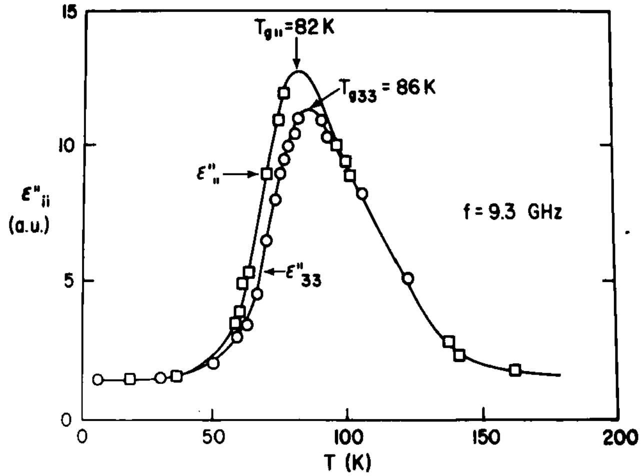


FIGURE 3 Temperature dependences of the imaginary part of electric permittivity in arbitrary units for two orientations of microwave electric field: $\varepsilon''_{33}$ and $\varepsilon''_{11}$ .

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