# Effect of Radiation Damage on Ferroelectric Phase Transition in $(NH_4)_2BeF_4$

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**Abstract**

Dielectric properties of the ferroelectric material, ammonium fluoroberyllate, irradiated by $\gamma$-ray were studied in the range of 30 Mrad. The ferroelectric phase transition is displaced towards low temperatures and its maximum dielectric constants are reduced with the increase of doses. The results are compared with published data for triglycine sulfate.

## Introduction

The ferroelectricity of ammonium fluoroberyllate, $(NH_4)_2BeF_4$ (AFB) have been known for quite a long time. At about 176 K this material undergoes a phase transition of the first order close to one of the second order.[1,2] The ferroelectrics, $(NH_4)_2BeF_4$, is classified as the order-disorder type and has no peizoeffect in the paraelectric phase[1,3]. Recently the space groups of the polar and nonpolar phases were established by X-ray analysis[4,5].

The physical properties of $(NH_4)_2BeF_4$ are rather unusual. For example, the Curie-Weiss law for the dielectric constant $\varepsilon$ is only satisfied in the immediate vicinity of the transition point $T_c$, and the Curie-Weiss constant is very low.[2] The anomaly in $\varepsilon$ is small and so is the spontaneous polarization,[2] while a considerable change in birefringence occurs at the transition and are not described by the spontaneous quadratic electrooptical effect[6]. The crystal structures of $(NH_4)_2BeF_4$ and $(NH_4)_2SO_4$ are similar and both would seem to belong to the improper type in such ferroelectrics as gadolimium molybdate and boracite. The characteristics of the imporper ferroelectrics are small Curier-Weiss constants, small variation of dielectric constants, small spontaneous polarization and narrow temperature regions where the Curie-Weiss law fist. However, none of the improper ferroelectrics have been reported on the influence of radiation damage on their ferroelectricities. Several papers on proper ferroelectrics, e. g., tryglycine sulfate, have been published for the investigation on radiation damage effect.[7,8,9]

The present article contains an effect of radiation damage on the characteristics of $(NH_4)_2BeF_4$ by the dielectric measurement and discussions of radiolysis in comparison with the results of electron spin nresonance.[10]

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## Experiment

$(NH_4)_2BeF_4$ single crystals were grown by slow evaporation from acqueous saturated solution and deuterated crystals were also grown by evaporation from the reagent previously subjected to isotope exchange in heavy water. The specimens were wafers $7\times7\times0.5$ mm cut perpendicular to the ferroelectric axis (b axis), polished and provided with silver paste electrodes. The capacity of the specimen was measured with a 100 kHz Q meter (YEW Model QM 102A) using isopentane in a cell as a means for obtaining a homogeneous temperature environment surrounding the specimen and also preventing temperature measurement and control from fluctuations. Temperature was measured with a copper-constantan thermocouple, one junction of which was placed in the vicinity of the specimen. Temperature was varied by controlled transfer of cooling gas from liquid nitrogen, which electric heat was fed to. With the cooling gas flow at a constant rate, a heater attached to the transfer tube permits precise control of temperature with stability of $\pm0.05$K. Raising or cooling rates of temperature were 0.05 K/min. in the vicinity of the phase transition. Absorption doses used at room temperature were from 5 up to 30 Mard with $Co^{60}$ $\gamma$-rays at a dose rate of 0.9 Mrad/hour.

## Results and Discussion

Fig. 1 shows the temperature dependences of dielectric constant $\varepsilon$ correspond-

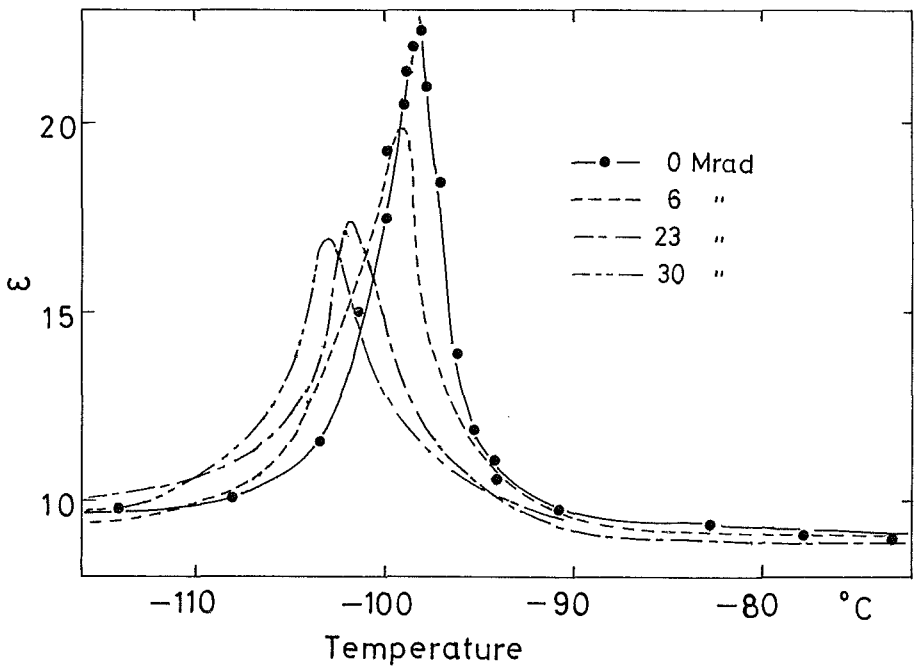


**Fig. 1.** Temperature dependence of the dielectric constant of ammonium fluoroberyllate for various absorbed doses. The observed data except for nonirradiated sample were omitted from the lines.

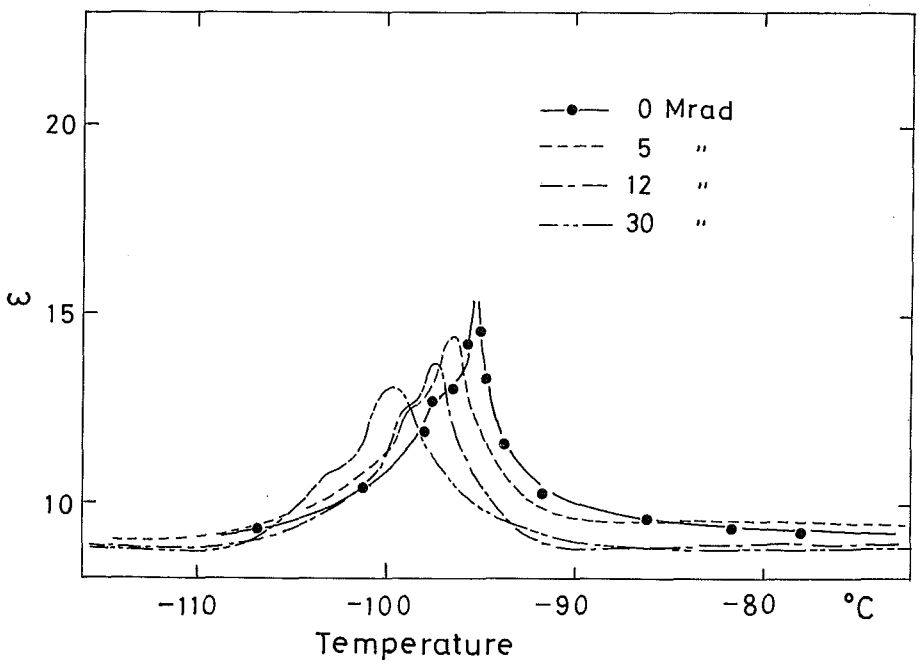


**Fig. 2.** Temperature dependence of the dielectric constant of partialy deuterated ammonium fluoroberyllate.

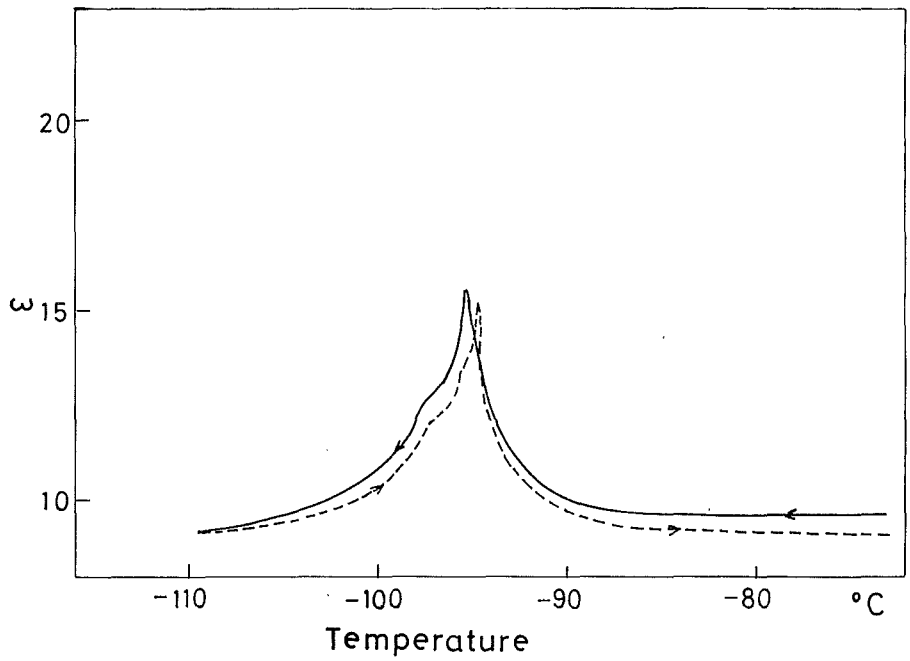


**Fig. 3.** Thermal hysteresis for the temperature dependence of dielectric constant of the ammonium fluoroberyllate.

ing to various radiation doses. It is confirmed from the figure that the temperature dependence before irradiation is identical to those known in literatures except for a rather broad peak width.[1,2] With the increase in the dose the Curie point $T_c$ is displaced toward lower temperature. This is accompanied by a considerable reduction in the peak value of $\varepsilon$. The behaviour of the temperature dependence in $\varepsilon$ are very similar to that of triglycine sulfate.

To observe the isotope effect, deuterated specimens were examined with the same procedure, as shown in Fig. 2. The Curie point of the deutrated sample shifts to a higher temperature, 177K than that of the normal one before the irradiation. Appearance of a slight shoulder on the low temperature side is presumably due to the superposition of the transition of the $(NH_4)_2BeF_4$, because this temperature of the shoulder is near the transition point of the normal one. Thus, this shoulder indicates partial deuteration of the sample. The behaviour of $\varepsilon$ in $\gamma$-irradiated $(ND_4)_2BeF_4$ is the same as that of $(NH_4)_2BeF_4$ except for the reduction of maximum $\varepsilon_{max}$. A thermal hysteresis of $\varepsilon$ was observed as shown in Fig. 3. In Fig. 4, 5,

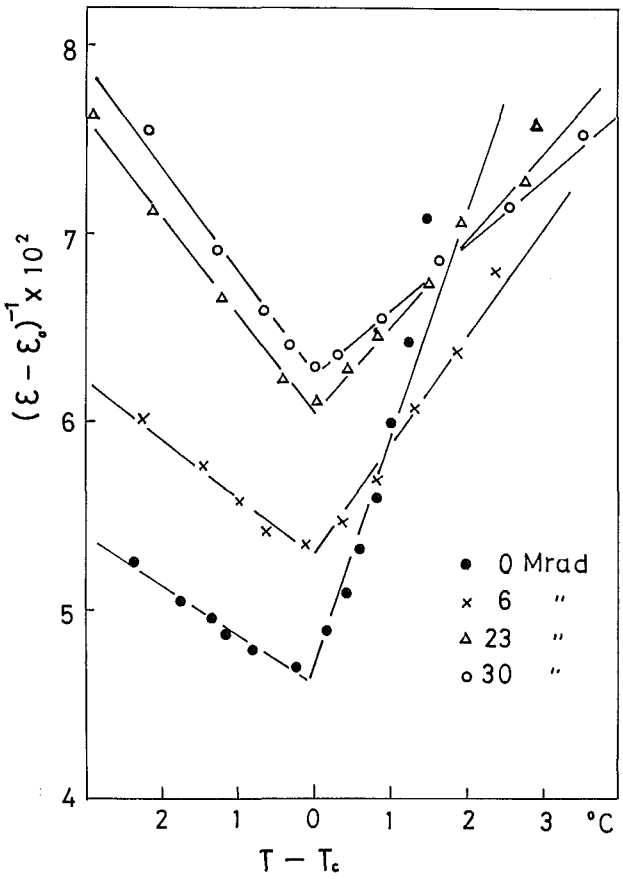


**Fig. 4.** Temperature dependence of the reciprocal dielectric constant of ammonium fluoroberyllate.

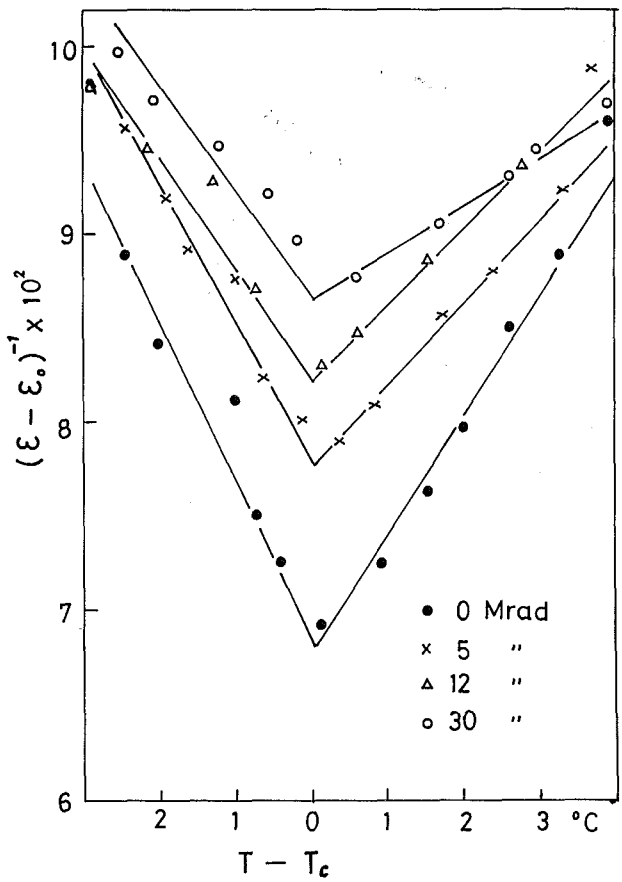


**Fig. 5.** Temperature dependence of the reciprocal dielectric constant of partialy deuterated ammonium fluoroberyllate.

the temperature dependence against inverse temperature made clear the decrease of Curie-Weiss constants with increasing doses.

It was reported earlier that ionizing radiations (X-rays and electrons) cause a considerable change in the ferroelectric hysteresis loops triglycine sulfate $(NH_2CH_2COOH)_3 \cdot H_2SO_4$ crystals which is not improper ferroelectrics, but belongs to an other group possessing a few thousands (°K) as the Curie-Weiss constants.[7~9]. According to Chynoweth's results,[9] the main damage producing these effects seems not to be by atomic displacements but by ionization followed by chemical reactions resulting in molecular rearrangement. However, the local damage can not be the origin of the observed bias effects for several reasons. Ultimately, the authors have merely suggested a hypothetical phenomenological model that accounts for the major changes in the ferroelectric properties with increasing bombardment.

Yrin et al.[7,8] also performed studies on the effect of $\gamma$-irrdiation on the hysteresis loop in this substance and obtained a more detailed description of its ferroelectric properties. The observed effect is quite similar to that produced by X-ray

and electrons irradiation. The concept of a proper bias field was used, which is produced in specimens during irradiation. They measured the effect of applied electric fields superposed with the bias field, the effect on the hysteresis loop, and temperature dependence of $\varepsilon$ and the Curie point of irradiated crystals. Based on these results they concluded that in the case of formation of double loop under irradiation these crystals have a stable polydomain state, while in the case of formation of displaced loop there is a stable monodomain state. The comparison of the properties of Rochelle salt crystals containing copper ions $Cu^{2+}$ with that of irradiated triglycine sulfate crystals indicates that the radiolysis products of triglycine sulfate presumably have an electric charge and their position in the crystal are determined by the directions of these amounts interacting with the field of spontaneous dipole moments. Taking a similar view-point the results obtained in our experiments could be explained in spite of the imporper ferroelectrics.

To determine the origins of radiation damages influencing the phase transition, ESR measurement was carried out,[10] and the hydrogen atom and $F_2^-$ radical produced by $\gamma$-rays were identified, but these radicals which decay out on warming to the transition point can not directly cause any effect on the phase transition. A few radicals centered at $g \simeq 2.00$, survive above the Curie point $T_c$ but almost all of them decay out and change into non-paramagnetic species on warming up to room temperature. From the comparison of their ESR patterns between AFB and partly deuterated one of these radicals might be identified as $NH_3^+$ ion. The results of recent magnetic resonance studies on ammonium fluoroberllate[13] show that the ferroelectricity in these substances arises from the distortion of the ammonium ions. The consideration of phenomena mentioned above leads to the central radical to be deeply related to the characteristic of sample suffered to radiation.

**Acknowledgement**

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