Effects of Gamma-Ray Irradiation on Rochelle Salt

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The property changes of Rochelle salt irradiated with γ-rays are studied. It has been found that the ferroelectric region became narrower as a result of irradiation, and that ferroelectricity has disappeared after prolonged irradiation. Most striking changes appear in the ferroelectric hysteresis loop, *i. e.*, the double loop pattern is revealed in the irradiated crystal. It has been also found that the piezoelectricity is affected as a result of irradiation.

INTRODUCTION

Recently the property changes of ferroelectric crystals with hydrogen bonds have been investigated by several workers, when the crystals were subjected to ionizing radiations. It has been reported by the present authors[1] and Iurin[2] that peculiar changes occurred in the ferroelectricity of Rochelle salt crystal irradiated with γ-rays. It is noteworthy that peculiar changes occurred in their ferroelectric polarization behavior after irradiation, *i. e.*, the crystal revealed the normal hysteresis loop before irradiation, but in the irradiated crystal the typical double loop was observed under strong electric field, and also the ferroelectricity disappeared after prolonged irradiation. It is known that the X-ray irradiation has the similar effect to the γ-ray irradiation.[3] It is also reported that the triglycine sulfate crystal is affected similarly as results of γ-ray irradiation,[4] and of X-ray irradiation[5]. These behaviors of polarization phenomena of irradiation-damaged ferroelectric crystals are very similar to those of impurity-doped ferroelectric crystals, and the results obtained from both cases will be complementary. In the dosage range under 10^5 roentgens sufficient to give peculiar changes in the electric properties, little or no remarkable change is observed in X-ray diffraction pattern, but the observable changes are found under a sufficient large dosage, *i. e.*, the diffuse scattering of X-rays in heavily damaged Rochelle salt crystal are observed by two of the present authors.[6]

The present paper report some results to give some information on the possible mechanism for the ferroelectric behaviors of Rochelle salt crystal affected by γ-ray irradiation.

EXPERIMENTAL PROCEDURE AND RESULTS**

The crystals used in these experiments were 45° x-cut crystals, of which dimensions were about $3\times0.9\times0.07\text{cm}^3$, and silver electrodes were evaporated *in vacuo* on both

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sides of the major surfaces. They were irradiated with γ-rays in the ICR 2000 curie Co^{60}-irradiation facility, at an ambient temperature of about 5°C, and the intensity of this source was estimated by Fricke's chemical method to be about 1.9×10^{5} roentgens per hour. The specimens were sealed in polyethylene envelopes during the irradiation, since their physical properties are very sensitive to humidity. All the measurements were made over the temperature range from about 30°C down to -30°C. The results are plotted before and after a wide range of irradiation levels.

The dielectric constants have been measured by a usual bridge method with AC field of 1 kcps at weak field intensity. Figure 1 shows the temperature dependence of dielectric constant along the *a*-axis of the crystal. The dielectric constant was

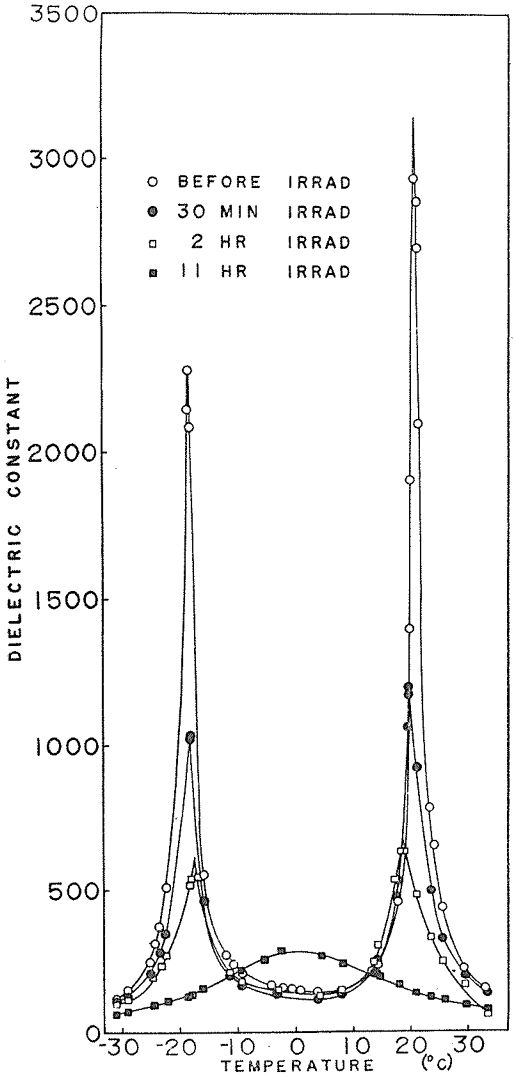


Fig. 1. Dielectric constant along the *a*-axis of Rochelle salt, before and after γ-ray irradiation.

found to decrease rapidly with increasing dosages. Most strikingly, the sharp peaks at both the Curie points, associated with the orthorhombic-monoclinic transitions, are reduced and moved closer to each other, *i. e.*, the ferroelectric region became narrow, and have disappeared after prolonged irradiation. The dielectric loss showed an increase as a result of irradiation.

Under a high AC field of 60 cps applied parallel to the *a*-axis, the ferroelectric hysteresis loop was observed by the well-known Sawyer-Tower circuit. The crystals before irradiation revealed normal ferroelectric hysteresis loops at temperatures between their two transition points (*e. g.*, Fig. 3 (a)). After short irradiation, the hysteresis loop tended to deform near the middle, and has splitted into two separate loops. Increasing the dosage, the deforming was enhanced to the state where a linear part appeared, *i. e.*, the typical double hysteresis loop have been observed. This anomalous hysteresis behavior is very similar to those observed in Na$(K\text{-}NH_4)$-tartrate crystals.[7] However, there exist a notable difference: in the irradiation-damaged crystals the lifetime of double loop is permanent, while in the case of Na$(K\text{-}NH_4)$-tartrate it is usually very short after some treatments. With further irradiation the length of the linear part increased, while the terminal loops became smaller, and the hysteresis loop lead to linear polarization with a little curvature after prolonged irradiation. Figure 2 shows the double loops at various temperatures for 4 hour irradiated crystals. The results obtained from hysteresis loop established that coercive and biasing fields increased, and spontaneous polarization came to decrease, with the increasing dosages. The biasing field has a weak temperature dependence. Typical examples are given in Table 1. In the case of crystal irradiated at a temperature higher than its upper Curie point, the hysteresis loop was different from that of the crystal irradiated at the ferroelectric region, as sh-

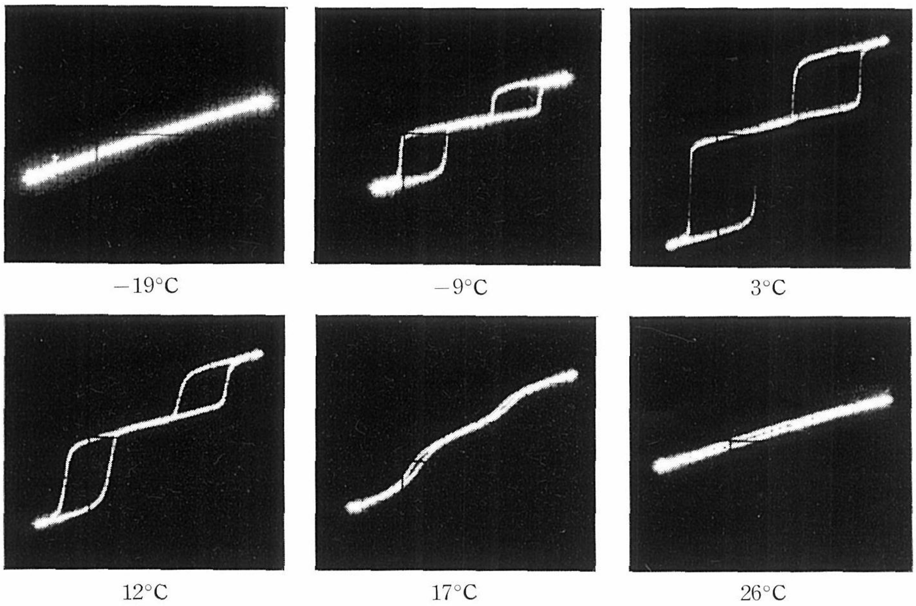
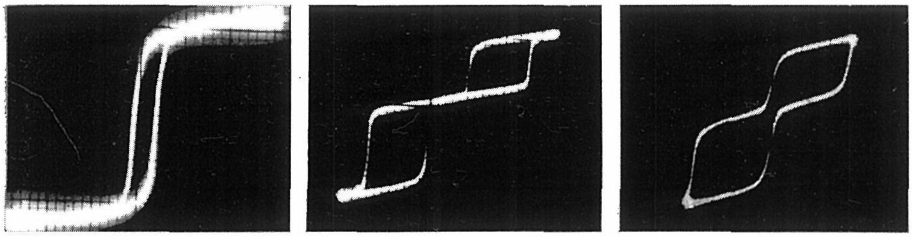


Fig. 2. A series of the ferroelectric hysteresis loops in the 4 hour irradiated Rochelle salt, under the applied field parallel to the *a*-axis ($E=2.5$kV/cm).

Table 1. Changes in polarization behavior of Rochelle salt, as a function of γ-ray irradiation.

Dose (hr)	Coercive field (V/cm)	Biasing field (V/cm)	Height of loop
0	150	0	141
1	300	350	112
2	520	650	105
4	610	1200	98



(a) (b) (c)

Fig. 3. Ferroelectric hysteresis loops of Rochelle salt : (a) before irradiation, (b) irradiated at the ferroelectric region, and (c) irradiated above its upper Curie point (4 hour irradiation).

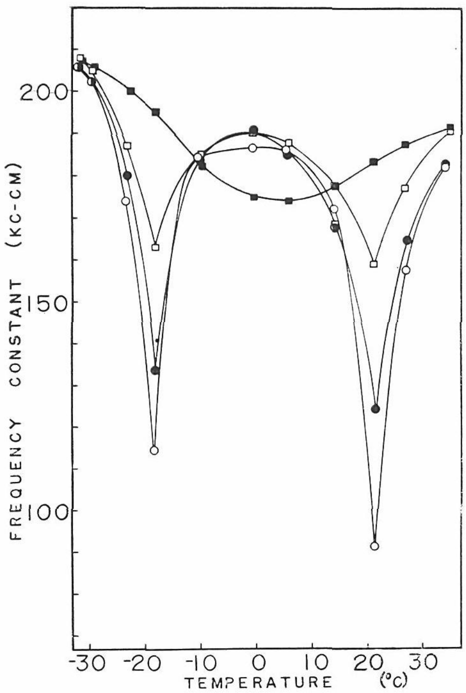


Fig. 4. Resonant frequency of Rochelle salt, before and after γ-ray irradiation.

own in Figure 3, *i. e.*, at the same dosage the latter revealed the typical double loop pattern, while the former revealed the deformed loop pattern. It may be supposed that the imperfection of crystal introduced at the paraelectric phase give more pronounced effects than that introduced at the ferroelectric phase.

It is well known that the polarization process of the ferroelectric crystals are closely associated with reorientation and rearrangement of the domain. The domain in specimens revealing double loop were observed under the electric field by means of a polarization microscope. The results showed that movement of domain wall began at the field equal to the threshold value for the appearance of terminal loops in the double loop. More detailed behaviors of the polarization phenomena in the irradiation-damaged crystals will be reported subsequently.

The piezoelectric properties of the crystals were also measured, by the resonance-antiresonance method for many vibrating modes. The resonant frequency was affected in the same way as dielectric constant, *e. g.*, temperature dependence of resonant frequency at longitudinal vibration in the longer side of the slab are shown in Figure 4. With increasing dosage, the resonant frequency increased rapidly, and both the sharp minima at transition points became flatter and moved closer to each other, and have disappeared after prolonged irradiation.

It will be noted that these changes occurred rather rapidly in short irradiation compared with long irradiation. Their appearances changed gradually in the course of irradiation: the yellow-coloring and opacity of crystals and the evolution of water were clearly found under high dosages.

DISCUSSION

The peculiar changes of electric properties found in those experiments are also observed, when the phase transition occurs in ferroelectric crystal under the influence of electric field, or when the antiferroelectric domains exist in the crystal. However, it may be supposed that the cause of these changes observed in the irradiation-damaged crystal might have different characters. There might be several explanations to interprete these changes.

The ionizing radiation, γ- or X-rays, would not displace the atoms in the crystal, but induce ionization of molecules or ions followed by chemical decomposition resulting in molecular rearrangements, *i. e.*, the most part of the property changes induced by γ-rays must be a chemical nature. It will be supposed that the γ-rays destroy or fix some hydrogen bond in the crystal. However, it does not explain the fact that the anomalous polarization behaviors might be produced by fixed dipole, or by local damage. A possible explanation for the peculiar changes in the ferroelectricity induced by the radiation is ascribed to the fact that the γ-rays change the shape of the double minimum potential energy curve usually used for phenomenological interpretation of ferroelectricity. The fact that the changes are enhanced continuously with increasing dosage, may suggest that the γ-rays produce a homogeneous defect over the irradiated area. At the beginning of irradiation, the most weak bond in a crystal is destroyed and then the rearrangement comes to have a new weak bond, which would be a secondarily decomposed.

It is another attempt to explain the possibility that the anomalous hysteresis behavior might be induced by polar anisotropy produced in the crystal. The ions or atoms surrounding crystal defects, which are produced by irradiation in the crystal, are difficult to rearrange tending to lower their contribution to the spontaneous polarization. These rearrangements occurred gradually with a relaxation time, and then the structure produced as results of rearrangements has become a polar anisotropy center. It will be supposed that these polar anisotropy show paraelectric behavior apparently. With irradiation, the apparent paraelectric phase will be produced in the ferroelectric phase, and as a result of mutual interaction between two phases double or deformed hysteresis loop appeared.

Third possibility is that the changes in ferroelectricity induced by the radiation might be ascribed to the migration of lattice defects into the domain walls, hence clamping domain walls, or the difficulty to make the new domain nucleation. This process is feasible assuming that the stress field around existing sites are modified by the irradiation to make the polarization revarsal harder. However, it has shown that the ferroelectric behavior of irradiated barium titanate[8] is different from that of irradiated Rochelle salt or triglycine sulfate crystals. The influence of crystal imperfection upon its physical properties depends on the bonding nature of the crystal, and it is generally hard to correlate the imperfection with changes of ferroelectricity of the crystal.

But these explanations of radiation effects mentioned above would be too speculative at the present status, and more experiments will be necessary.

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