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EFFECT OF PILE NEUTRON IRRADIATION ON THE DIELECTRIC PROPERTIES OF $PbZrO_3$

By B. Hilczer and J. Kułek

Dielectric Department, Institute of Physics, Polish Academy of Sciences, Poznań*

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Ferroelectric and antiferroelectric properties are very sensitive to crystal lattice defects. The influence of defects engendered by pile neutron irradiation in $PbZrO_3$ is studied. The antiferroelectric Curie temperature was found to be shifted towards lower temperatures and the thermal hysteresis of dielectric permittivity was found to increase. Moreover, the dielectric polarization measured from the hysteresis loop in the vicinity of the phase transition temperature was found to decrease due to neutron irradiation, and the temperature range in which the hysteresis loop appears becomes narrower.

1. *Introduction*

The dielectric and structural properties of lead zirconate were studied by many authors [1–14]. Dielectric anomalies near the phase transition temperature (about 230°C) were independently reported by Smolenski [2] and Roberts [1] in 1950. In 1951 Shirane, Sawaguchi and Takagi observed a double hysteresis loop in high electric fields [3]; finally, the antiferroelectric structure of lead zirconate was estiblished by Sawaguchi, Maniva and Hoshino [4].

In the paraelectric phase, above 230°C, the structure of lead zirconate was found to be cubic of the perovskite type. Below 230°C lead zirconate is antiferroelectric, with orthorhombic structure [4, 5]. X-ray and neutron diffraction studies of the orthorhombic phase lead zirconate [4, 7] permitted the determination of compensated antiparallel shifts of the lead and oxygen ions in the (001) plane and a small uncompensated shift of oxygen ions in the direction perpendicular to this plane.

Dielectric investigations show that the temperature dependence of the dielectric permittivity attains a maximum at about 230°C [1–3]; above this temperature the dielectric permittivity follows the Curie-Weiss law. Moreover, a thermal hysteresis of the dielectric

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[*] Address: Instytut Fizyki, Polska Akademia Nauk, Poznań, Grunwaldzka 6, Poland.

permittivity was observed. Accurate measurements of the temperature dependence of dielectric permittivity made by Goulpeau [12] point to the presence, at 227°C, af yet another phase transition. A similar bend on the temperature dependence curve of the dielectric permittivity was also observed [16].

The dielectric polarization at room temperature is a linear function of the electric field strength, but at temperatures near the phase transition a high external electric field gives rise to a double hysteresis loop [6], which can be related with a field-induced ferroelectric phase. The threshold field strength inducing the double hysteresis loop was found to decrease linearly with increasing temperature [6] from about 60 kV/cm at 200°C to 20 kV/cm at 225°C. The symmetry of the induced ferroelectric phase is rhomboedric [8]. Moreover, in the near neighbourhood of the phase transition, a normal hysteresis loop in electric fields of about 10 kV/cm can be obtained [16].

The bends on the dielectric permittivity *versus* temperature curves seem to suggest the existence of a ferroelectric phase in the vicinity of 230°C [12, 14, 16]. This is convincingly demonstrated by the latest results of Samara [17] regarding the effect of hydrostatic pressure on the temperature dependence of dielectric permittivity.

It is a well-known fact that crystal lattice defects cause significant changes in the dielectric properties of ferroelectrics. Similarly, an influence of crystal lattice defects on the dielectric properties of antiferroelectric lead zirconate was observed as a result of doping with foreign ions by Krajnik and Benguigi [14, 17, 18] as well as by Hilczer, Kułek and Lekki in the case of gamma Co-60 irradiation [16]. Moreover, Hauser and Schenk studied the effect of fast neutron irradiation on the phase transition of lead zirconate by X-rays and calorimetric methods [19, 20].

This paper deals with the effect of pile neutron irradiation on the dielectric properties of $PbZrO_3$.

2. *Experimental results*

1. Preparation of samples

The lead zirconate samples were sintered from substances of 99.9% purity and processed by conventional ceramic technology with esspecial care for lead stechiometry. For the measurements, the samples were formed into discs 0.3 to 0.5 mm thick and about 50 mm^2 in area. Each sample was cut in two parts, one of which was irradiated with pile neutrons in the reactor EWA at Świerk in channels where fast neutrons amounted to about 10 per cent of the total flux, whereas the other part was the control sample. The integrated pile neutron flux Φt varied from 10^{17} to 10^{19} n/cm^2. The dielectric properties of the irradiated samples were measured after about 3 months of "cooling", because of radioactivity. Previous to the measurements, both parts of the sample were coated with silver electrodes without heating, using Degussa silver paste or other methods. The capacity of the samples was measured by resonance methods at a generator frequency of 1 Mc/s. The hysteresis loops were investigated with a 50 c/s AC field. The temperature was measured with a chromel-alumel thermocouple.

2. Dielectric permittivity measurements

In Fig. 1, the dielectric permittivity of a nonirradiated $PbZrO_3$ sample is shown. Dielectric permittivity reaches its maximum value for rising temperature at 230°C, denoted further as the antiferroelectric Curie temperature T_c. The maximum value of dielectric permittivity measured for falling temperature is shifted towards lower temperatures with respect to T_c by an ammount of ΔT_c^h, which was found to be 1 degree. This temperature difference ΔT_c^h, measured at a constant rate of temperature variation, can be taken as a measure of the thermal hysteresis of dielectric permittivity. Moreover, the maximum permittivity value was higher when measured at falling temperature. Above 230°C, the permittivity obeys a Curie-Weiss law. On the permittivity *versus* temperature curves, some bends can

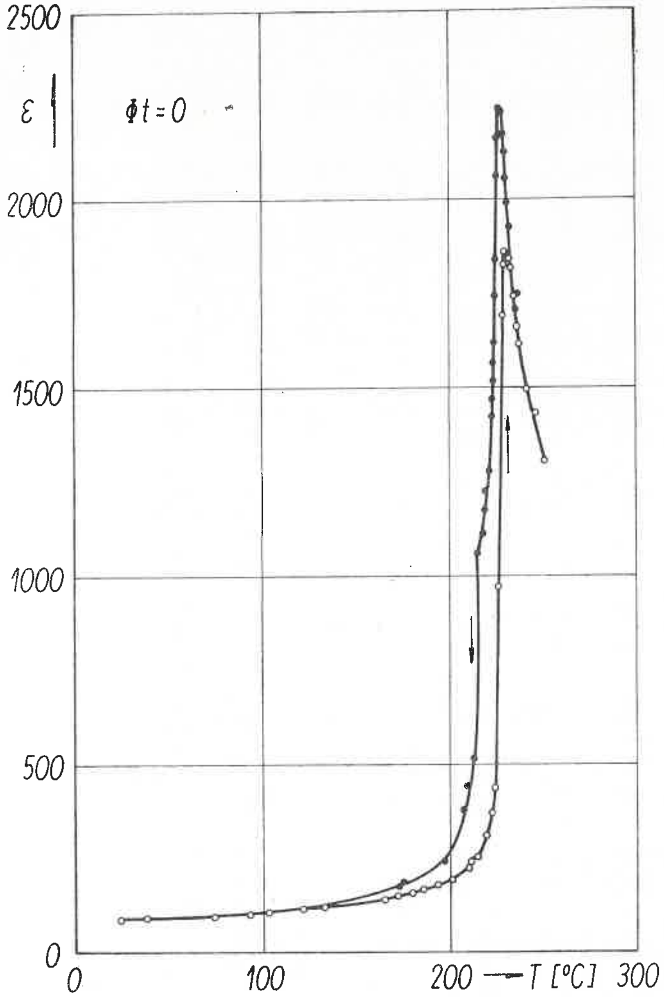

Fig. 1. Temperature dependence of dielectric permittivity of nonirradiated $PbZrO_3$ sample

be noticed at a temperature several degrees lower than the temperature of the dielectric permittivity maximum.

Fig. 2 shows the temperature dependence of dielectric permittivity of a lead zirconate sample irradiated with an integrated pile neutron flux of 10^{19} n/cm^2. The permittivity maximum is shifted towards lower temperatures. Moreover, the two maximum values of dielectric permittivity were found to decrease, and the peaks became diffused.

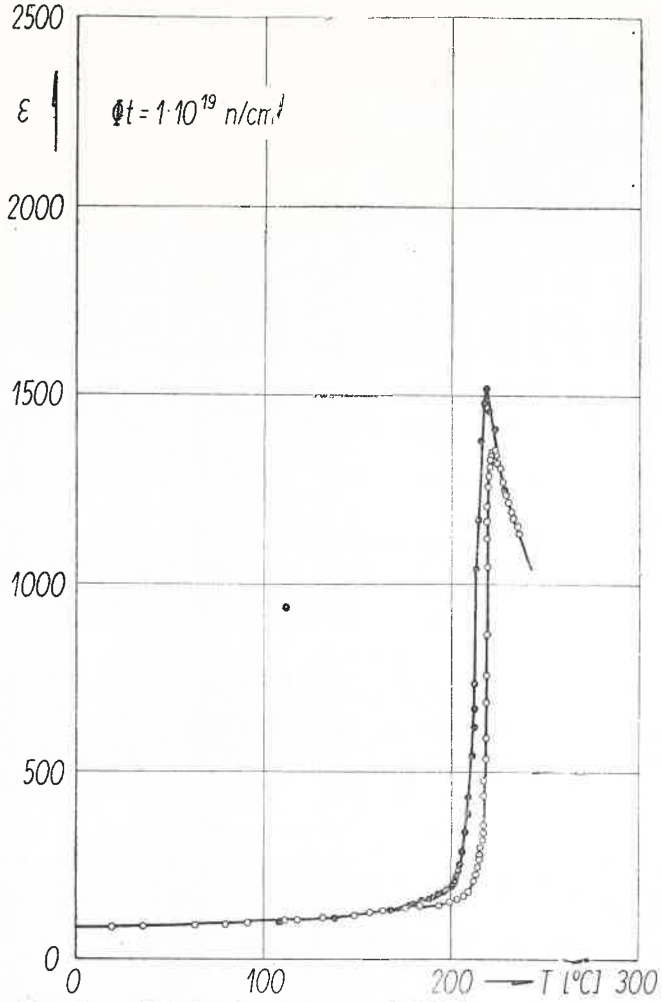

Fig. 2. Temperature dependence of dielectric permittivity of PbZrO$_3$ sample irradiated with integrated pile neutron flux 1.10^{19} n/cm^2

The antiferroelectric Curie temperatures T_c in their dependence on the integrated pile neutron flux are depicted with circles on the curve of Fig. 3*a*. For comparison, the phase transition temperatures of pure and neutron irradiated lead zirconate determined by differential thermal analysis by Schenk [20] are denoted by crosses. The results obtained by quite different methods (dielectric and thermal) are seen to be in good agreement.

After pile neutron irradiation, the ΔT_c^h value characterizing the thermal hysteresis of dielectric permittivity was found to increase. This is shown in Fig. 3*b* *versus* the integrated pile neutron flux.

In Fig. 3*c*, the Curie-Weiss temperatures Θ of nonirradiated and irradiated $PbZrO_3$ samples are plotted *versus* the integrated pile neutron flux. Similarly to the shift in Curie temperature T_c (Fig. 3*a*), the Curie-Weiss temperature Θ was found to be shifted towards lower temperatures.

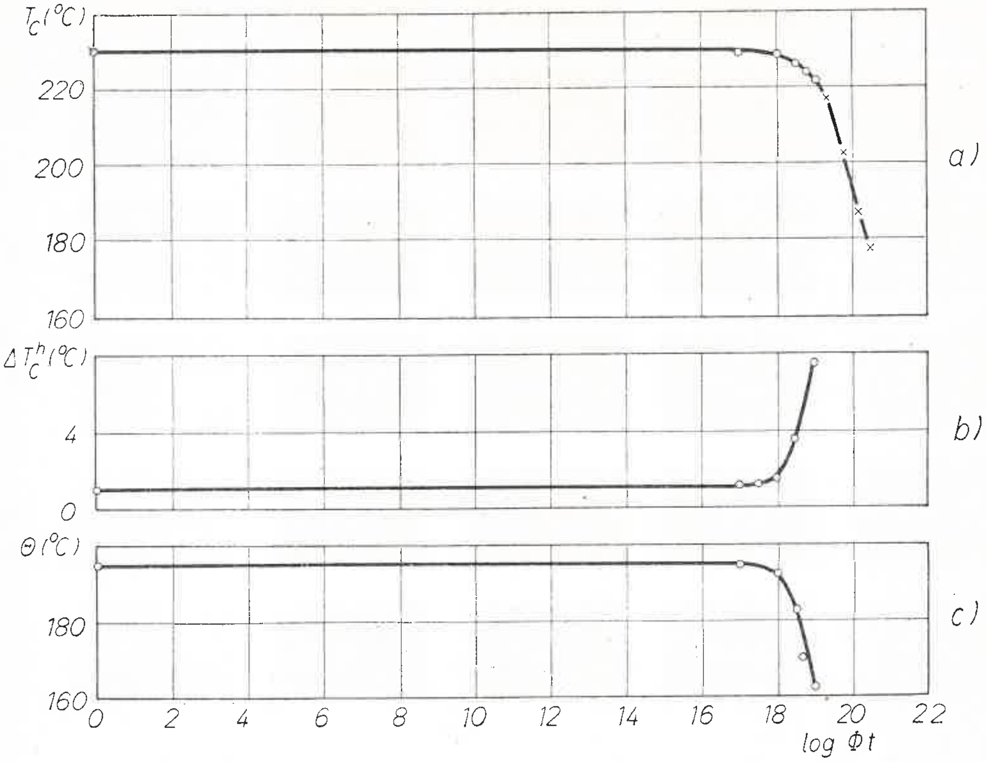

Fig. 3. Curie temperature T_c (*a*), ΔT_c^h(*b*), Curie-Weiss temperature Θ (*c*) of $PbZrO_3$ as dependent on integrated pile neutron flux (○ — dielectric measurements, × — differential thermal analysis measurements [20])

3. *Dielectric polarization measurements*

As already mentioned, in the vicinity of the phase transition temperature 230°C of lead zirconate a normal ferroelectric hysteresis loop can be obtained in AC fields of about 10 kV/cm.

Fig. 4 shows a Table of hysteresis loops obtained at various temperatures for pure and pile neutron irradiated lead zirconate. The pictures were obtained for samples of different thickness and area, and hence the loops cannot be compared directly.

The maximum value of total polarization measured from hysteresis loops of pure samples was found to be 14.5 μC/cm² in field strengths of 10 kV/cm, and 18.5 μC/cm² in

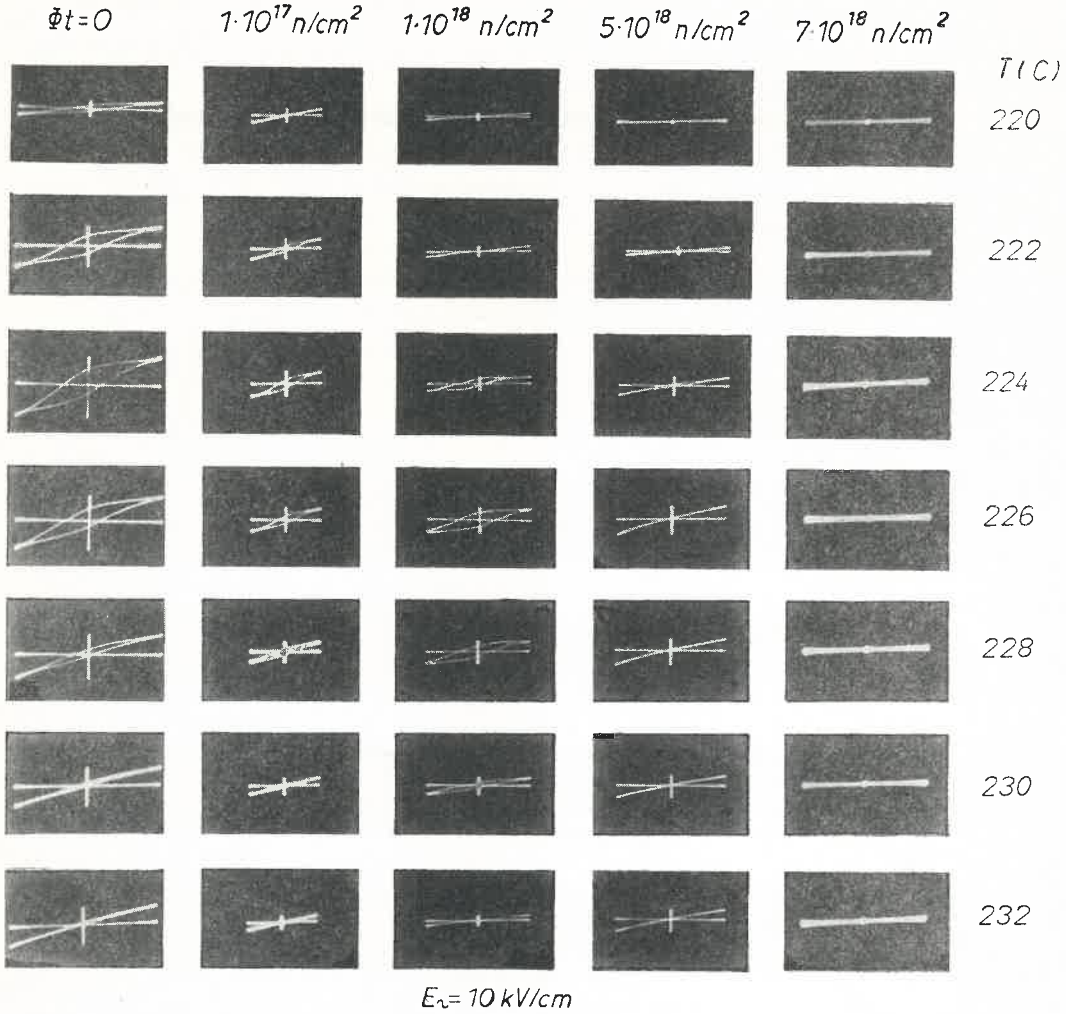

Fig. 4. Hysteresis loop oscillograms of $PbZrO_3$ at various temperatures near the Curie point for nonirradiated and neutron irradiated samples

field strengths of 15 kV/cm. After neutron irradiation, this value was found to decrease. Moreover, the temperature range in which the normal hysteresis loop appears was found to diminish. In field strengths of 10 kV/cm, no hysteresis loop can be observed for samples irradiated with 5.10^{18} n/cm^2. However, after heating at 300°C, a small hysteresis loop reappears. In Fig. 5 the maximum polarization value obtained from the hysteresis loops of samples rejuvenated in paraelectric phase is plotted in function of the integrated neutron flux.

The temperature dependence of the total polarization measured from the hysteresis loops of rejuvenated lead zirconate, pure and irradiated with an integrated neutron flux of 1.10^{18} and 5.10^{18} n/cm^2, is presented in Fig. 6.

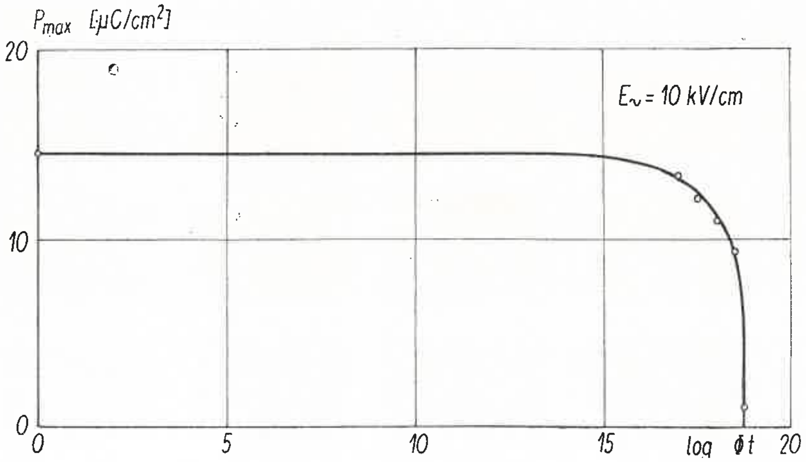

Fig. 5. Maximum polarization value of $PbZrO_3$ near the Curie point as dependent on integrated pile neutron flux

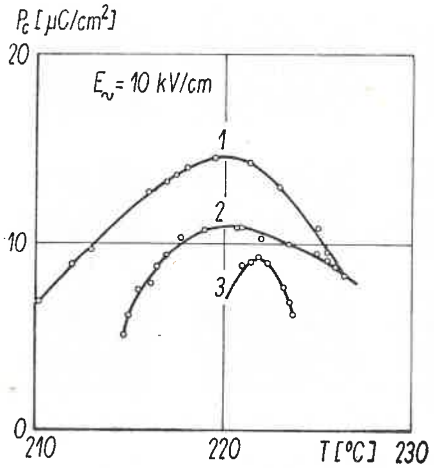

Fig. 6. Temperature dependence of total polarization of nonirradiated $PbZrO_3$ sample (*1*), and samples irradiated with integrated pile neutron flux of 1.10^{18} n/cm² — (*2*) and 5.10^{18} n/cm² — (*3*)

4. *Discussion*

The reported changes in dielectric properties of lead zirconate are due to crystal lattice defects engendered by pile neutron irradiation. These are generally point defects such as vacancies and interstitials, atom interchanges, admixtures and their agglomerates, such as thermal and displacement spikes.

The pile neutron flux consisted chiefly of fast neutrons (of energy 1 MeV and higher) and thermal neutrons. The cross-section for fast neutrons is essentially the cross-section for elastic collision with crystal lattice atoms. Therefore, fast neutrons will produce a number of point defects. By elastic collision and resorting to certain approximations and the model of Kinchin and Pease [21, 22], we calculated the density of point defects created in lead zirconate by fast neutrons in an integrated pile neutron flux of 10^{19} n/cm^2. The cross-sections for neutron elastic scattering by the oxygen, zirconium and lead atoms were taken from Altomirado and Perkins [23] to be:

$$\sigma_{\mathrm{O}} = 5.52b$$

$$\sigma_{\mathrm{Zr}} = 6.9b$$

$$\sigma_{\mathrm{Pb}} = 4.6b.$$

The density of Frenkel defects was calculated as:

$$N_{\mathrm{O}} = 7.23.10^{20}\ \mathrm{cm}^{-3}$$

$$N_{\mathrm{Pb}} = 1.86.10^{19}\ \mathrm{cm}^{-3}$$

$$N_{\mathrm{Zr}} = 7.1.10^{19}\ \mathrm{cm}^{-3}.$$

For thermal neutrons, the most probable interaction with lattice atoms is the (n, γ) reaction:

$$ {}^{A}X + {}^{1}n \rightarrow {}^{A+1}X = \gamma, \qquad \text{(I)}$$

$$ {}^{A+1}X \rightarrow {}^{A+1}Y + \beta + \gamma. \qquad \text{(II)}$$

In this case, defects can be produced by

1. recoil of atoms which, on emitting a gamma cascade, return to the ground state after neutron capture (I),
2. recoil after beta emission (II),
3. admixture from the process of activation.

The admixtures introduced in $PbZrO_3$ by neutron activation process are ${}^{18}_{8}$F and ${}^{95}_{42}$Mo. In 1 cm^3 of $PbZrO_3$, the integrated pile neutron flux of 10^{19} n/cm^2 produces 3.10^{11} atoms of F–18 and 3.10^{15} atoms of isotope Mo-95. The order of the total defect density produced by thermal neutrons in an integrated pile neutron flux of 10^{19} n/cm^2 is 10^{18} cm^{-3}.

From a comparison with the density of defects introduced by fast neutrons, it is evident that the main changes in the properties of lead zirconate are due to the fast neutrons of the flux. Because of the small deviation from cubic structure in the antiferroelectric phase of lead zirconate ($c/a = 0.988$, amounting to about 1%), there is no ground for anisotropic formation of interstitials, and a uniform distribution of crystal lattice defects can be assumed.

The observed hysteresis loops in the vicinity of the transition temperature from antiferroelectric to paraelectric phase and the temperature dependence of the dielectric polarization can be interpreted on the basis of the mathematical model of antiferroelectrics proposed by Piekara [24]. The energy of the external electric field induces a shift in the polarization *versus* temperature curve of either antiferroelectric sublattice in the opposite direction. Accordingly, in the vicinity of the antiferroelectric phase transition a resultant polarization with a maximum can be obtained [25]. The defects created by neutrons reduce the action of the externally applied field. At the some external electric field strength, the shifts in $P(T)$ curves of the sublattices are smaller, and therefore the resultant polarization decreases. This fact was observed and is demonstrated in Fig. 5. Moreover, the present analysis shows that, for defected antiferroelectrics, the temperature range of induced polarization is also narrower and the temperature at which the hysteresis loop appears is shifted towards higher temperatures. These facts were observed in reality and are demonstrated in Figs 4 and 6. In an electric field of 10 kV/cm the hysteresis loop can be observed already from 220.5°C, whereas for samples irradiated with 5.10^{18} n/cm^2 the hysteresis loop appears only at 225.5°C. On the other hand, the defects engendered by neutron irradiation reduce the number of polar unit cells of either sublattice causing a decrease in the polarization of the sublattices and, consequently in the experimental dielectric permittivity value.

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