Application of measurements of internal friction amplitude dependences for tests of ceramic materials

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An aim of this work was to show possibilities of the application of internal friction (IF) measurements in investigations of processes taking place in ceramic materials responsible for dissipation of energy and an application of IF for an interpretation of maxima observed for the temperature dependences of the IF. For the measurements, ceramic specimens of a PZT type were used. Three peaks of IF, relaxation P_{R1}, P_{R2} and phase transition P_F, were observed for the IF temperature dependences obtained. In order to determine the mechanisms responsible for relaxation and phase transition peak formation, measurements of amplitude of internal friction (AIF) relationships were performed. An explanation of the $Q^{-1} = f(\varepsilon_{am})$ AIF dependences was made on the basis of the Granato–Lücke model.

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1 Introduction In order to widen the scope of applications of ceramic materials it is necessary to learn about the physical, chemical and mechanical properties, the real structure and relaxation properties of these materials. Detailed knowledge about relationships between chemical composition, crystal structure, electrophysical properties and domain structure enables one to obtain ceramics with even better properties. The rapid growth of modern investigation methods, mainly non-destructive ones, is observed in examinations of ceramic materials. Methods of mechanical spectroscopy are often used; the internal friction method in particular.

Internal friction (IF) is caused by irreversible energy losses occurring in solid bodies as a result of many processes in which crystal lattice defects participate. It is characterized by inelastic behaviour of bodies when external stresses act on them and it manifests in the form of losses of some energy of mechanical vibrations (a part of the mechanical energy changes into thermal energy) [1–3].

Much of the interest in the IF method in examinations of the real structure of ceramic materials is caused by the fact that, by observing macroscopic vibrations of speci-mens, information on the behaviour of a material at the atomic level can be obtained.

This method is characterized by high sensitivity to changes in the concentration of point defects, to interaction between defects of the crystal structure and to changes in the real structure of materials [4–6]. Examinations using the IF method can be conducted depending on [7, 8]:

– temperature at constant measurement frequency;

– frequency at constant temperature – infrasonic methods (10^{-4}–10 Hz), acoustic methods (10^2–10^4 Hz), ultrasonic methods (10^5–10^8 Hz), hypersonic methods (10^9–10^{11} Hz);

– deformation amplitude at constant temperature.

In the temperature relationships of IF obtained for ceramic materials, the presence of one, two or more maxima is observed (for $\omega\tau_n = 1$, where ω is the frequency of specimen vibrations and τ_n the relaxation time). In order to determine the mechanisms of processes occurring in ceramic materials and the mechanisms responsible for formation of the IF maxima, a series of other measurements should be carried out, e.g. measurements of temperature dependence of the electric permittivity and measurements of temperature dependence of the IF at different rates of

temperature changes and at different measurement frequencies [5, 9–11].

A method that enables one to determine precisely the mechanisms responsible for the formation of the IF peaks of the $Q^{-1}(T)$ dependences is the measurement of the $Q^{-1} = f(\varepsilon_{am})$ amplitude relationships of the internal friction (AIF). For a ferroelectric ceramic isothermal AIF measurements are made in the ferroelectric phase in the area of the occurrence of the IF peak maxima and in the paraelectric phase.

The aim of the work reported here was to show possibilities of an application of IF measurements in investigations of processes taking place in ceramic materials responsible for dissipation of energy and an application of IF for an interpretation of the maxima observed in the temperature dependences of the IF.

2 Materials and methods For the measurements, ceramic specimens of a PZT type were used with the following chemical compositions: specimen 1, $0.47PbTiO_3-0.51PbZrO_3-0.02[Pb(Cd_{0.5}W_{0.5})O_3]$; specimen 2, $Pb_{0.975}Ba_{0.01}Ca_{0.01}Sr_{0.005}(Zr_{0.52}Ti_{0.48})O_3 + 1.4$ wt% Bi_2O_3 + 0.3 wt% GeO; specimen 3, $(Pb_{0.9}Ba_{0.1})(Zr_{0.53}Ti_{0.47})O_3$ + 2 wt% Nb_2O_5.

Test specimens were obtained by conducting a synthesis reaction in the solid phase at 1223 K for 6 h in the first stage. The specimens thus obtained were then granulated and ground again. In the last stage the specimens were obtained by a free sintering method (specimens 1 and 3) at 1423 K within 6 h and by a hot pressing method (specimen 2) at 20 MPa pressure at 1400 K within 1 h. After completing the sintering process the specimens were ground, polished and then electrodes were positioned on their surfaces by a silver paste burning method. Specimens in the shape of cubicoid plates with dimensions $(30 \times 0.9 \times 1)$ mm³ were tested. An automatic relaxator of acoustic frequencies (RAK-3) was used for tests [12]. Measurements of IF depending on the $Q^{-1}(T)$ temperature during heating at a rate of 3 K/min and depending on the $Q^{-1}(\varepsilon_{am})$ deformation amplitude were made.

3 Results and discussion The IF temperature dependences obtained for specimens 1 and 2 are presented in Fig. 1. Three IF peaks, P_{R1}, P_{R2} and P_F, were observed in the IF temperature dependences obtained for specimen 1; two peaks, P_{R1} and P_F, were observed in the $Q^{-1}(T)$ dependences obtained for specimen 2. Measurements at different frequencies enabled us to determine that peaks P_{R1} and P_{R2} have relaxation character, because a change in the temperature orientation of their maximum with a change in the measurement frequency was observed. However, the P_F peak, for which stability of the temperature orientation is observed, is connected with a change from a ferroelectric phase into a paraelectric phase, for both $0.47PbTiO_3-0.51PbZrO_3-0.02[Pb(Ti_{0.5}Zr_{0.5})O_3]$ and $Pb_{0.975}Ba_{0.01}Ca_{0.01}Sr_{0.005}(Zr_{0.52}Ti_{0.48})O_3 + 1.4$ wt% Bi_2O_3 + 0.3 wt% GeO [9, 10, 13].
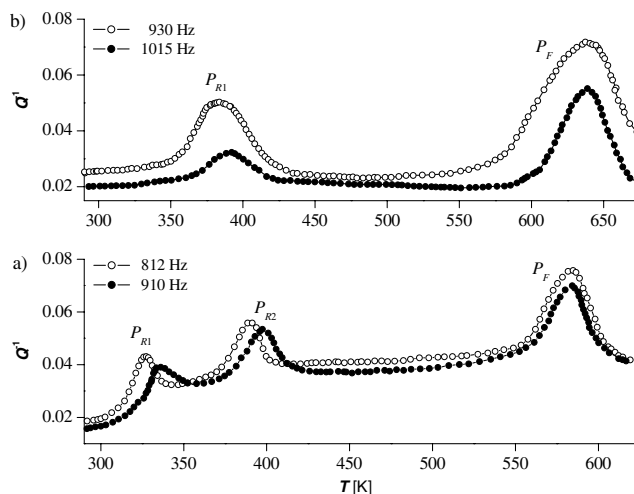

Figure 1 Temperature dependences of IF obtained for a) specimen 1 and b) specimen 2 during heating at a rate of 3 K/min for two measurement frequencies.

In order to confirm this hypothesis and to determine the mechanisms responsible for relaxation peak formation, measurements of AIF relationships were performed. The AIF relationships obtained at constant temperature (isothermal measurements) are presented in Fig. 2, as an example. This temperature corresponds with the peak maximum and also corresponds with the maximum intensity of the given phenomena: $T_{R1} = 327$ K for P_{R1}, $T_{R2} = 386$ K for P_{R2} and $T = 620$ K in the paraelectric phase.

Values of the deformation amplitude were determined on the basis of the following relationship [14]:

$$\varepsilon_{am} = \frac{4d}{\pi m l^2} \frac{\alpha_n^2}{f_r^2} \frac{C_e V_e \upsilon_1}{g \delta} \times 10^{-5} , \qquad (1)$$

where d is the specimen thickness (cm), α_n a constant (0.879), C_e the capacitance formed between a fixed elec-
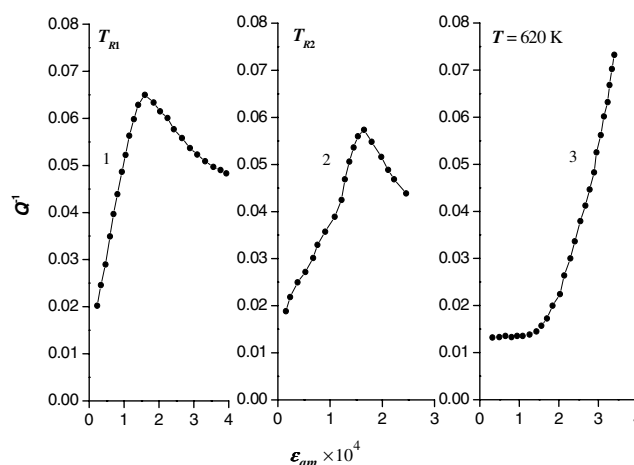

Figure 2 Amplitude dependences of the IF obtained for specimen 1: curve 1 was determined at 327 K, curve 2 at 386 K and curve 3 at 620 K.

trode and the grounded reed (pF), V_e the voltage on the electrodes (V), l^2 the surface of the vibrating part of the specimen (cm^2), υ_l the amplitude of the ac drive voltage (V), m the mass of the vibrating part of the sample (g), f_r the frequency of specimen vibrations (Hz), g the gap distance between the sample and electrode (cm) and δ the damping decrement.

An explanation of the course of the $Q^{-1} = f(\varepsilon_{am})$ dependence in Fig. 2 is made on the basis of the Granato–Lücke model [15, 16]. In this model, developed for metals, it is assumed that in the undeformed crystal dislocations are anchored by dislocation lattice nodes and by foreign atoms, at sufficiently high concentration of admixtures. Therefore, there are two characteristic lengths of the dislocation line (Fig. 3): the dislocation line length L_N between points of strong anchoring determined by the dislocation lattice and the dislocation line length L_C between points of weak anchoring determined by admixture atoms ($L_N \gg L_C$).

Under the influence of an external stress segments of the dislocation line contained between weak anchoring points begin to bend. If the external force exceeds the value of the force interacting between anchoring defects and the dislocation, detachment of the dislocation from the anchoring point takes place. Further increase in the stress leads to bending of a loop with the L_N length. Thus, there are two types of IF depending on the deformation amplitude: dependent and independent of ε_{am} (observed at the moment of the detachment of the dislocation from the weak anchoring points).

This model was used for tests of ceramic materials assuming that the domain walls in the ceramics, like dislocations in metals, can be anchored in strong and weak anchoring points (admixture atoms). The presence of the straight-line segment in curve 1 of Fig. 2, in accordance with the Granato–Lücke model, confirms the interaction of point defects and domain walls. It is also confirmed by values of activation energy H (characterizing the height of potential barriers, which atoms overcome during migration in the relaxation process) and a pre-exponential factor determined by the Arrhenius law and a condition on the IF peak maximum ($\omega\tau_n = 1$) for specimen 1 (Table 1). However, the present maximum confirms the presence of micro-deformations formed as a result of specimen deforma-
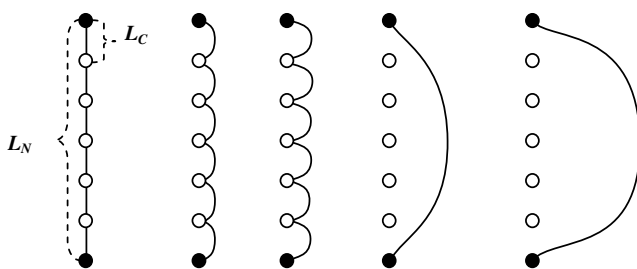
Table 1 Values of the activation energy H and pre-exponential factor τ_0 determined for the P_{R1} relaxation peak.

specimen type	H (eV)	τ_0 (s)
specimen 1 – peak P_{R1}	1.18 ± 0.02	$(4.38 \pm 0.04) \times 10^{-15}$
specimen 1 – peak P_{R2}	1.50 ± 0.02	$(8.05 \pm 0.04) \times 10^{-16}$
specimen 2 – peak P_{R1}	0.86 ± 0.02	$(1.43 \pm 0.04) \times 10^{-15}$

tion during vibrations and domain wall displacement in the ceramic materials [17].

Curve 2 in Fig. 2 shows the amplitude dependence of the IF in the area of peak P_{R2}. A decrease in the concentration of oxygen vacancies with an increase in the temperature and a decrease in internal stresses lead to an increase in domain wall mobility. This is confirmed by a change of the angle of inclination of the linear segment of curve 2 in the range of the amplitude deformations to $1.5 \times 10^{-4}\varepsilon_{am}$. The mechanism of the maximum formation for curve 2 is analogous to the maximum for curve 1.

At 620 K (the paraelectric phase) the IF amplitude dependence, which is connected with structure defects such as dislocations and grain boundaries, was also observed. The AIF curves observed in the ferroelectric phase have higher IF background than the curve observed in the paraelectric phase. In the ferroelectric phase several processes giving total contribution to the height of the IF background are responsible for dissipation of energy of mechanical vibrations in the ceramic materials. Its value is influenced by interactions originating from dislocations and grain boundaries, and also interactions coming from the domain structure [18]. A phase change of piezoceramics from the ferroelectric phase to the paraelectric phase is connected with the disappearance of the domain structure. The character of curve 3 for the amplitude dependence of the IF (Fig. 2) confirms the disappearance of the domain structure after exceeding the Curie temperature. For that reason a decrease in the value of the IF caused by a component related to the presence of the domain walls is observed. The linear segment of curve 3 in Fig. 2 in the range of low ε_{am} values is caused by the interaction of point defects only and dislocations present in the material.

The amplitude dependence of the IF, in accordance with the Granato–Lücke theory, is described by the following formula [15]:

$$Q^{-1} = \frac{C_1}{\varepsilon_{am}} \exp\left(-\frac{C_2}{\varepsilon_{am}}\right), \qquad (2)$$

where ε_{am} is the amplitude of deformations. Constants C_1 and C_2 can be determined from the relationships

$$C_1 = \frac{4\Omega(1-\nu)\,\Lambda L_N^3}{\pi^4 L_C}\,C_2\,, \qquad (3)$$

$$C_2 = \frac{Ka_0\delta_n}{L_C}\,, \qquad (4)$$

Figure 3 Diagram of the mechanism describing the Granato–Lücke model: ○, point of weak anchoring; ●, point of strong anchoring.

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where Ω is a factor characterizing the total contribution of dislocations located in different slip planes, K a constant taking into account anisotropy of elasticity coefficients and orientation of the specimen in relation to the stress applied, a_0 a constant of the crystal lattice, δ_n a factor characterizing maladjustment of atom rays of the matrix and dissolved admixtures, ν Poisson's coefficient and Λ the dislocation density.

Multiplying Eq. (2) on both sides by the deformation amplitude ε_{am} we obtain an equation of the form

$$Q^{-1} \cdot \varepsilon_{am} = C_1 \exp\left(-\frac{C_2}{\varepsilon_{am}}\right), \tag{5}$$

which, after finding the logarithm and simple transformation, has the form

$$-\ln\left(Q^{-1} \cdot \varepsilon_{am}\right) = \frac{C_2}{\varepsilon_{am}} - \ln C_1. \tag{6}$$

From Eq. (6) it can be seen that $\ln\left(Q^{-1} \cdot \varepsilon_{am}\right)$ depends linearly on $1/\varepsilon_{am}$. By plotting $-\ln\left(Q^{-1} \cdot \varepsilon_{am}\right)$ versus $1/\varepsilon_{am}$, C_2 values can be read directly from the diagram (Fig. 4). $C_2 = 0.69 \pm 0.04$ for specimen 1 and $C_2 = 0.87 \pm 0.04$ for specimen 2.

On the basis of the linear $-\ln\left(Q^{-1} \cdot \varepsilon_{am}\right) = 1/\varepsilon_{am}$ relationships obtained for the different ceramics tested, it can be said that the domain wall can be treated as a set of dislocation lines. It can also be determined if the observed peaks of relaxation character come from the same process or from different types of relaxation processes. The parallel character of the straight lines obtained for specimens 1 and 2 (Fig. 4) confirms the origin of peaks from the same type of relaxation process.

Measurements of the amplitude dependences of the IF can also be applied to evaluate changes in the distance between the points of weak or strong anchoring of the domain walls in the ceramic materials after treatment influencing the concentration of defects in the material in question, e.g. after vacuum-thermal treatment or after irradiation. Knowing the C_2 values and taking as the critical deformation value (which can be read directly from the $Q^{-1} = f(\varepsilon_{am})$ dependence) $\varepsilon_{kr} = b/L_N$ (where b is the Burger's vector), equal to a value of the stress needed to detach the domain wall segments from strong anchoring points, information on changes in the length of L_N, L_C dislocation lines and changes in the domain wall density can be obtained.

Subjecting ceramic materials to vacuum-thermal treatment or irradiation changes the concentration of defects which can anchor weakly or strongly the domain walls. Irradiation of ceramics with γ-radiation causes the introduction of additional point defects anchoring the domain walls. In ceramics of PZT type there are predominantly oxygen vacancies, because oxygen atoms, present in the structure of perovskite type, are susceptible to movements as a result of bombardment, e.g. with an integral stream of the γ-radiation quanta [5, 19, 20].

The temperature dependences of the IF for specimen 3 obtained before and after γ-irradiation with dosage of 5 R and 20 R are presented in Fig. 5. The ^{192}Ir isotope was the source of radiation. The $Q^{-1} = f(\varepsilon_{am})$ dependences for specimen 2 are presented in Fig. 6. Three IF peaks are observed: P_{R1}, connected with the interaction of defects and domain walls; P_{R2}, connected with viscoelastic movement of the domain walls; and P_F, connected with a phase transformation from the ferroelectric phase to the paraelectric phase and the simultaneous change of the tetragonal structure into a regular one. Those mechanisms were discussed in detail in earlier works [21−23]. The H and τ_0 values confirm also the mechanisms of the peak formation (Table 2).
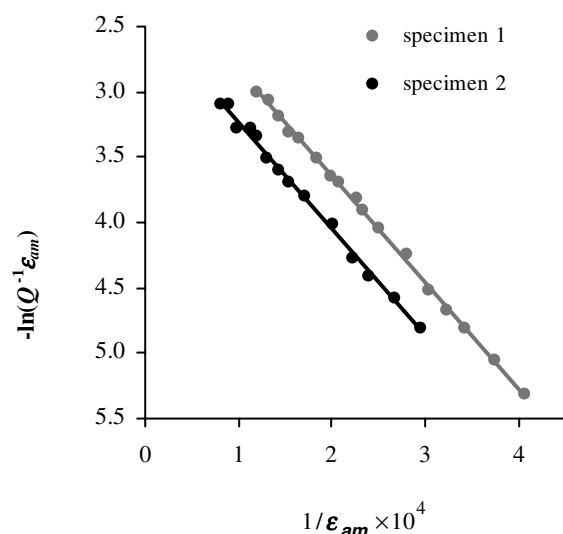

Figure 4 Plots of $-\ln\left(Q^{-1} \cdot \varepsilon_{am}\right)$ versus $1/\varepsilon_{am}$ obtained at the temperature of the P_{R1} peak for specimens 1 and 2.
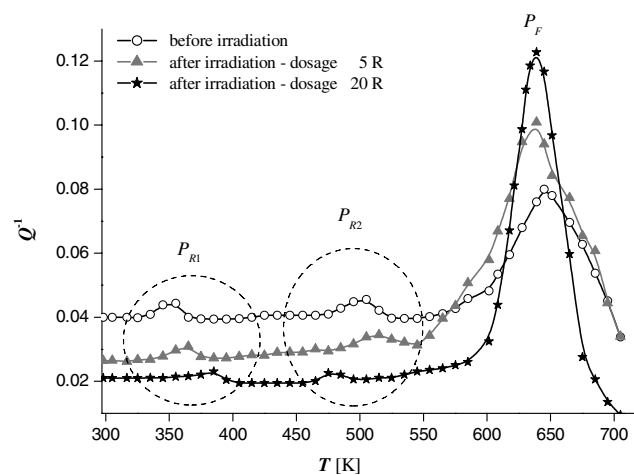

Figure 5 Temperature dependences of the IF obtained during heating of specimen 3 before and after irradiation for different dosages of γ-radiation from 0 R to 20 R.
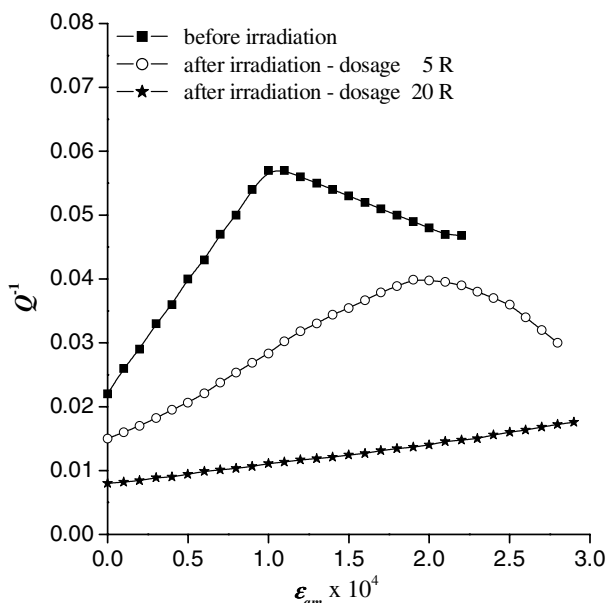
Figure 6 $Q^{-1} = f(\varepsilon_{am})$ dependences obtained at room temperature for specimen 3.

Table 2 Values of the activation energy H and pre-exponential factor τ_0 determined for specimen 3 for the P_{R1} relaxation peak.

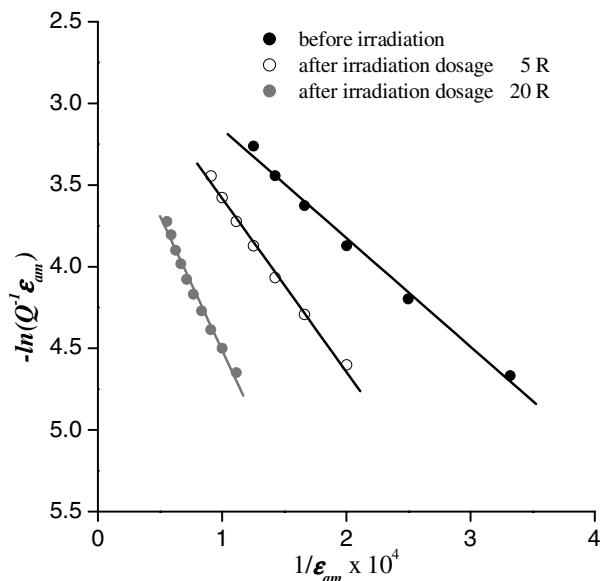| dosage (R)	H (eV)	τ_0 (s)
0	1.14 ± 0.02	$(6.81 \pm 0.04) \times 10^{-15}$
5	0.98 ± 0.02	$(7.72 \pm 0.04) \times 10^{-16}$
20	0.60 ± 0.02	$(3.06 \pm 0.04) \times 10^{-16}$

Figure 7 Granato–Lücke diagrams obtained on the basis of curves of the IF amplitude dependences for specimen 3.

Table 3 Values of the coefficient C_2 and length L_C/L_{C0} for specimen 3 before and after the irradiation with different dosages.

dosage (R)	before irradiation	5	20
coefficient C_2	0.67 ± 0.04	1.06 ± 0.04	1.63 ± 0.04
L_C/L_{C0}	1.00	0.63	0.41

From Fig. 6 it can be seen that the $Q^{-1} = f(\varepsilon_{am})$ curves show linear segments in the area of small amplitudes of deformation; thus they can be analysed on the basis of the Granato–Lücke model. For bigger ε_{am} deformations on the $Q^{-1} = f(\varepsilon_{am})$ curve the characteristic maximum, which disappears at higher dosages of radiation, is visible. In the case of the specimen irradiated with the highest dosage of 20 R the linear $Q^{-1} = f(\varepsilon_{am})$ dependence is observed over the whole range of the ε_{am} deformations. A decrease in the value of the IF background from 0.022 for the non-irradiated specimen to 0.008 for that radiated with a dosage of 20 R is observed simultaneously with an increase in the radiation dosage. This is caused by a decrease in mobility of the domain walls as a result of introducing additional point defects anchoring the domain walls.

With an increase in the irradiation dosage the Granato–Lücke diagrams have progressively higher values of the C_2 direction coefficient, which results in shortening of the L_C segment (Fig. 7, Table 3). This fact points to a greater number of anchoring points of the domain walls, a greater number of point defects introduced by irradiation, leading to (for further increase in dosage) a change in the character of interactions influencing P_{R1} formation in specimen 3. Denoting as L_{C0} the distances between points of weak anchoring of the domain walls in the non-irradiated ceramics, and L_C those in the irradiated ceramics, it is possible to follow changes in those distances as a result of introducing additional effects on irradiation.

4 Summary and conclusions Investigations of the amplitude dependences of the IF and their analysis using the Granato–Lücke model enable one to obtain much important information on processes taking place in ceramic materials. They give information on changes in distribution of the anchoring points of the domain walls as a result of changes in the defect concentration after different treatment processes of a material (e.g. irradiation) contributing to learning about changes taking place in the real structure of ceramics. The AIF measurements allow precise specification of the processes responsible for formation of the relaxation peaks of the IF and determining factors that have an influence on the IF background. They constitute a very precise tool to analyse temperature dependences of the IF. They enable one to follow changes in mobility of the domain walls in ceramic materials.

Measurements of the amplitude dependences of the IF also enable one to determine values of the critical deformation ε_{kr} corresponding to the value of stress needed for detachment of the domain wall from strong anchoring points.

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