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STRUCTURAL, OPTICAL, AND DIELECTRIC INVESTIGATIONS OF THE RELAXOR **PLZT** 9,75/65/35 CERAMICS IRRADIATED BY HIGH-CURRENT PULSED ELECTRON BEAM

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INTRODUCTION

Transparent ceramics of lanthanum modified lead zirconate - titanate PLZT X/65/35 has been extensively studied because of their excellent optical, dielectric, electrooptical and piezoelectric properties [1, 2]. Ceramics of composition line PLZT 7÷12/65/35 possessing a broad set of unusual properties belongs to the ferroelectric relaxors characterized by a wide frequency dependent maximum of the dielectric permittivity [1], and a complex phase diagram [2], incorporating a morphotropic phase boundary between the high and low temperature rhombohedral phases. All these properties are a subject of interest for applied and fundamental investigations. Such a variety of properties of PLZT ceramics is associated with the existence of polar nanoregions causing spontaneous polarization. Switching kinetics in the external field of polar nanoclusters determines the nature of phase transition from the ferroelectric polar state to the paraelectric nonpolar one [3, 4, 5]. The study of influence of different external actions on the phase transitions as well as on the behavior of polar nanoregions leading to the change of metastable state, is of great interest. The irradiation effects caused by particles with various ionizing ability: γ-rays, electrons, multicharge ions, neutrons [7, 8] can be referred to the external actions as well. The kind of defects in lattice depends on the type of irradiating particles and by studying their influence on ferroelectric properties it is expected to reveal the excitation and damage mechanisms of the local polar nanoregions. Exposure of transparent PLZT ceramics to static radiation field, such as by γ - rays, electrons, multycharge ions, neutrons leads to an essential decreasing of interaction forces between the ferroelectrically active dipoles, simultaneously reducing a ferroelectric distortion that gives rise to a gradual shift of the absorption edge in optical spectra to longer wavelengths, decrease of polarization and dielectric permittivity as well as in broadening of phase transition [9]. However, recently influence of the lattice structural and dynamic transformation of PLZT ceramics caused by the pulsed electron and ion beams irradiation treatment was found [10]. The aim of this work is to study the effect of pulsed electron beam irradiation on structural, optical and dielectric properties of relaxor PLZT 9,75/65/35 ceramics. One of the most effective and informative method to investigate the nature of the pulsed electron beam interaction with a sample is combined X-ray and neutron diffraction methods, dielectric and IR spectroscopic studies. These methods allow to obtain not only the most completed information about the lattice deformation, but also on lattice dynamics in polar nanoregions.

EXPERIMENTAL

Ceramic samples of PLZT 9,75/65/35 were prepared by a two-stage hot-pressing technique from chemically coprecipitated raw materials [3]. The IR reflectivity measurements in the spectral range 100 - 2000 cm^{-1} were made by using Bruker IFS66v Fourier transform spectrometer at room temperature. Neutron diffraction data were carried out by using High resolution Fourier diffractometer at the IBR-2

Neutron diffraction data were carried out by using High resolution Fourier diffractometer at the IBR-2 pulsed nuclear reactor. X-ray diffraction measurements were done on the DRON - 2 M diffractometer by using CuK_α radiation. Dielectric permittivity ε(T) were measured at frequency 1 kHz using an E7-8 instrument. Sputtered silver electrodes on ceramics were exploited. The parameters of electron beam produced by accelerator facility as a source were: energy E = 250 keV, current density J = 1000 A, pulse duration τ=300 ns, beam density - 10^{15} electrons/cm^2 per pulse.

STRUCTURAL DATA

The X-ray powder diffraction measurements were carried out on the unirradiated, irradiated by 1500 electron pulses and on the annealed at 500^0C PLZT 9,75/65/35 ceramic to find out the correlation changes between the phonon modes and the static position of ions in the lattice under irradiation. Figures 1, 2 show some X-ray diffraction lines of PLZT 9,75/65/35 ceramic before and after irradiation and after annealing. The instrumental error of X-ray diffractometer is equal to ± 0,002 deg.

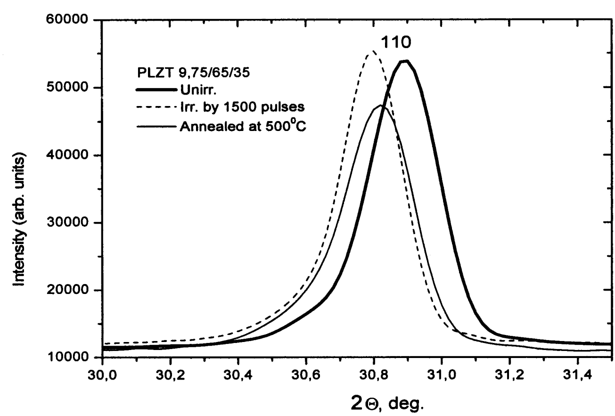


Figure 1. The profile of diffraction lines (110) in PLZT 9,75/65/35 ceramics before and after irradiation and after annealing at 500^0C.

It should be noted that the shape of (222) diffraction line is most sensitive to the unit cell distortions. In our case the peaks for unirradiated, irradiated and annealed samples mentioned above don't have any split that could correspond to the "quasicubic" structure ($\alpha \approx 90^0$) [11]. X-ray diffraction data (see Table 1 and Fig. 1, 2) coinside rather well with those obtained by Keve [12].

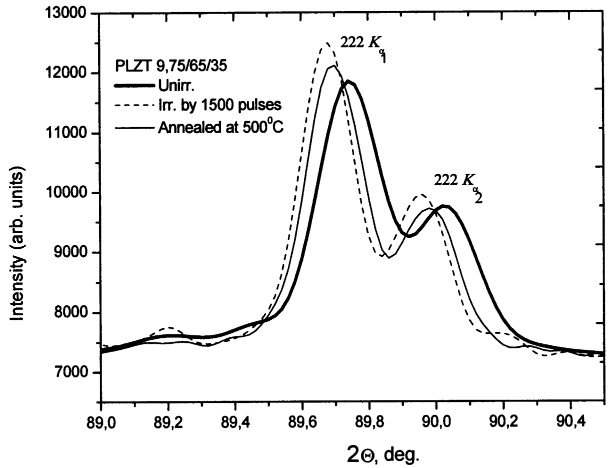


Figure 2. The profile of diffraction lines (222) in PLZT 9,75/65/35 ceramics before and after irradiation and after annealing at 500^0C.

According to the Table I and Fig. 1, 2 the irradiation of PLZT ceramic by using the pulsed electron beam leads to the shifts of the main X-ray reflections to the smaller angles 2Θ.

Table 1. Unit cell parameter values (in Å) of PLZT 9,75/65/35 ceramic before and after irradiation and isochronic annealing.

Initial lattice parameters	**Parameters after irradiation by 1500 pulses**	**Parameters after annealing at 500^0C**
a = 4,087 (4,0801)	a = 4,100	a =4,096
b = 4,087 (4,0801)	b = 4,100	b = 4,096
c = 4,087 (4,0801)	c = 4,100	c = 4,096
$V_{lattice}$=68,27 (67,923)	$V_{lattice}$= 68,94	$V_{lattice}$= 68,73

It means that electron beam irradiation in studied ceramic samples course change of the lattice parameter and increase of the lattice volume. In addition, the unit cell symmetry and single phase state of irradiated and annealed samples are preserved.

Neutron diffraction results (see Table I; in brackets) correlate well with X-ray diffraction data (carried out only on unirradited sample) (see Table I). It is interesting to note that after annealing of irradiated PLZT 9,75/65/35 ceramic at 500^0C the both unit cell parameters and lattice volume are not completely restored (Fig. 1, 2, Table I) as well as position of phonon modes and their intensities - from IR spectroscopy data (Table II, and Fig. 2, 3).

INFRARED SPECTROSCOPY

Infrared reflectivity spectra were obtained in the region 100 – 2000 cm^{-1} for unirradiated and irradiated by 1500 pulses PLZT 9,75/65/35 ceramic as well as for annealed at 500^0C. In Fig. 3 the polar mode reflection bands (below 800 cm^{-1}) are showed. All IR reflection spectra were measured at room temperature. Our IR reflectivity spectra for unirradiated PLZT 9,75/65/35 ceramic agree fairly well with those obtained in Refs. [13,14].

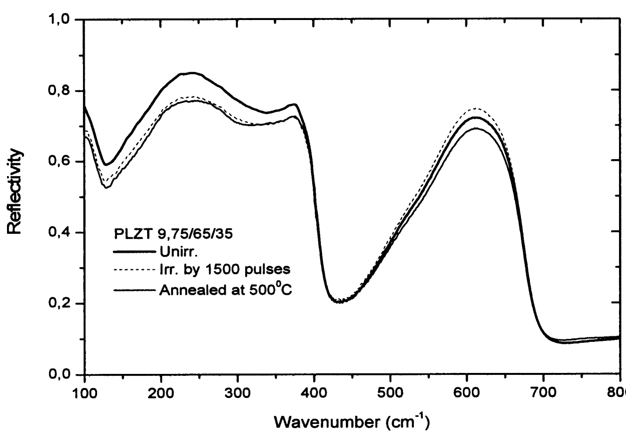


Figure 3. IR reflectivity spectra before and after irradiation and annealing in PLZT 9,75/65/35 ceramics at room temperature.

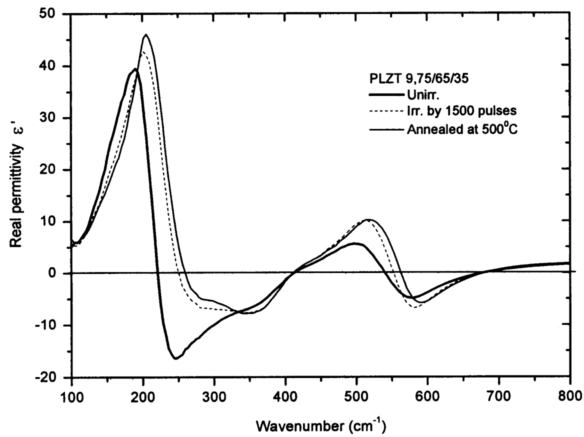
The reflectivity spectra were fitted with the well known formula [15]:

$$R(\omega) = \left| \frac{\sqrt{\varepsilon^*(\omega)} - 1}{\sqrt{\varepsilon^*(\omega)} + 1} \right|^2 ,$$

where $\varepsilon^*(\omega)$ denotes complex dielectric permittivity which is equal

$$\varepsilon^*(\omega) = \mathrm{Re}\,\varepsilon\ (\omega) + \mathrm{Im}\,\varepsilon\ (\omega) .$$

To determine the real and imaginary dielectric permittivity, the Kramers - Kronig relations have been used. In case of lattice's reflection the maxima in $\omega \cdot Im(-\varepsilon^{-1}) = f'(\omega)$ and $\omega \cdot Re(\varepsilon)$ dependencies correspond to the transverse and longitudinal phonon modes, and half-widths relate to the damping parameter γ_{LO} and γ_{TO}, respectively. Thus, the transverse and longitudinal phonon modes, the damping parameters and oscillators strength were obtained using by the Kramers - Kronigs method as well as the dispersive analysis by using Lorenz oscillators model provided. The resulting $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$ spectra (Fig. 4, 5) demonstrate the calculated dependencies of Re(ε) and Im(ε) of the unirradiated, irradiated and annealed PLZT 9,75/65/35 ceramics, respectively.



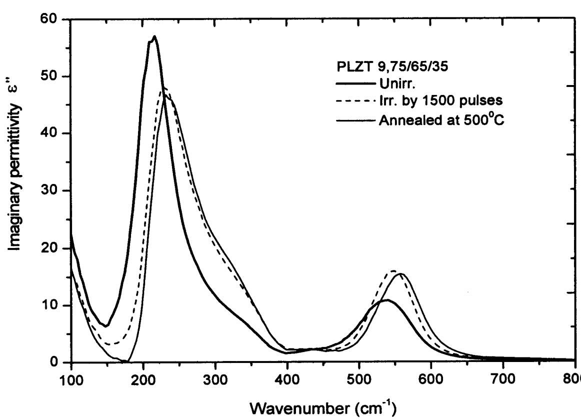


Figure 4. Real and imaginary part of dielectric permittivity before and after irradiation and annealing of PLZT 9,75/65/35 ceramics obtained from the fit of IR reflectivity.

The fitted mode parameters for the same samples are listed in Table II. The assignment of normal-mode spectrum in PLZT 9,75/65/35 has been achieved from [17].

Table 2. Mode parameters obtained from the fit of reflectivity spectra using Kramers-Kronig expressions of unirradiated (**Un**), irradiated (**Irr**) and annealed (**An**) PLZT 9,75/65/35 ceramic. All mode parameters are expressed in cm^{-1}.

ω_{TO}			γ_{TO}			ω_{LO}			γ_{LO}			$\Delta\varepsilon$		
Un	**Irr**	**An**	**Un**	**Irr**	**An**	**Un**	**Irr**	**An**	**Un**	**Irr**	**An**	**Un**	**Irr**	**An**
197	208	205	44	49	44	232	241	238	16	19	18	801	872	858
315	336	320	56	58	52	405	416	408	21	25	24	420	500	486
525	531	535	45	43	47	633	628	535	15	39	16	582	608	585
564	567	572	28	25	33	688	681	803	18	26	17	295	333	307

On the base of these results (from Fig. 4, 5 and Table II), one can get that torsion modes Ti/Zr – O_2 as well as bend ones O – (Ti, Zr) – O at 232 cm^{-1} and the stretch modes Ti/Zr – O in the range of 530 ÷ 580 cm^{-1} are slightly shifted towards the higher wavelength region about 7÷16 cm^{-1}. The change of intensities of above mentioned modes can be related to variation of oscillator strength. They could be attributed to appearance of an essential intrinsic radiation-induced bias field, which is obviously responsible for the change position of ions in lattice after exposure (see Table I). However, after annealing at 500^0C both the phonon mode parameters and those intensities are only partly restored.

DIELECTRIC PROPERTIES

Temperature behavior ε (T) at 1 kHz for unirradiated, for the same irradiated and annealed sample (Fig.6) reveals radiation-induced shift of maximum temperature T_m of dielectric permittivity ε as well as in value and in the shape of the curve.

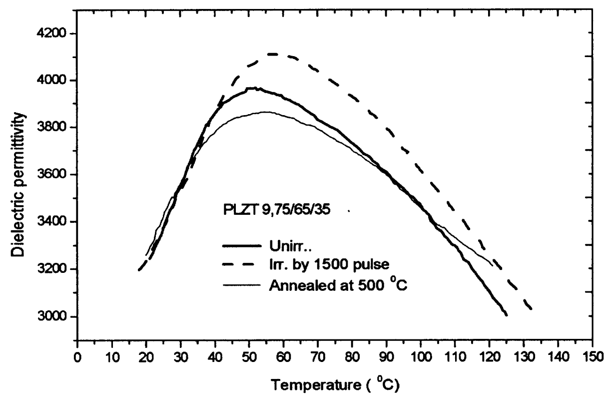


Figure 5. Dielectric permittivity of the PLZT 9,75/65/35 ceramics: 1 – unirradiated (T_m = 52^{0}C); 2 – irradiated (T_m = 59^{0}C); after annealing at 500^{0}C (T_m = 55^{0}C). f = 1 kHz.

After pulsed electron irradiation the behavior of ε(T) shows an increase of dielectric constant ε, a small broadening of ε(T) maximum and a shift T_m of higher values (about 7^{0}C). However, after annealing at 500^{0}C the ε(T) behavior is not completely restored compare to that for unirradiated sample while the values essentially decreases.

RESULTS AND DISSCUSSION

We have observed significant changes in X-ray diffraction data as well as in IR spectra and dielectric properties of relaxor PLZT 9,75/65/35 ceramics after irradiation with electron pulses. It should be noted that changes of structural parameters (see Table I) for unirradiated, irradiated and annealed samples correlate well with ones of phonon modes behavior for the same sample (Fig. 4, 5 and Table II). With regard to dielectric properties, we have found that pulsed electron irradiation leads to significant effects showing growth of ε value and the shift T_m to higher temperature.

In literature there is a lack of data on high-current pulsed electron irradiation of ferroelectrics. However, there are many articles devoted to different kinds of investigations of ferroelectrics by using stationary irradiation sources [7-10]. They do not show similar results as obtained by using the high-current pulsed charge particles beam with duration τ = 300 nsec. Summarizing the results mentioned above it is possible to suppose that this effect of pulsed electrons relates in value to the duration of high-current pulsed electron beam and characteristic relaxation times of secondary electrons produced in result of ionizing losses of initial electrons beam, which penetrate into the sample. In this case obviously a trapping of electrons on vacancies in the A and B sublattices take place. It has been calculated by us, that the penetration depth of the pulsed electrons with energy E_e = 250 keV is equal to about 200 μm. Thus, it is easy to find the electron density within their penetration depth in the sample. Taking into account the value of current density $J_e = 1000\ A/cm^2$, duration of pulses $\tau = 300$ nsec, the quantity of pulses and penetration depth R = 150 μm, the density of electrons is equal to about $n_e \approx 5\cdot10^{19}$.

Thus, more probable that the increase of electron density within the penetration depth in the sample can lead to the charge transfer – the change of ion charge, e.g., La^{3+} and Ti^{4+} by La^{2+} and Ti^{3+}, Ti^{2+} as well as the appearance of charged radiation-induced vacancies in A and B sublattice causing significant intrinsic fields in the sample. The latter assumptions correlate well with obtained above X-ray diffraction data (an increase of unit cell volume) and the shift of the stretch modes Ti/Zr – O in the range 530 ÷ 580 cm^{-1} towards the high wavelength region in IR reflectivity spectra. The change of intensities of this modes can be related to additional ordering of Ti (Zr) and oxygen ions in B – O sublattice. Regarding dielectric measurements, both dielectric permittivity maximum T_m shift to higher temperature and an increase of dielectric constant ε could be attributed to an increase of domain walls mobility [18,19] and, as a consequence, some transformation of domain structure.

In order to reveal the nature of the electron pulse radiation – induced effects on of PLZT X/65/35 relaxor ceramic more detailed studies, including X-ray and neutron diffraction experiments as well as UV, visible and IR spectroscopy and extended investigations of dielectric properties are in progress.

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Структурные, оптические и диэлектрические исследования релаксорной PLZT 9,75/65/35-керамики, облученной сильноточным импульсным пучком электронов

Проведены структурные, оптические и диэлектрические исследования релаксорной $(Pb_{(1-x)}La_x)(Zr_{0,65}Ti_{0,35})_{1-x/4}O_3$-керамики ($x=9{,}75\%$), облученной сильноточным импульсным электронным пучком. Электронный пучок имел следующие параметры: энергию $E_e = 250$ кэВ, плотность тока $J_e = 1000$ А/см^2, длительность импульса $\tau = 300$ нс, плотность пучка 10^{15} электронов/см^2 за один импульс. Получены ИК-спектры отражения в области 100–2000 см$^{-1}$ для необлученного образца и облученного 1500 импульсами, а затем отожженного при $t=500\,^\circ$C. Из рентгеноструктурных измерений и данных ИК-спектроскопии обнаружен эффект перестройки перовскитной ABO_3-структуры облученной PLZT-керамики и как следствие этого — смещение поперечных и продольных фононных мод, измерение сил осцилляторов и величин их затухания. Эффекты радиационного воздействия изучены по температурной зависимости диэлектрической проницаемости ε в области фазового перехода. Анализируются механизмы эффекта импульсного электронного облучения для релаксорной PLZT-керамики.

Работа выполнена в Лаборатории физики частиц ОИЯИ.

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Structural, Optical, and Dielectric Investigations of the Relaxor PLZT 9,75/65/35 Ceramics Irradiated by High-Current Pulsed Electron Beam

First time comprehensive study of high-current pulsed electron irradiation effects on the structural, optical and dielectric properties of relaxor $(Pb_{(1-x)}La_x)(Zr_{0,65}Ti_{0,35})_{1-x/4}O_3$ ceramics with ($x=9{,}75\%$) has been provided. The electron beam had the following parameters: energy $E_e=250$ keV, current density $J_e=1000$ A/cm^2, pulse duration $\tau=300$ ns, density 10^{15} electrons/cm^2 per pulse. Infrared reflectivity spectra in the region of 100–2000 cm^{-1} were obtained in virgin, irradiated by 1500 pulses and annealed up to $t=500\,^\circ$C ceramics. The reconstruction of perovskite ABO_3 structure in irradiated samples has been studied by complex use of X-ray and neutron scattering and IR spectroscopy techniques revealing the changes in transverse and longitudinal phonon modes, oscillators strength and damping of modes. Radiation effects on temperature behaviour of dielectric permittivity ε in the region of phase transition were studied. The possible mechanisms of pulsed electron irradiation effect in relaxor PLZT ceramics are discussed.

The investigation has been performed at the Laboratory of Particle Physics, JINR.

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