PIEZOCERAMICS UNDER ELECTRON IRRADIATION

Irinela CHILIBON[1]

Lucrarea prezintă aspecte privind comportarea piezoceramicelor PZT la iradiere cu electroni de putere scazuta. Probele PZT au fost iradiate într-un accelerator liniar de electroni cu doze diferite de electroni, şi anume: 10 kGy; 15 kGy; 20 kGy; 25 kGy. Aceste ceramice îşi schimbă puţin performanţele după iradierea cu electroni de putere scazută, însă la 25 kGy constantele piezoelectrice de sarcină şi de tensiune cresc mai mult. Totuşi, descompunerea parţială a PZT ar putea să apară la iradierea cu electroni de putere ridicată şi în consecinţă creşterea coeficienţilor de pierdere. O remarcă, probele experimentale iradiate prezintă proprietăţi dielectrice şi piezoelectrice cu variaţii mici, iar coeficienţii de cuplaj descresc chiar la doze mici de iradiere (sub 25 kGy). Rezultatele obtinute constituie punctul de plecare pentru proiectarea de materiale ceramice superioare cu parametrii îmbunătăţiţi, optime pentru aplicaţiile diverse ale traductoarelor piezoelectrice.

Paper presents aspects concerning the behaviour of PZT piezoceramics at low power electron irradiation. The PZT samples were irradiated into a linear accelerator of electrons with different electron doses, namely: 10 kGy; 15 kGy; 20 kGy; 25 kGy. These ceramics change slightly their performances after low power electron irradiation, but at 25kGy the piezoelectric charge and voltage constants increase more. However, PZT partial decomposition could occur at high power electron irradiation doses and consequently the loosing coefficients enhance. As remark, the experimental irradiated PZT samples present piezoelectric and dielectric properties with small variations, and the coupling coefficients decrease even at small irradiation doses (below 25 kGy). The obtained results could be an excellent starting point in designing superior ceramic materials with improved parameters, suitable for various piezoelectric transducers applications.

Keywords: piezoceramic, PZT, electron irradiation, electron accelerator

1. Introduction

Piezoceramics represent a well-proven technology for fabrication of electromechanical transducers. However, despite their widespread applications there are still many aspects of their behaviour that poorly understood this is particular true of nonlinear effects that characterize their dielectric, elastic, and piezoelectric properties [1]. The piezoceramics are crystallite conglomerate ferroelectrics materials with random orienting and the piezoceramic materials

[1] Researcher, National Institute of R&D for Optoelectronics, INOE-2000, Bucharest-Magurele, ROMANIA, e-mail: qilib@yahoo.com

$Pb(Zr_xTi_{1-x})O_3$ are solid solutions, obtained in the classical technology [2], utilizing oxide powders and impurities as base materials. The properties of piezoceramics are function of the preparation process [3] and the fluctuations may be caused by inhomogeneous chemical composition, mechanical differences in the forming process, varying shrinkage and chemical modification during firing, and by varying response to the poling treatment. A high degree of process control is essential in the manufacture of piezoceramics in order to insure a consistent product with respect to electrical and mechanical properties [4]. PZT ceramics are piezoelectric material with the perovskit structure. The internal stress of PZT is induced by the para- to ferro-electric phase transition at the Curie point during cooling process after firing and the additional anisotropic internal stress is induced in perpendicular direction. Their physical, chemical, and piezoelectric characteristics can be tailored to specific applications. These materials are used as electromechanical transducers in various applications.

The purpose of this study is to investigate the dependence of dielectric, piezoelectric and mechanical properties of hard PZT ceramic at electron irradiation dose variation, produced by an electron linear accelerator.

2. Piezoelectric coefficients and relations

Piezoelectric ceramics produce an electrical charge when a load is applied and deformation occurs. Piezoelectric ceramics can also produce force or deformation when an electrical charge is applied. A piezoceramic is therefore capable of acting as either a sensing or transmitting element, or both. Since piezoceramic elements are capable of generating very high voltages, they are compatible with today's generation of solid-state devices - rugged, compact, reliable, and efficient. Relationships between applied forces and the resultant responses depend upon: the piezoelectric properties of the ceramic; the size and shape of the piece; and the direction of the electrical and mechanical excitation.

To identify directions in a piezoceramic element, three axes are used (Figure 1). These axes, termed 1, 2, and 3, are analogous to X, Y, and Z of the classical three dimensional orthogonal set of axes. The polar, or 3 axis, is taken parallel to the direction of polarization within the ceramic. This direction is established during manufacturing by a high DC voltage that is applied between a pair of electroded faces to activate the material. In shear operations, these poling electrodes are later removed and replaced by electrodes deposited on a second pair of faces. In this event, the 3 axis is not altered, but is then parallel to the electroded faces found on the finished element. When the mechanical stress or strain is shear, the subscript 5 is used in the second place.

Piezoelectric coefficients with double subscripts link electrical and mechanical quantities. The first subscript gives the direction of the electrical field associated with the voltage applied, or the charge produced. The second subscript gives the direction of the mechanical stress or strain. Several piezoceramic material constants may be written with a "superscript" which specifies either a mechanical or electrical boundary condition. The superscripts are T, E, D, and S, signifying: T = constant stress = mechanically free; E = constant field = short circuit; D = constant electrical displacement = open circuit; S = constant strain = mechanically clamped.

As an example, K^T_3 expresses the *relative dielectric constant* (K), measured in the polar direction ($_3$) with no mechanical clamping applied.

The electrical behaviour of an unstressed medium under the influence of an electric field is defined by two quantities - the field strength *E* and the dielectric displacement *D.* Their relationship is:

$$D = \varepsilon E \qquad (1)$$

in which ε is the material permittivity.

The mechanical behaviour of the same medium at zero electric field strength is defined by two mechanical quantities - the stress applied *T* and the strain *S*. The relationship here is:

$$S = sT \qquad (2)$$

in which *s* denotes the compliance of the medium. Piezoelectricity involves the interaction between the electrical and mechanical behaviour of the medium. To a good approximation this interaction can be described by linear relations between two electrical and mechanical variables:

$$S = s^E T + dE \qquad (3)$$
$$D = dT + \varepsilon^T E$$

The choice of the independent variables (*T* - mechanical, and *E* - electrical*)* is arbitrary. A given pair of piezoelectric equations corresponds to a particular choice of independent variables. In a similar way it is possible to arrive at the following formulae:

$$E = -gT + \frac{D}{\varepsilon^T}; \qquad S = s^D + gD \qquad (4)$$

$$E = -hS + \frac{D}{\varepsilon^S}; \qquad T = c^D S - hD \qquad (5)$$

$$D = dS + \varepsilon^S E\ ; \qquad T = c^E S - eE \qquad (6)$$

In these equations, S^D, S^E, ε^T, ε^S, d and g are the main practical constants. The superscripts to the symbols denote the quantity kept constant under boundary conditions. In reality, Eqs 3 to 6 are tensor equations with, in the general case, 3 electrical quantities (in the X, Y and Z directions) and 6 mechanical ones including shear about the three axes. So, of each piezoelectric parameter, up to 18 varieties can exist and are indicated by subscripts. For piezoelectric materials the direction of polarization is usually taken to be that of the Z-axis (direction 3) (see

Fig. 1). Methods of measurement and piezoelectric properties of ceramic materials and components are described by [5] – [8].

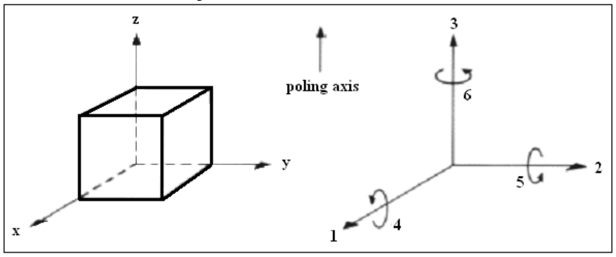

Fig. 1 Designation of the axis and directions of deformation

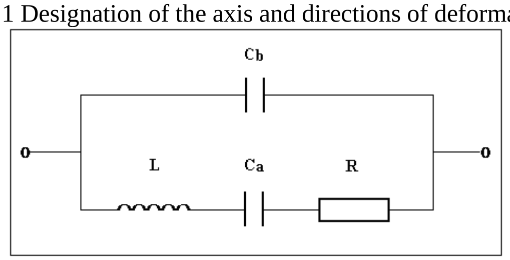

Fig. 2 Equivalent electrical circuit of PZT disc

The equivalent electrical circuit of PZT disc is a resonant circuit (Fig. 2) and is characterized by two frequencies: $\boldsymbol{f_s}$ and $\boldsymbol{f_p}$. At the series resonance, branch L - C_a is in resonance, the lower branch of the equivalent circuit diagram becomes low-resistive and the impedance shows a minimum $\boldsymbol{Z_{min}}$. At the parallel resonance, the branch L - (C_b + C_a) is in resonance, the resonant circuit becomes high-resistive and the impedance has a maximum $\boldsymbol{Z_{max}}$.

Modern impedance analyzers (e.g. HP 4192A) can be combined with a computer and programmed to find $\boldsymbol{f_s}$, $\boldsymbol{f_p}$, $\boldsymbol{Z_{min}}$ and $\boldsymbol{Z_{max}}$ The effective coupling factor $\boldsymbol{k_{eff}}$ then follows from the formula (Fig. 3):

$$k_{eff} = \sqrt{\frac{f_p^2 - f_s^2}{f_p^2}} \quad (7)$$

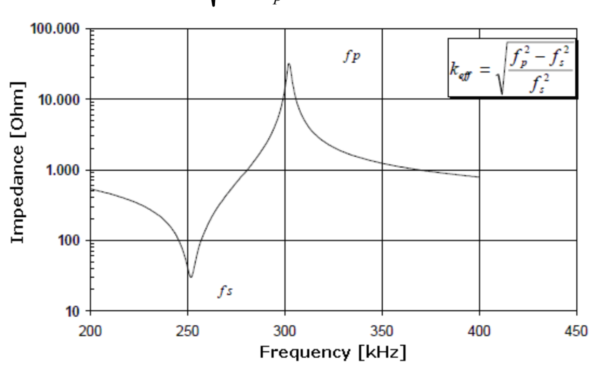

Fig. 3 Impedance at the planar resonance (measured at a disc ϕ 5 x 1 mm)

It is also possible to determine k_{eff} of more complicated devices like bimorphs or PZT discs or plates glued on some substrate. Depending on the construction different values of k_{eff} will be found. The translation to the *absolute* quality level is often very complicated or impossible. However k_{eff} is always a useful *relative* measure for the effectiveness of a device.

$$k_{eff}^2 = \frac{C_a}{C_b + C_a} \tag{8}$$

By using equations:

$$f_s = \frac{1}{2\pi}\sqrt{\frac{1}{LC_a}} \tag{9}$$

and

$$f_p = \frac{1}{2\pi}\sqrt{\frac{C_a + C_b}{L\ C_a C_b}} \tag{10}$$

This ratio can be expressed as a function of series- and parallel resonant frequency,

$$k^2 = \frac{f_p^2 - f_s^2}{f_p^2} \tag{11}$$

So it is possible to derive the coupling factor from these resonant frequencies. As an approximation, when *keff <<1* one may write:

$$k_{eff}^2 \approx 2\frac{f_p - f_s}{f_s} = 2\frac{\Delta f}{f_s} \tag{12}$$

The piezoelectric voltage constant ***g*** is defined as the electric field generated in a material per unit mechanical stress applied to it. Alternatively, it is the mechanical strain experienced by the material per unit electric displacement applied to it. The first subscript refers to the direction of the electric field generated in the material or to the applied electric displacement the second refers respectively to the direction of the applied stress or to the direction of the induced strain.

The piezoelectric charge constants ***d*** is defined as the electric polarization generated in a material per unit mechanical stress applied to it. Alternatively, it is the mechanical strain experienced by the material per unit electric field applied to it. The first subscript refers to the direction of polarization generated in the material (at $E = 0$) or to the applied field strength, the second refers respectively to the direction of the applied stress or to the direction of the induced strain.

The ***g*** and ***d*** constants of a material are inter-related by their dielectric constant. Thus

$$g = \frac{d}{k\varepsilon_0} \text{ or } g\,k\varepsilon_0 = d \tag{13}$$

where ***K*** is the dielectric constant and $\boldsymbol{\varepsilon_o}$ is the permittivity of space, 9 x 10^{-12} Farads per meter. For a given level of ***d*** constant, the ***g*** is high if the dielectric constant is low and vice-versa.

The compliance ***s*** of a material is defined as the strain produced per unit stress. It's the reciprocal of the modulus of elasticity. The first subscript refers to the direction of strain, the second to direction of stress. For example, the compliance ***s*** of a material determined for the piezoceramic plate is:

$$s_{11}^{E} = \frac{1}{4\rho f_r^2 L^2} \tag{14}$$

$$s_{11}^{D} = s_{11}^{E}\left(1 - k_{31}^2\right) \tag{15}$$

where $\boldsymbol{\rho}$ is the piezoceramic density, $\boldsymbol{f_r}$ is the resonance frequency, ***L*** is the thickness of disc.

The relation between d_{31}, k_{31} and s_{11} is the following:

$$d_{31} = k_{31}\sqrt{\varepsilon_{33}^{T} s_{11}^{E}} \tag{16}$$

Whereas the relative dielectric constant is strictly a material property, the capacitance is a quantity dependent on the type of material and its dimensions. The capacitance is calculated by multiplying the relative dielectric constant by the permittivity of free space ($\varepsilon_0 = 8.9 \cdot 10^{-12}\, farads/meter$) and ***A*** electrode surface area, then dividing by the ***t*** thickness separating the electrodes. Units are expressed in farads.

$$C = \frac{k\varepsilon_0 A}{t} \tag{17}$$

K_3 is related to the capacitance between the original poling electrodes. K_1 is related to the capacitance between the second pair of electrodes applied after removal of the poling electrodes for the purposes of shear excitation.

The mechanical losses can be determined from the mechanical quality or damping factor, $\boldsymbol{Q_M}$ (18).

$$\mathrm{Q_M} = \frac{f_a^2}{2\pi f_r Z_r C\left(f_a^2 - f_r^2\right)} \tag{18}$$

Where ***C*** is the low frequency capacitance and $\boldsymbol{Z_r}$ is the minimum impedance, $\boldsymbol{f_r}$ is the resonance frequency and $\boldsymbol{f_a}$ is the antiresonance frequency.

Also, when $Q_M > 3$, $\boldsymbol{Q_M}$ can also be determined approximately from the frequency response curve and the bandwidth at 3 dB ($f_2 - f_1$) as follows:

$$\mathrm{Q_M} = \frac{f_r}{f_2 - f_1} \tag{19}$$

3. Experiments and results

The piezoceramic materials under study are solid solutions of PZT (lead titanate zirconate) $Pb(Zr_xTi_{1-x})O_3$ obtained by classic technology in laboratory, using as raw materials oxide. Material selection should be based on the conditions of a given application. PZT ceramic is the active element into various piezoceramic transducers. Therefore, it is important to understand the behaviour of this material at the variation of electron irradiation doses. PZT material parameters were measured for two modes: planar and thickness, for complete characterization, by using disc samples of hard PZT material (7600 Kg/m^3 density), with small size (15 mm diameter, and 1.06 mm thickness). The research was made on many PZT samples, in order to have an accurate evaluation. After each electron irradiation the main electric, piezoelectric and dielectric characteristics of the piezoceramic materials were measured, namely: coupling coefficients (K_{eff}, k), piezoelectric coefficients (g_{31}, d_{31}), strain coefficients, and mechanical quality factor (Q_m). Referring to the equivalent circuit of PZT disc, the dependence of (f_s and f_p) serial and parallel resonant frequencies (in the planar and thickness modes), R impedance at resonant frequency (in the planar and thickness modes) and the capacities (C_a and C_b) upon irradiation doses are determined. The PZT disc samples were irradiated by an electron accelerator with different doses (between 10 and 25 kGy), and then the main electric, piezoelectric and dielectric characteristics of the PZT disc were measured. Electron accelerator has the following parameters: energy 7 MeV, average beam current 7 mA, pulse width 2.5 ms, pulse repetition rate 150 Hz, electron irradiation dose 4 W10^3 Gy/min at 1 m. The PZT samples were irradiated by different electron doses, namely: 10 kGy; 15 kGy; 20 kGy; 25 kGy.

According to [5], [6], the main parameters and characteristics of PZT piezoceramic were determined by HP 4194 Impedance/Gain-Phase Analyzer, Hewlett Packard, USA. The main measured or calculated parameters of the experimental PZT materials were: coupling coefficients, piezoelectric voltage coefficients, free dielectric constant, mechanical quality factor in thickness mode and the elements of the equivalent electrical circuit (resonant frequencies, resistance, and capacities).

For better understanding of results, the main material parameters and characteristics as function of electron irradiation doses are illustrated in the Figures 4 to 14.

For the planar mode of PZT disc, the curves frequency as function of electron irradiation doses show small variations of parallel and serial frequencies (f_p and f_s), (Fig. 4). However, in the thickness mode of PZT disc f_p decreases, and f_s increases (Fig. 5).

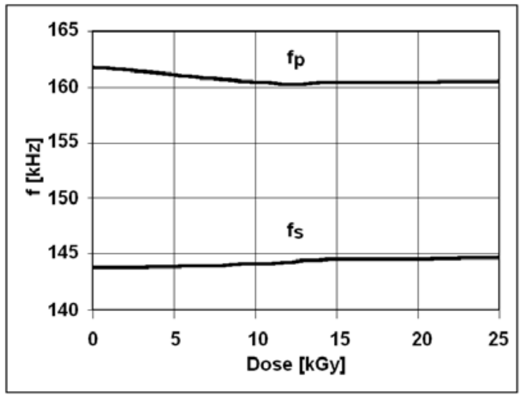

Fig. 4 Frequency as function of Dose in the Planar Mode for PZT disc

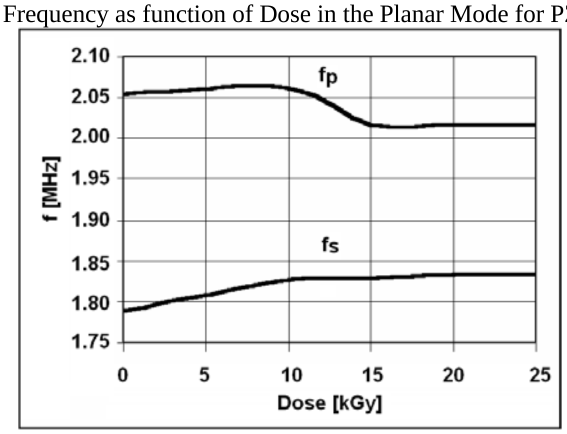

Fig. 5 Frequency as function of Dose in Thickness Mode for PZT disc

For the planar and thickness modes of PZT disc, the curves ***R*** resistance as function of electron irradiation doses increase (Fig. 6).

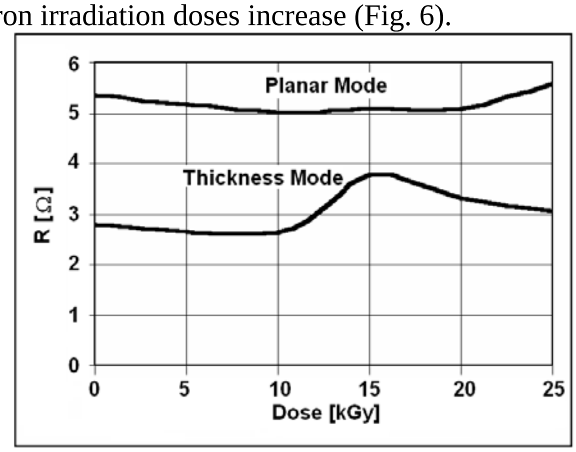

Fig. 6 Resistance as function of Dose for PZT disc

Referring to the equivalent circuit of the PZT disc (Fig. 2), the curves of C_a and C_b capacities function of electron irradiation doses increase for the planar and thickness modes, with small variations (Fig. 7 and 8).

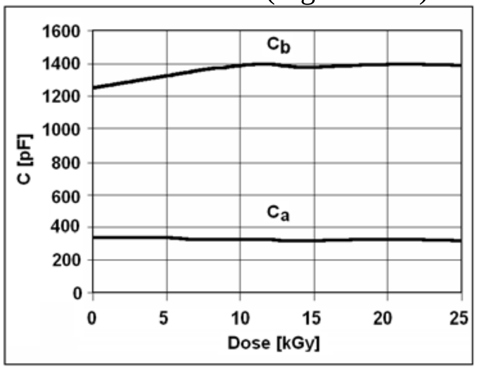

Fig. 7 Capacity as function of Dose in Planar Mode for PZT disc

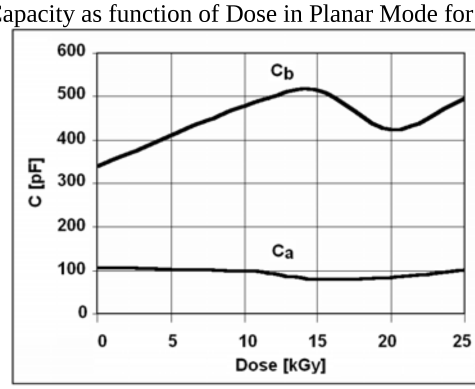

Fig. 8 Capacity as function of Dose in Thickness Mode for PZT disc

For the planar and thickness modes of the PZT disc, the mechanical quality factors Q_m as function of electron irradiation doses present small variations (Fig. 9).

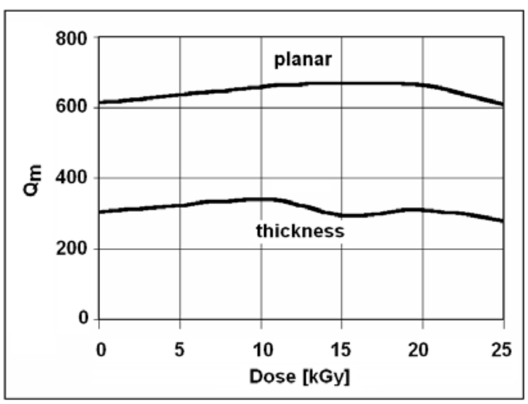

Fig. 9 Mechanical Quality Factor as function of Dose for PZT disc

For the planar and thickness modes, the effective coupling coefficients as function of electron irradiation doses decrease that means the electromechanical efficiencies are smaller (Fig. 10 and 11).

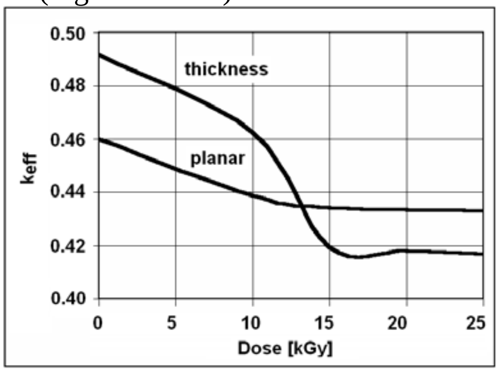

Fig. 10 Effective Coupling Coefficient as function of Dose for PZT disc

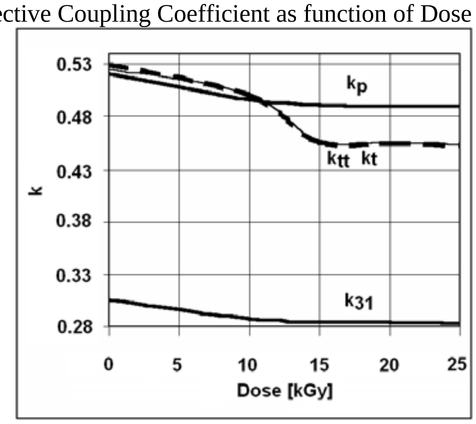

Fig. 11 Coupling Coefficients as function of Dose for PZT disc

The piezoelectric charge constant d_{31} as function of electron irradiation doses increases by 3% (Fig. 12).

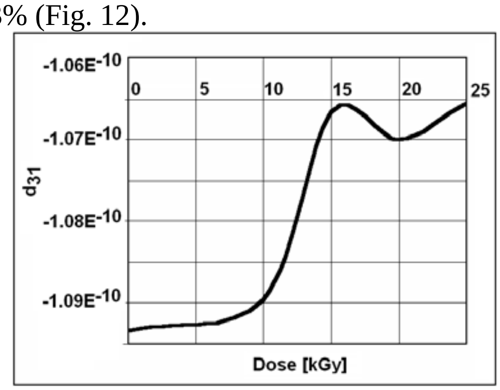

Fig. 12 Piezoelectric Charge Constant as function of Dose for PZT disc

The piezoelectric voltage constant g_{31} as function of electron irradiation doses increases by 14% (Fig. 13).

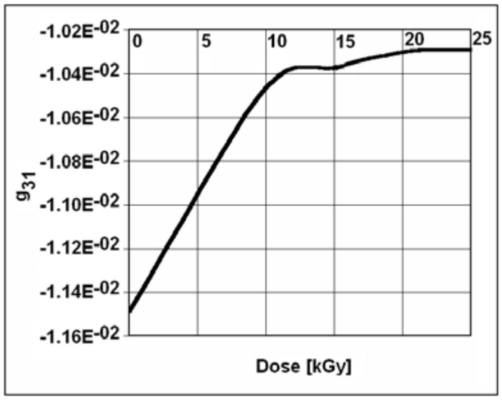

Fig. 13 Piezoelectric Voltage Constants as function of Dose for PZT disc

The elastic constants (compliances) s_{11e}, s_{11d}, s_{12e}, and s_{12e} as function of electron irradiation doses present small variations (Fig. 14).

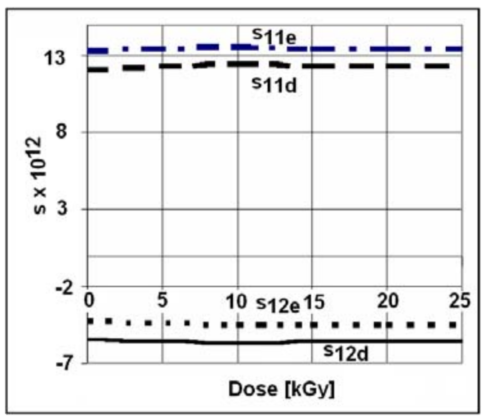

Fig. 14 Elastic Constants as function of Dose for PZT disc

As important result the values of piezoelectric coefficients increase in the range of 10 to 25 kGy electron irradiation doses. However, the values of coupling coefficients decrease. At 25 kGy electron irradiation doses, the piezoelectric charge constant d_{31} increases by 3%, and the piezoelectric voltage constant g_{31} increases by 14%. The other parameters present an acceptable stability with the irradiation doses.

4. Conclusions

As experimental results, the irradiated PZT samples change their piezoelectric and dielectric properties, especially piezoelectric and voltage charge constants. These PZT materials are stable in time and can be successfully utilized into piezoceramic transducers and devices which work in radiation environment, such as: nuclear reactors and centrals, etc. The coupling coefficients decrease at 25 kGy irradiation doses, and the piezoelectric charge and voltage constants increase. Usual, high g constants are wanted. However, the connections to the element, such as cables, act as suplimentary capacities, increase the losses and decrease the output voltage. Therefore, high dielectric and piezoelectric constants are also desirables to minimize the effects of the capacitive loads.

In consequence, the study of piezoceramics at electron irradiation could promote research for superior ceramic materials with improved characteristics, suitable for various piezoelectric transducer applications [9].

REFERENCES

[1] *D. A. Hall*, Piezoelectric Materials: Advances in Science, Technology and Applications, NATO Science Series, Kluwer Academic Publisher, **76**, 2000

[2] *K. Okazaki*, Ferroelectrics, **41**, 77-96, 1982

[3] Z. Surowiak, D. Czekj, Influence of the chemical composition on the physical properties of PZT-type piezoceramic, Molecular and Quantum Acoustics, 183-209, 2003

[4] *M. Brissaud*, IEEE Transaction on Ultrasonics, **38**, 6, 1991

[5] *IEEE Standards on Piezoelectricity. Special Issue of Trans. Sonics Ultrason*, SU 31.2, pt.II, 1984, ANSI-IEEE Std. 176, 1987

[6] *IEC 61994-4-2 TS Ed. 1.0 B 1CD,* Piezoelectric and dielectric devices for frequency control and selection - Glossary - Part 4-2: Piezoelectric materials - Piezoelectric ceramics, 1994

[7] *prEN 50324-2:2001*, Piezoelectric properties of ceramic materials and components - Part 2: Methods of measurement and properties - Low power

[8] *prEN 50324-3:2001*, Piezoelectric properties of ceramic materials and components - Part 3: Methods of measurement - High power

[9] *M. Musu-Coman, H. Ispas, M.I. Petrescu, E. Jianu*, Improved retention of surface treated diamonds in sintered tools for processing ornamental stones, U.P.B. Sci. Bull., Series B, **68**, No. 4, 47-56, 2006