# EFFECT OF NEUTRON IRRADIATION ON SOME PIEZOELECTRIC PROPERTIES OF PZT TYPE CERAMICS

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## 1. INTRODUCTION

The strong interest in piezoelectric ceramics is due to their extraordinary property to convert the electrical energy into mechanical strain and *vice-versa* at high yields. These materials are used as active elements for a wide variety of sensors and transducers. In some instances these sensors and transducers are due to operate under rather “unfriendly” environmental conditions. Among them the temperature, electrical field, mechanical stress and nuclear irradiation are the most important factors that can affect the basic properties of the piezoactive element, sometimes producing irreversible damages. The effect of temperature, electrical field and stress on the piezoelectric properties is rather known. But little is known about the influence of nuclear irradiation on the main parameters of piezoceramic materials. Quite recently, some theoretical approaches of the degradation of ferroelectric properties produced by neutron irradiation were undertaken. The main defects produced by neutron irradiation in perovskite type ceramics are oxygen vacancies and interstitials which play an important role in changing the properties of materials. But it seems that there are some other associated factors that can influence the changes of the properties. The present work investigated the changes of the main piezoelectric properties of two typical PZT type materials brought about by neutron irradiation fluxes of high intensities up to $10^{18}$ neutron per square centimeter.

## 2. EXPERIMENTAL

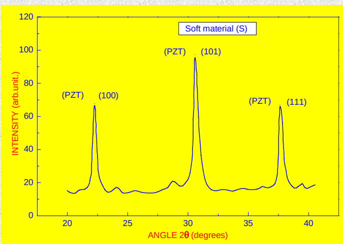


*Figure 1*
*X-ray diffractograms of calcined powder of the soft material*

The materials selected for the experiment were a typical “soft” and a typical ”hard” lead titanate zirconate materials. The corresponding chemical formulae were:

$PbZr_{0.51}Ti_{0.463}Nb_{0.02}Li_{0.007}O_3$ (soft) and $PbZr_{0.45}Ti_{0.49}Mn_{0.17}Nb_{0.033}O_3$ (hard).

The preparation method was the usual mixed oxide route. High purity oxides were used. The mixings were carried out in a planetary ball mill, in methanol, using agate vials and balls of 10 mm diameter and a ball/powder weighted ratio of 2/1. After mixing for 3 h, the products were dried and double calcined at 850 ºC and 900 ºC respectively with an intermediate milling of 1 h and a final wet milling of 10 h. This processing procedure produced a single phase perovskite compound as can be seen in figure 1. Morphologic evaluation by BET measurements gave a specific surface area of about 1.6 $m^2/g$ corresponding to an average spherical equivalent diameter of about 0.6 µm, a value confirmed by SEM micrographs as shoun in figure 2. These powders were compacted in a cylindrical die, as discs of 13 mm diameter and about 1.5 mm thick using uniaxial pressing and a pressure of about 50 MPa. No organic binder was used but a slight wetting, by spraying, using distilled water (about 5% wt). The pressed samples were sintered in covered alumina crucibles at temperatures between 1150⌦1350 ºC with a dwell time of 4 h. The sintered samples were then mechanically processed by grinding as discs with 10 mm diameters and 1mm thick having flat plan parallel surfaces. The irradiations were carried out in a VVRS nuclear reactor, in fluxes up to $10^{18}$ n/$cm^2$.

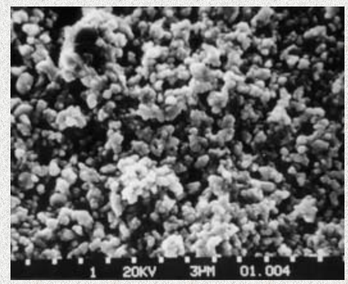


*Figure 2*
*SEM micrograph of the calcined and milled powder of the soft piezoceramic material*

## 3. RESULTS

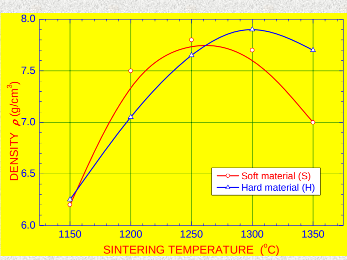


*Figure 3*
*The dependence of the densities of sintered samples, for the soft and hard piezoceramic materials, on the sintering temperature*

Fig. 3 displays the densities of the sintered samples for the two materials as a function of the sintering temperature. Each material shows a maximum value of the density centered around 1250 ºC for the soft material and around 1300 ºC for the hard one. This means that at this temperature the densification process is complete and the densities reach about 97% of the theoretical density. Figure 4 shows the changes of the electromechanical coupling factors $k_P$ produced by neutron irradiation. One can see that neutron fluxes up to about $10^{15}$ n/$cm^2$ do not change significantly the $k_P$, but greater fluxes do. The decrease of $k_p$ for both materials were about 30% for soft and 25% for hard material respectively, when fluxes were $10^{18}$ n/$cm^2$. This means that some damages into the crystal lattice took place. The behavior of the mechanical quality factor $Q_m$ shows an important increase with increasing neutron flux, for both materials, as it is shown in fig. 5. Thus for the soft material $Q_m$ increases with about 130% while for the hard one the increase reaches 230% so that both materials become harder. The relative dielectric constants decrease with about 75% for both materials at fluxes of $10^{18}$ n/$cm^2$ as it is shown in fig. 6. At the same time the loss factor $tg\delta$ decreases with 40-50% for both materials as illustrated in fig. 7. All these changes indicate clearly that the main defects brought about by neutron irradiation is the oxygen vacancies and perhaps interstitials. Measuring the cell constants for irradiated samples of the soft material, we have found the values shown in figure 8. Unfortunately no noticeable changes were found for **a** and **c** except for a slight increase of the constants for irradiated samples at high fluxes of $10^{17}$-$10^{18}$ n/$cm^2$. Such an increase of the cell constants tends to modify the tetragonally deformed cell into the cubic one. This tendency is also visible in fig. 9 where a refinement of (002) T and the (200) T reflections is shown in details for angles around 2υ = 44 º in the case of the soft samples. One can see a slight decrease of these maxima after irradiation indicating the tendency to cubic cell. In addition, the decrease of tetragonality is accompanied by a corresponding decrease of the polarization associated with the presence of oxygen vacancies considered to be the most mobile and abundant in perovskite ferroelectrics and playing an essential role in polarization degradation.

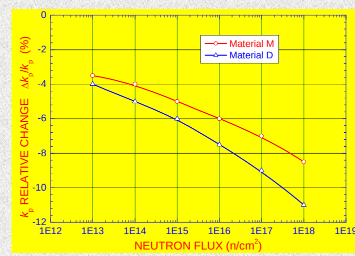


*Figure 4*
*The changes of electromechanical coupling factors kp as a function of the neutron flux for irradiated samples of the two materials*

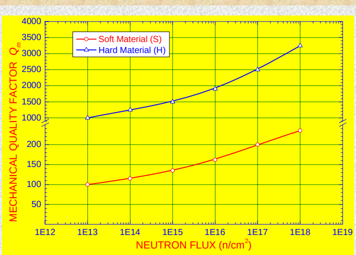


*Figure 5*
*The changes of the mechanical quality factor Qm as a function of the neutron flux for irradiated samples of the two materials*

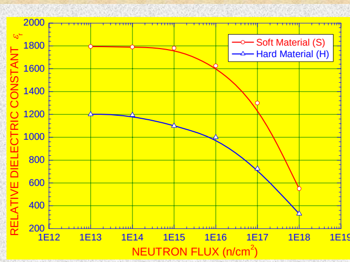


*Figure 6*
*The changes of the relative dielectric permittivity εr as a function of the neutron flux for irradiated samples of the two materials*

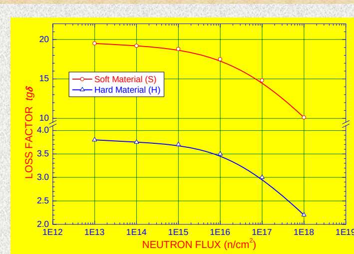


*Figure 7*
*The changes of the loss factor tan δ as a function of the neutron flux for irradiated samples of the two materials*

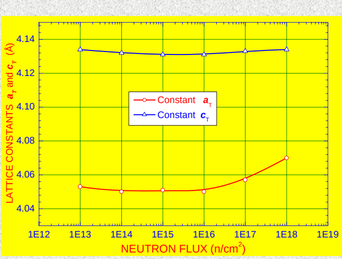


*Figure 8*
*The modifications of the lattice constants c and a produced by neutron irradiation in the soft material*

## Summary

Sintered samples of a soft and a hard piezoceramic materials were prepared by the usual mixed oxide route and were irradiated by neutrons in a VVRS nuclear reactor in fluxes up to $10^{18}$ n/$cm^2$. As a result of irradiation their basic properties changes as follows: the electromechanical coupling factor, the dielectric permittivity and the loss factor decreased with 30 %, 75 % and 50 % respectively, while the mechanical quality factor increased with up to 230 %. The main defects produced by irradiation were oxygen vacancies, but some other factors such as domain pinning, lattice deformation or charged vacancies have to be taken into consideration.

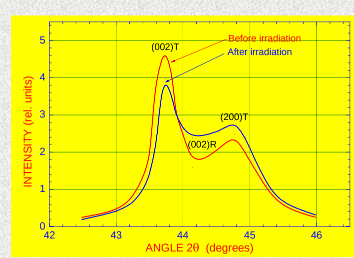


*Figure 9*
*The refinement of the (002) T and (200)T reflexions around 2θ = 44º for the soft material*