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Journal of the European Ceramic Society 24 (2004) 1653–1657

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Antiferroelectric $PbZrO_3$ thin films: structure, properties and irradiation effects

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Abstract

Irradiation effects on highly oriented antiferroelectric $PbZrO_3$ and ferroelectric $Pb_{0.92}La_{0.08}(Zr_{0.65}Ti_{0.35})O_3$ thin films are investigated being exposed to neutron irradiation up to fluence $2*10^{22}$ m^{-2}. The higher resistance of antiferroelectric $PbZrO_3$ thin films as compared to ferroelectric heterostructures to large fluences of neutron irradiation is recognized and discussed. Influence of two factors (structural and charge) was taken into account analysing irradiation effects on materials of different polarization states: ferroelectric PLZT (ceramics and thin films) and antiferroelectric $PbZrO_3$ films.

Keywords: Antiferroelectric and ferroelectric thin films; Dielectric properties; Neutron irradiation; Oxygen vacancies; Radiation-induced charges

1. Introduction

Advanced multifunctional ferroelectrics are distinguished by pronounced dielectric, electromechanical, optic and non-linear optic properties and are proved to be comparably radiation hard materials, e.g.,[1] some applications are needed in areas where the design requires a high radiation tolerance of the material e.g., as an active element in an alternative bolometer system for ITER. Currently only a limited amount of data on the irradiation response of ferroelectric (FE) thin films is available.[2–4] For the particular application the composition should be used in its paraelectric phase, but the operating regime should not to be too close to the dielectric permittivity (ε) maximum temperature T_m, because the FE material is more sensitive to neutron irradiation exactly near T_m.[5] In this work results on high fluency (up to $2*10^{22}$ m^{-2}) neutron irradiation effects in sol-gel and pulsed laser deposited $PbZrO_3$ and PLZT thin films are reported.

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doi:10.1016/S0955-2219(03)00450-3

2. Experimental

The $PbZrO_3$ (PZ) thin films (thickness 1–1.4 μm) were prepared by sol-gel technique[6] on $TiO_2/Pt/TiO_2/SiO_2/Si$ substrates (Au top electrodes) as well as by pulsed laser deposition (PLD) on a $Si/Ti/SiO_2/Pt$ substrate (thickness ~400 nm) with Pt top electrode pads. The $Pb_{0.92}La_{0.08}(Zr_{0.65}Ti_{0.35})O_3$ (PLZT-8) heterostructures investigated as a reference FE material were obtained by PLD. The dielectric properties (in the frequency range of 20 Hz–1 MHz) were investigated by use of a HP4284A LCR meter and a Perkin-Elmer 7265 lock-in amplifier before and after irradiation to neutron fluence up to $2*10^{22}$ m^{-2} ($E > 0.1$ MeV). After irradiation the samples were annealed in air for 1 h at several temperatures (250, 300, and 380 °C). "Zero field" dielectric permittivity (at 20 mV) was measured during stepwise heating and cooling at 2.0 °C*min^{-1} in the temperature interval of 20–400 °C. Polarization was evaluated from dielectric hysteresis loops obtained on a modified Sawyer-Tower circuit (at frequency 15 Hz) or recorded at 20 Hz with a RT6000 HVS testing system.

3. Results and discussion

The dielectric hysteresis (Fig. 1a) of the unirradiated PLZT-8 heterostructure shows a pronounced FE-behaviour with a maximum polarization P_{max} of 32 μC/cm^2 and a remnant polarisation P_r of 8.5 μC/cm^2. After irradiation (to a fluence of 1*10^{22} m^{-2}) a significant decrease of P_{max} and P_r was observed. The hysteresis loop changes to an "AFE shape" with P_r nearly zero. It is assumed that radiation-induced oxygen vacancies (VO) represent the most significant defects in neutron irradiated FE materials.[7,14] They play the role of donors and cause radiation-induced charges. In addition, an antiphase polarization (like in AFE materials) is induced in the surrounding volume of such a vacancy, which will reduce the total polarization near VO to nearly zero.[8] Thus the net polarization of the FE film is reduced. Furthermore, the domains are pinned by these VO clusters. Both effects lead to the observed reduction of P_{max}. The loop shows a FE shape with increased P_r and P_{max} after the last annealing step at 450 °C. P_r has approximately the same value as prior to irradiation, even though P_{max} still remains reduced. This indicates that the radiation-induced charges, which cause the internal bias field, disappear completely. However, some small clusters of oxygen vacancies could remain after annealing at 450 °C.

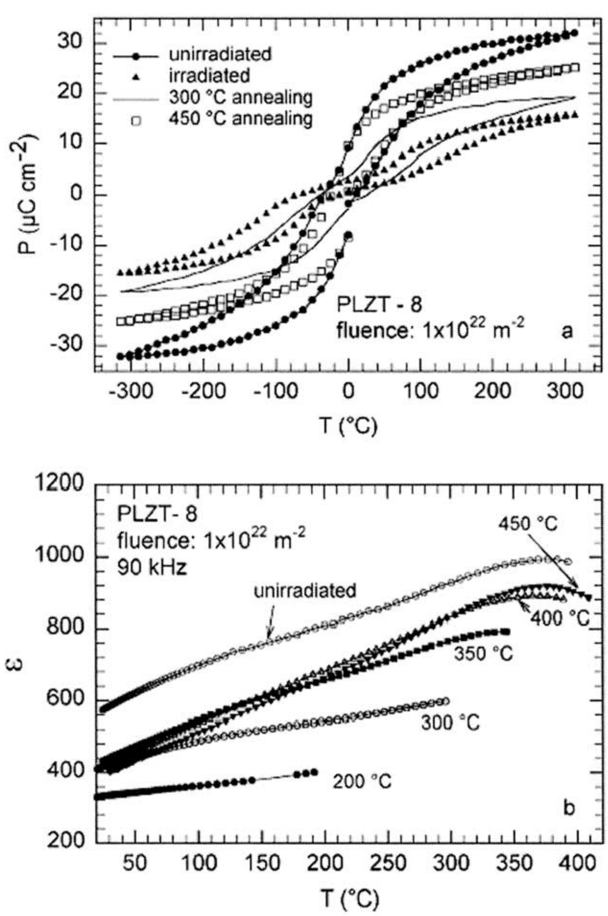

Fig. 1. Hysteresis loops (a) and temperature dependence of the dielectric permittivity $\varepsilon(T)$ (b) of the PLZT-8 film prior to and after irradiation to a fast neutron fluence of 1*10^{22} m^{-2} and after several annealing steps (200, 300, 350, 400 and 450 °C). $\varepsilon(T)$ was measured at 90 kHz during cooling.

Fig. 1b shows $\varepsilon(T)$ for PLZT-8 film measured at 90 kHz prior to and after irradiation and after some annealing steps. The ε_{max} at 370 °C might indicate the phase transition (PT), in contrast to previous measurements on PLZT-8 films prepared by PLD.[9] After irradiation and annealing at 200 °C the ε is reduced by a factor of two. Further annealing at 300 °C results in a large increase of ε. A decrease of T_c is also observed after irradiation (see the annealing curve at 350 °C in Fig. 1b), but T_c returns to its preirradiation value after annealing at 450 °C. In order to explain this behaviour, radiation-induced charges near the electrodes are taken into consideration. It is shown[10] that radiation-induced charges cause a nonswitchable internal polarization ("built-in polarization"), which is temperature-independent and reduces T_c. During annealing the charges recombine and the "built-in polarization" becomes smaller resulting in an increased T_c. At higher temperatures (around 400 °C) a sharp increase of ε is observed indicating the influence of the interfaces and an increased electrical conductivity.

Fig. 2 shows the hysteresis loops for two PZ films before and after neutron irradiation to fluences of 1*10^{22} m^{-2} (Fig. 2a) and 2*10^{22} m^{-2} (Fig. 2b). The PZ film denoted L89 (Fig. 2a) was irradiated to 1*10^{22} m^{-2} and afterwards annealed in several steps up to 350 °C. After the last step the P_r as well as the P_{max} remain slightly enhanced. This broader hysteresis loop of L89 seems to be related to radiation-induced charges causing an enhanced space charge polarization. In comparison to the FE film (Fig. 1a) the radiation-induced charges do not lead to such drastic changes of the hysteresis loop.

Fig. 3 shows the $\varepsilon(T)$ dependence in PZ film before and after irradiation and after some annealing steps. T_c is about 223 °C in the unirradiated state. After irradiation to fluence of 2*10^{22} m^{-2} T_c decreases to 217 °C, but ε increases, in contrast to the FE film (Fig. 1b). This behaviour could be explained by radiation-induced charges as in the case of the hysteresis loop in the PZ films. An increase of charges leads to an increase of ε at a certain grain size.[11] Also a radiation-induced internal bias field leads to an increase of ε, in contrast to irradiated FE films.[12] A bias field forces the surrounding area to change from the AFE into the FE state. Furthermore, the $\varepsilon(T)$ measured at 1.1 kHz is different from that at 250 kHz after irradiation, also below T_c (Fig. 3). This could be related to the increased space charge polarization at the grain boundaries and between heavily radiation-damaged areas of the film (cascades) and less damaged areas, which leads to an increase of ε. The dielectric properties at lower frequencies are more influenced by grain boundary effects than those measured at higher frequencies (here up to 250 kHz), where the response is mainly determined by the bulk properties .[12] During further annealing, T_c increases to 220 °C (at 300 °C annealing) and finally to its preirradiation value of 223 °C.

Fig. 4 shows the hysteresis loop of the PLD PZ heterostructure before and after irradiation to $2*10^{22}$ m^{-2}. The unirradiated PZ film possesses pronounced AFE behaviour with P_{max} of 22 μC/cm^2 and a well-defined P_r. The hysteresis and the values of ε above (Fig. 5) prove the high quality of the film. After annealing at 380 °C (Fig. 4) the hysteresis loop measured at 85 °C shows a distorted and broadened AFE like shape indicating that the film maintains the AFE phase structure also after irradiation. $\varepsilon(T)$ (Fig. 5) indicates a pronounced sharp PT from the AFE to the paraelectric phase at $T_c = 217$ °C with ε_{max} of about 1160. After irradiation and annealing at 250 °C, ε_{max} decreases and T_c increases (~5 °C) in contrast to results on sol-gel PZ thin films. During the next annealing step at 380 °C, a certain part of the radiation-induced defects, i.e. oxygen vacancies and of the charges, recombine, thus reducing the influence of the space-charge polarization on ε.

Despite of neutron induced cascades, many of the individual (radiation-induced) vacancies VO form clusters due to diffusion, which starts at room temperature.[13] This leads to the observed degradation of the net polarization. It is proposed that two different sorts of vacancies VO[8] exist; one is switchable and does not decrease the polarization of the domain, and the other forms a ‘‘tail-to-tail’’ configuration of the polarization vector in the surrounding area of such vacancies and pins the polarization domain. Due to annealing, such a ‘‘tail-to-tail’’ configuration will transform into a switchable vacancy or recombines with oxygen interstitials, thus leading to a restoration of the net polarization. The AFE shape of the hysteresis loop in FE can be explained by radiation-induced and trapped charges, which form an internal bias field.[3] During annealing, the charges are

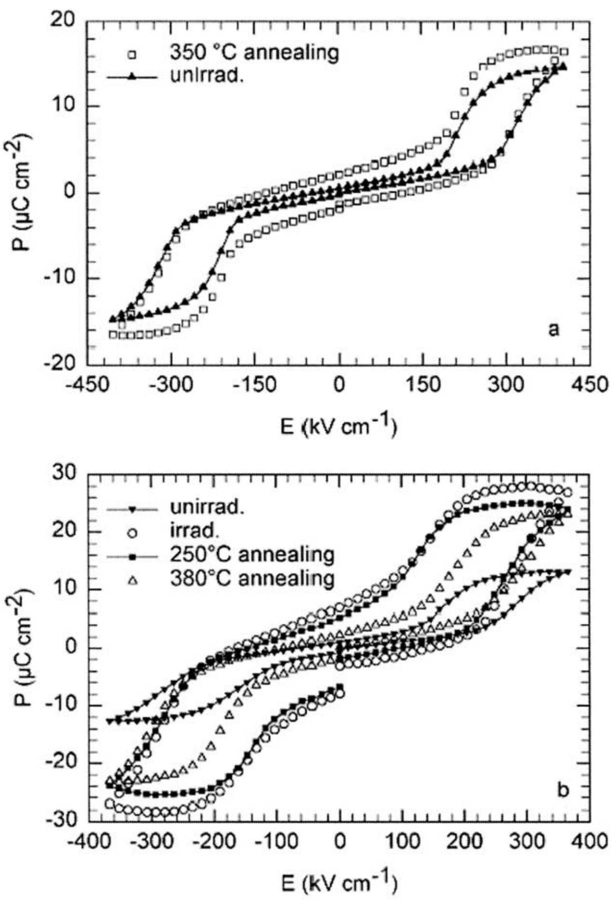

Fig. 2. Hysteresis loops of the PZ films L89 (a) and L85 (b) before and after irradiation to a fast neutron fluence of $1*10^{22}$ m^{-2} for the L89 film (a) and of $2*10^{22}$ m^{-2} for the L85 film (b) and after several annealing steps.

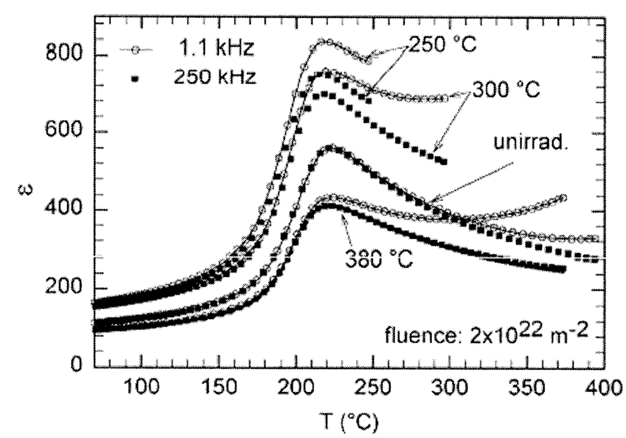

Fig. 3. $\epsilon(T)$ of the L85 PZ film measured during cooling at 250 kHz and 1.1 kHz before and after irradiation to a fast neutron fluence of $2*10^{22}$ m^{-2} and after several annealing steps (250, 300 and 380 °C).

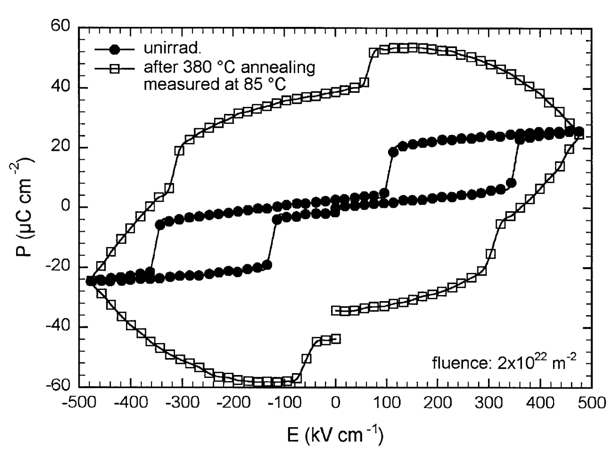

Fig. 4. Hysteresis loops of the pulsed laser deposited PZ film before and after irradiation to a fast neutron fluence of $2*10^{22}$ m^{-2}. The hysteresis after irradiation and 380 °C annealing for 1 h was measured at 85 °C.

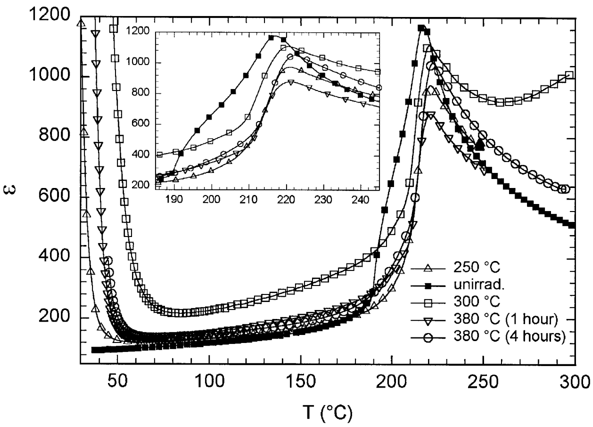

Fig. 5. $\varepsilon(T)$ of the pulsed laser deposited PZ film measured during cooling at 2 kHz before and after irradiation to fast neutron fluence of $2*10^{22}$ m^{-2} and after several annealing steps.

released and the loop returns to its FE shape. The radiation-induced T_c shift can also be explained by radiation-induced charges. It is expected that a depletion zone with the corresponding (depletion) charge distribution is formed at the metal-ferroelectric interface.[12] The model described above should also be applicable to the AFE PZ film. However, in contrast to the FE film, it seems that the oxygen atom position is less critical in the AFE phase. Behaviour of FE and AFE thin films under neutron irradiation is different. Polarization of the AFE practically does not change after neutron irradiation (see above). This may be due to the fact that in AFE before irradiation the polarization in each unit cell has two components, which are directional opposite, that is very close to the polarization structure proposed in the model.[7,8] Therefore the appearance of the radiation induced oxygen vacancies changing polarization to the ‘‘tail-to-tail’’ configuration in neighbouring area does not effect very much the full polarization of a sample. Thus, the PZ film is more radiation resistant than the FE (PLZT-8) film. This is confirmed by our previous measurements[13] on neutron irradiated and annealed PZ films irradiated to a fluence of $5*10^{21}$ m^{-2} and by the results presented in Fig. 2a for $1*10^{22}$ m^{-2}. It is also expected that the radiation-induced charges influence the AFE material in a different way because of the remnant polarization P_r, which is approximately zero in AFE heterostructures. This difference is indeed observed in the ε (Fig. 3), where ε increases after irradiation (250 °C annealing) as well as after 300 °C annealing.

4. Conclusions

The presented results demonstrate a significant difference between PLD and sol-gel AFE PZ thin films. It can be explained mainly by the higher structural quality of the PLD film. The PLD film is epitaxially grown and more or less single-crystalline, whereas the sol-gel is highly oriented but with a columnar polycrystalline grain structure. Therefore, the radiation-induced charges cannot build up an internal bias field or additional defect clusters at the grain boundaries in the entire temperature regime, which causes the behaviour observed in the AFE PZ sol-gel heterostructures.

Pronounced irradiation effects in PZ (sol-gel prepared) thin film occur above a neutron fluence of $1*10^{22}$ m^{-2}, where the defect structure becomes more complex. The charge induced shift of T_c to lower temperatures is observed in AFE PZ films as in FE films and seems to represent a general feature of thin FE and AFE films with metallic electrodes and with a considerably increased amount of mobile charges.[10] Additional annealing at higher temperatures (>380 °C) will not restore the dielectric properties of the PZ film[13] but only enhance the influence of the interfaces.

Acknowledgements

This work has been carried out within the association EURATOM-OEAW and EURATOM-University of Latvia.

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