

Water-induced degradation in $0.91\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.09\text{PbTiO}_3$ single crystals

W. P. Chen,^{a)} J. Q. Qi, Y. Wang, X. P. Jiang, and H. L. W. Chan

Department of Applied Physics and Materials Research Center, The Hong Kong Polytechnic University, Hong Kong, People's Republic of China

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Water-induced degradation in $0.91\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.09\text{PbTiO}_3$ (PZN-PT) single crystals was studied through an electrochemical hydrogen charging process, in which silver electrodes were fired onto the single crystals and hydrogen was deposited on the electrodes via electrolysis of water in 0.01 M NaOH solution. The degradation was characterized by dramatic increases in the leakage current and in the dielectric loss of the crystals. X-ray diffraction analysis showed that the crystals were decomposed into metallic lead, zinc, and a niobium-rich face-centered-cubic phase. Water-induced degradation limits the application of PZN-PT single crystals. © 2004 American Institute of Physics. [DOI: 10.1063/1.1702095]

Lead-based relaxor perovskite oxides are very attractive for applications in high-dielectric constant ceramic capacitors due to their high dielectric constants, broad dielectric maxima, and relatively low firing temperatures. In recent years, single crystals of lead-based relaxors are found to possess some exceptionally high piezoelectric constants and extensive researches are being conducted to apply them in various piezoelectric devices.¹ As they find more and more important applications, the reliability of lead-based relaxor components and devices has become an important concern.

For lead-based relaxor ceramic capacitors, electroplating sometimes induces serious resistance degradation, i.e., the insulation resistance is greatly decreased after electroplating. We found that the degradation is due to the reduction of hydrogen generated in electroplating.² Through x-ray photoelectron spectroscopy analysis, Cao *et al.* showed that in $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ -based ceramics Nb^{5+} and Pb^{2+} are partially reduced to Nb^{4+} and metallic Pb.³ They assumed that the lattice remained unchanged though the valence of some elements changed. As a matter of fact, our previous studies showed that sometimes the lattice will decompose and phases are formed after the reduction of hydrogen.⁴ So presently, we have carried out an in-depth study on the reaction between relaxor oxides and hydrogen by adopting an electrochemical hydrogen-charging procedure, in which the material under test is made a cathode in a dilute NaOH solution to evolve hydrogen via electrolysis of water. This procedure highlights the coexistence of water and electricity, such as in electroplating or when components operate under some voltages while water is condensed from environmental moisture. Our study reveals that some relaxor oxides exhibit an extremely poor stability against water in the presence of electricity. Water-induced degradation must be examined for relaxor oxides before they are applied in components and devices.

Several $0.91\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.09\text{PbTiO}_3$ (001) single crystals were used in the present investigation. The crystals

were $5 \times 5 \times 1 \text{ mm}^3$ in size and 2 mm diameter silver electrodes (Dupont 1183) were fired onto the centers of the two major surfaces of the crystals. The crystals were placed in a 0.01 M NaOH solution and dc voltages were imposed between the silver electrodes of the crystals and a counter Pt electrode in the solution. All the silver electrodes of the crystals acted as the cathode and the counter Pt electrode acted as the anode. Hydrogen was deposited on the silver electrodes of the crystals as the applied dc voltages induced electrolysis of water. This treatment is hereafter referred to as hydrogen charging. The dc voltages were removed after designated periods of time and the crystals were taken out, cleaned with de-ionized water and dried. An Agilent 4294A impedance analyzer was used to measure the frequency spectra of capacitance and dielectric loss of the crystals. The $I-V$ characteristics of the crystals were measured through a Keithley 6517 electrometer/high resistance meter. Chemical reactions were studied using an x-ray diffractometer (Philips PW 3719) with $\text{Cu } K_\alpha$ radiation.

For reference, some crystals had been immersed in the NaOH solution for 20 h. No changes were observed in the appearance or in the properties of the crystals after the immersion. It indicates that the crystals were chemically stable in water. In contrast, hydrogen charging greatly changed the crystals. The as-received single crystals were greenish-yellow. Two 1 mm wide dark rings were formed around the two silver electrodes of a crystal after 30 min of hydrogen charging with the application of a 4.5 V dc voltage and the cathodic current density of 0.6 mA/cm². The dark rings spread outwards as hydrogen charging proceeded and the whole crystal changed dark after 120 min of hydrogen charging. After 30 min of hydrogen charging, the crystal had been taken out, cleaned and dried to measure dielectric properties and $I-V$ curve, which are shown in Figs. 1 and 2, respectively. It is clear that both the dielectric loss and the leakage current were greatly increased after hydrogen charging, which are serious degradations for various components and devices.

The x-ray diffraction patterns taken on the (001) surface of an as-received single crystal and the (001) surface of the

^{a)}Electronic mail: apchenwp@polyu.edu.hk

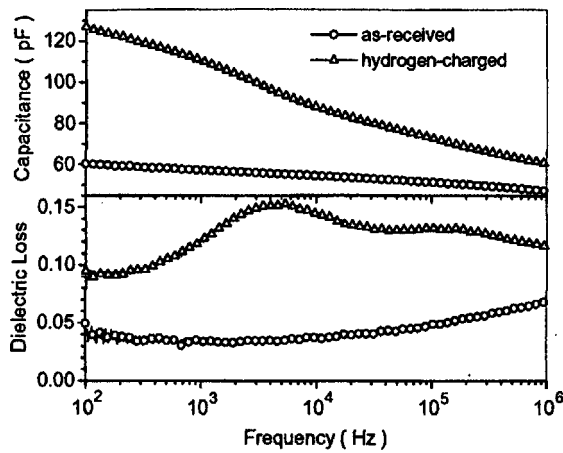
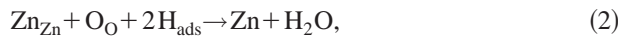


FIG. 1. Frequency spectra of capacitance and dielectric loss of a $0.91\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.09\text{PbTiO}_3$ single crystal before and after 30 min of hydrogen charging.

single crystal with 120 min of hydrogen charging are shown in Fig. 3. For the hydrogen-charged single crystal, the surface was dark and the x-ray diffraction pattern shows that its lattice had decomposed and some phases were formed. It is interesting to find that most strong peaks are from a single phase of $\text{Pb}_{1.83}\text{Nb}_{1.71}\text{Zn}_{0.29}\text{O}_{6.39}$ according to JCPDS file 34-374, which is of a face-centered-cubic lattice. Compared to $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$, this phase is niobium-rich while zinc and lead deficient. Correspondingly, some peaks of metallic lead and zinc can also be found. The peak of silver is from the silver electrode. It indicates that some Pb^{2+} and Zn^{2+} were reduced to a metallic state, while the remaining ions formed another phase, which can be expressed as



where H_{ads} represents an adsorbed hydrogen atom generated by the electrolysis of water. It is assumed that some hydrogen atoms had reacted with the crystal though most of them combined with one another and formed hydrogen molecules to evolve. A similar result has been reported for ZnO , which is reduced to metallic zinc by hydrogen generated from electrolysis of water.⁴

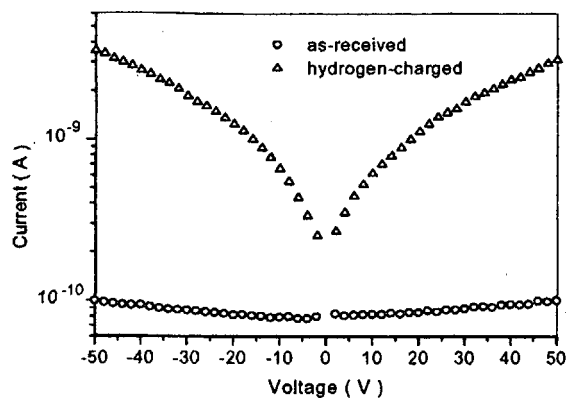


FIG. 2. $I-V$ characteristics obtained for a $0.91\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.09\text{PbTiO}_3$ single crystal before and after 30 min of hydrogen charging.

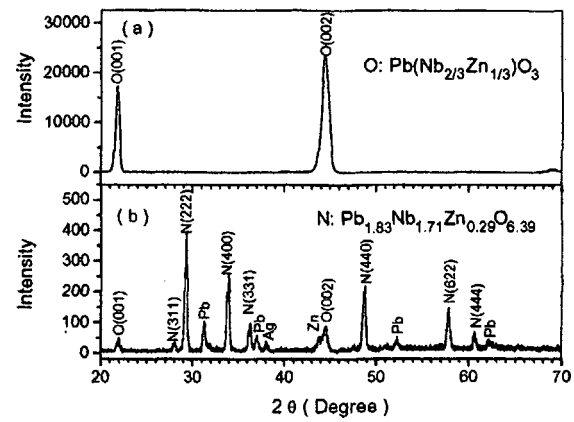


FIG. 3. X-ray diffraction patterns taken for the (001) surface of (a) an as-received $0.91\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.09\text{PbTiO}_3$ single crystal and (b) a $0.91\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.09\text{PbTiO}_3$ single crystal after 120 min of hydrogen charging.

It should be pointed out that the decomposition induced by hydrogen is very quick. This will be an obstacle for some applications of the relaxors. Due to its excellent dielectric properties, $0.90\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.05\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.05\text{PbTiO}_3$ had been used as the basic composition for some commercial ceramic capacitors. However, ceramic capacitors based on this composition were found affected greatly by electroplating.² As hydrogen is always generated in electroplating, hydrogen-induced decomposition of $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ must be an important cause for the influence of electroplating. So $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ is not suitable for capacitors application though it may have very high dielectric properties. $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ single crystals should not be applied in piezoelectric devices operating in humid environments, either. Some studies have shown that environmental moisture is also harmful to components and devices through the electrolysis of water.⁵ A further study is being conducted to compare water-induced degradations among different relaxor oxides, which will provide some guidance for material designing.

In summary, the dielectric loss and the leakage current of $0.91\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.09\text{PbTiO}_3$ single crystals were greatly increased by the reaction of hydrogen generated in electrolysis of water. The degradation resulted from the decomposition of the crystals and metallic lead, zinc, and a niobium-rich face-centered-cubic phase were formed. The stability against electrolysis of water should be taken into consideration before relaxor oxides are applied in various components and devices.

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