

Hydrogen-related dynamic dielectric behavior of barium titanate single crystals

W. P. Chen^{a)}

Department of Applied Physics, The Hong Kong Polytechnic University, Hong Kong, People's Republic of China and Department of Physics, Wuhan University, Wuhan 430072, People's Republic of China

Y. Wang and H. L. W. Chan

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

H. S. Luo

The State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 201800, People's Republic of China

(Received 23 January 2006; accepted 6 April 2006; published online 18 May 2006)

Barium titanate single crystals had been placed in 0.01M NaOH solution to deposit hydrogen on their electrodes through the electrolysis of water. Two kinds of time-dependent changes in dielectric properties of the single crystals were observed: One occurred in the course of hydrogen deposition and the other lasted for a long period of time after the deposition. The diffusion of hydrogen and in and out of the single crystals may be the cause for the changes. This hydrogen-related dynamic dielectric behavior clearly shows that hydrogen is an important mobile ion other than oxygen vacancy in perovskite-type lattice. Extra attention should be paid to the role of hydrogen in time-dependent property changes, including resistance degradation and ferroelectric aging, of perovskite-type ferroelectric titanates. © 2006 American Institute of Physics.

[DOI: [10.1063/1.2206686](https://doi.org/10.1063/1.2206686)]

A wide variety of point defects can be formed in perovskite-type titanate lattices and they play a vital role in tailoring perovskite-type titanates to many important and diverse applications—from high dielectric constant ceramic capacitors and piezoelectric ceramic devices of high resistivity,¹ to semiconducting thermistors with positive temperature coefficient of resistivity (PTCR), and to oxide superconductors. Point defects are normally characterized by concentration, and the relationship between the physical properties and the concentration of various point defects has been extensively investigated for perovskite-type titanates. On the other hand, the mobility or the movement of point defects in perovskite lattices has also attracted more and more attention. Waser *et al.* demonstrated that oxygen vacancies in perovskite-type titanates would electromigrate when a dc field is applied and a concentration polarization of oxygen vacancies between the anode and the cathode would be formed, which is believed to be responsible for the well known resistance degradation in perovskite-type titanates and the lifetime of components and devices based on them is greatly reduced.² Recently, Ren observed a huge recoverable electrostrain in aged barium titanate single crystals, and he ascribed this amazing phenomenon to the so-called symmetry-conforming property of point defects in perovskite-type titanate lattices.³ In the course of aging, oxygen vacancies migrate to a distribution conforming to the ferroelectric domain structure formed after the cubic to tetragonal transition and this distribution provides a restoring force for a reverse domain switching when electric field is removed. This discovery may lead to some applications in ultralarge stroke and nonlinear actuators for barium titanate

single crystals. The migration of oxygen vacancies in aging was also found to result in a stabilization effect in ferroelectric materials.⁴ Obviously, it is meaningful to establish a relatively full understanding of the behavior of various point defects in perovskite-type titanate lattices. In this letter, we report an interesting dynamic dielectric behavior of barium titanate single crystals induced by hydrogen. Hydrogen is an important point defect in many oxide lattices and its influence on perovskite-type titanates has been the subject of numerous investigations.^{5,6}

Prepared by a top-seeded solution growth technique, barium titanate (001) single crystals with the size of $10 \times 10 \times 2$ mm³ were used in our investigation. Two 3 mm diameter silver electrodes (Du Pont 1183) were fired onto the centers of the two major surfaces of the crystals and then the crystals were aged for one month to stabilize the properties after the heat treatment. The crystals were placed in a 0.01M NaOH solution and a 3 V dc voltage was applied between the silver electrodes of the crystals and an anode (Pt) in the solution. The electrolysis of water occurred due to the applied dc voltage and hydrogen was evolved on the silver electrodes of the crystals while oxygen was evolved on the anode. Hydrogen generated in this electrochemical process can diffuse into oxide lattices and this treatment has been known as electrochemical hydrogen charging.⁷ The solution was kept stirred using a magnetic agitator and the temperature was kept constant at 20 °C. The hydrogen charging was interrupted several times and the crystals were taken out, washed with de-ionized water and acetone, and dried for measurement. Using the two silver electrodes of the crystals, the frequency spectra of capacitance and dielectric loss were measured on an impedance analyzer (Agilent 4294 A), and the *I-V* characteristics were recorded through an

^{a)}Electronic mail: chenwp66@yahoo.com

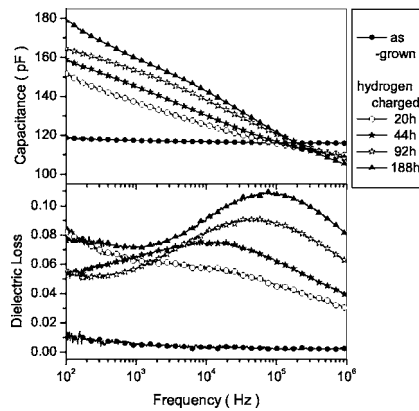


FIG. 1. Frequency spectra of capacitance and dielectric loss of a barium titanate single crystal measured at different times: as grown and after a series of periods of electrochemical hydrogen charging.

electrometer/high resistance meter (Keithley 6517). All measurements were done at ambient temperature (20 °C).

For the sake of contrast, some crystals had been immersed in the 0.01M NaOH solution for 100 h with no voltage applied. Measurements showed that the immersion had little influence on the properties of the crystals, indicating that the barium titanate single crystals used in this study were chemically stable against water. Electrochemical hydrogen charging, on the contrary, obviously changed the dielectric properties of the crystals. Figure 1 shows the dielectric properties obtained for a representative sample before (marked by as grown) and after different periods of electrochemical hydrogen charging, respectively. To be consistent, the frequency spectra were measured after the crystal was aged for 15 min when the electrochemical hydrogen charging was interrupted. It can be seen that for the as-grown crystal, the dielectric loss was very small and the capacitance almost had no variation over the measuring frequency range (10^2 – 10^6 Hz), while after electrochemical hydrogen charging, the dielectric loss was dramatically increased with a dielectric loss peak formed between 10^4 – 10^5 Hz and the capacitance showed an obvious dependence on frequency. This frequency dependence of capacitance arose from the fact that the capacitance was considerably increased at low frequencies but was obviously decreased at high frequencies after electrochemical hydrogen charging.

As regards to hydrogen-induced changes in dielectric properties, there is a striking similarity between the barium titanate single crystals and TiO_2 ceramic capacitors that we had studied before.⁷ For the TiO_2 capacitors, electrochemical hydrogen charging had also led to a great increase in dielectric loss with a peak formed and an obvious increase in the capacitance-frequency dependence. Through Fourier transform infrared (FTIR) analysis on rutile single crystals, interstitial hydrogen was observed in TiO_2 lattice and the following reaction had been proposed:



where H_{ads} represents an adsorbed hydrogen atom and H_i^+ an ionized hydrogen in an interstitial site. The increase in dielectric loss of the TiO_2 capacitors was explained by the formation of a free electron in Eq. (1), while H_i^+ formed in Eq. (1) accounted for the change in capacitance. H_i^+ makes an important contribution to the polarization in the low frequency region through forming dipoles, so the capacitance

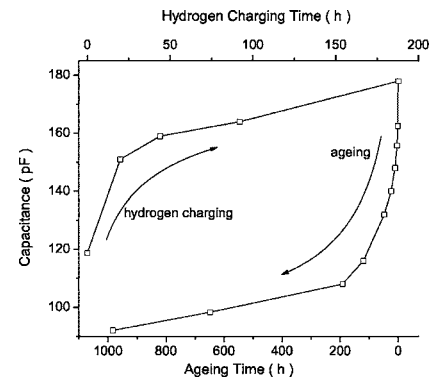


FIG. 2. Variations in the capacitance at 100 Hz for a barium titanate single crystal in the course of electrochemical hydrogen charging and a subsequent ageing process.

was obviously increased, especially at low frequencies. It is reasonable to assume that interstitial hydrogen can also be formed in perovskite barium titanate lattice through electrochemical hydrogen charging and result in the observed changes in dielectric properties. However, the decrease in capacitance at high frequencies in hydrogen-charged barium titanate single crystals was not observed in the hydrogen-charged TiO_2 capacitors. As we know, a major difference between BaTiO_3 and TiO_2 in their dielectric properties is that BaTiO_3 is ferroelectric with ferroelectric domains. Ferroelectric domains have great influences on dielectric properties and domain-wall pinning effect is generally believed to be responsible for the well known ferroelectric ageing phenomenon,⁸ which includes an obvious decrease in capacitance. The decrease in capacitance at high frequencies should also be related to some change in ferroelectric domains induced by interstitial hydrogen, whereas further investigations are needed to obtain a clearer picture.

The free electron formed in Eq. (1) should lead to a great increase in conductivity. However, I - V measurement showed that the leakage current in the barium titanate single crystal almost remained unchanged after 188 h of electrochemical hydrogen charging. Due to the great thickness of the single crystal, hydrogen must be distributed nonuniformly in the single crystal: two thin layers beneath the two silver electrodes were rich with hydrogen while the interior was undoped. The hydrogen-doped layers and the undoped interior were connected in series. The thickness of the hydrogen-doped layers was relatively small so the leakage current could not be effectively increased. On the other hand, the thickness of the hydrogen-doped layers increased with increasing time of electrochemical hydrogen charging, so the dielectric properties of the barium titanate single crystal changed continuously throughout the hydrogen charging process. As interstitial hydrogen increased the capacitance at low frequencies but decreased it at high frequencies, the capacitance was becoming bigger at 100 Hz and becoming smaller at 1 MHz. There must be a certain frequency at which the capacitance was not changed by interstitial hydrogen, and in Fig. 1 we can see that this frequency was around 30 kHz. The capacitance almost remained unchanged at 30 kHz but was either increased or decreased obviously at other frequencies. The relationship between the capacitance at 100 Hz and the time of electrochemical hydrogen charging is shown in Fig. 2. The increase in capacitance was particularly quick at the initial stage, and a 50% increase was obtained after 188 h of hydrogen charging. The relationship

between the dielectric loss and the time of electrochemical hydrogen charging was relatively complicated. The dielectric loss at 100 Hz showed a quite inconsistent dependence on the time of electrochemical hydrogen charging, while the movement of the dielectric loss peak was very clear. Both its height and its frequency increased with increasing time of electrochemical hydrogen charging.

The sample of Fig. 1 was kept at 20 °C for aging after electrochemical hydrogen charging had been conducted on it for a total time of 188 h. The moment, when the sample was finally disconnected from the dc voltage, was taken as the starting point of aging and its dielectric properties were measured successively with a series of periods of aging time. As shown in Fig. 3, the dielectric properties of the barium titanate single crystal were found to change systematically in the course of aging. With increasing time of aging, both the capacitance at 1 MHz and the slope of the capacitance-frequency curve decreased, while the dielectric loss peak moved to the low frequency side and the peak height decreased. After a long time of aging, the capacitance showed little frequency dependence and the dielectric loss could almost restore its original low value. It should be pointed out that this aging behavior was also very similar to that of the hydrogen-doped TiO₂ ceramic capacitors described above. It had been proposed that hydrogen does not form an O–H bond with oxygen ion in rutile and hydrogen is only metastable in the lattice.⁷ Obviously hydrogen must also be metastable in the lattice of barium titanate and its outdiffusion resulted in the observed aging behavior. The relationship between the capacitance at 100 Hz and the aging time is shown in Fig. 2. The capacitance decreased very quickly in the initial stage of aging and then the decrease slowed down with increasing time of aging. It can be seen that, compared to the as-grown capacitance, there was more than 20% decrease after 984 h of aging. As a matter of fact, the capacitance at 1 MHz decreased continuously during electrochemical hydrogen charging, and in the aging process it still decreased with increasing time of aging, showing no sign of recovery. This result indicates that the changes in ferroelectric domains induced by interstitial hydrogen must be irreversible, which could not be recovered naturally after the outdiffusion of hydrogen and the decrease in capacitance remained after aging for a long period of time.

As we can see clearly in Fig. 2, the dielectric properties of the barium titanate single crystals exhibited a quite dynamic behavior during electrochemical hydrogen charging and subsequent aging process, which was obviously related to the high mobility of hydrogen in the perovskite lattice. As a matter of fact, ferroelectric perovskite-type titanates are well known for resistance degradation under dc voltages, dramatic changes in dielectric properties after poling, and an obvious time dependence of dielectric properties during aging. A high stability in physical properties is of great importance for perovskite-type titanate single crystals, and polycrystals as well in view of practical applications and there have been extensive investigations on it. It is well known that under low dc voltages and high humidity, silver can enter into polycrystalline barium titanate through electromigration and act as the agent for changes in physical properties.⁹ As for mobile point defects, only oxygen vacancy has been paid much attention in most of these investigations. The role of hydrogen has been quite neglected. Our

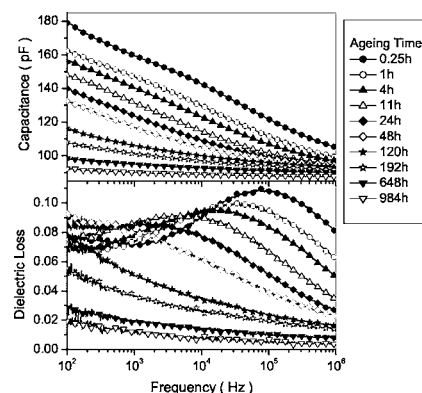


FIG. 3. Frequency spectra of capacitance and dielectric loss of a hydrogen-charged barium titanate single crystal in the course of an aging process.

result suggests that hydrogen is also an important factor for dielectric instability of perovskite-type titanates. Through a well-designed experiment, Ivker *et al.* found that interstitial hydrogen may fulfill the role of mobile ion usually attributed to oxygen vacancy in models of resistance degradation for perovskite-type oxides and a quantitative analysis of the competition between hydrogen and oxygen vacancy was expected.¹⁰ Though oxygen vacancy is ubiquitous in oxide materials, now more and more works have demonstrated that hydrogen also widely exists in many oxides, and as the smallest atom, it deserves extra attention due to its high mobility.¹¹

In summary, hydrogen from the electrolysis of water induced two kinds of time-dependent changes in dielectric properties of barium titanate single crystals: One was characterized by continuous increases in the slope of capacitance-frequency curve and in the height of a dielectric loss peak in the course of the electrolysis of water; the other was characterized by a continuous decrease in the slope of capacitance-frequency curve and continuous decreases in both the height and the frequency of the dielectric loss peak in subsequent aging process after the electrolysis of water. Obviously, hydrogen must have diffused into the single crystals during the electrolysis of water, and then gradually diffused out of the single crystals after the electrolysis of water, resulting in the observed dynamic dielectric behavior. Hydrogen is an important mobile ion other than oxygen vacancy in perovskite lattice and it may play a vital role in many time-dependent property changes, such as resistance degradation and ferroelectric aging, of perovskite-type ferroelectric titanates.

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