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Materials Letters 61 (2007) 4354–4357
materials letters
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Hydrogen-induced degradation in multiferroic $BiFeO_3$ ceramics

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Received 22 November 2006; accepted 1 February 2007
Available online 7 February 2007

Abstract

Chemical stability of multiferroic $BiFeO_3$ (BFO) ceramics has been studied through electrochemical hydrogen charging, in which BFO ceramic pellets were placed in 0.01 M NaOH solution with hydrogen deposited on their electrodes from the electrolysis of water. The properties of the samples were greatly degraded after the treatment: The leakage current was increased by orders of magnitude, the capacitance and the dielectric loss were dramatically increased in low frequency region. It was proposed that hydrogen entered into BFO lattice and existed at interstitial sites and the degradation was explained by hydrogen's reduction of some Fe^{3+} to Fe^{2+} in BFO. Hydrogen-induced degradation occurs relatively easily in BFO and much attention should be paid to it for BFO-based devices.

Keywords: $BiFeO_3$; Multiferroic; Hydrogen; Degradation

1. Introduction

With spontaneous electric and magnetic ordering in the same phase, multiferroics have been receiving more and more attention in recent years. The coupling between the electric and the magnetic polarizations in these materials not only provides an additional degree of freedom in device design, which may give rise to some new electronic devices, but also is of great interest to fundamental physics [1]. Perovskite-type $BiFeO_3$ (BFO) is one of the most widely studied multiferroic materials. It is antiferromagnetic with a relatively high Neel temperature ($T_N = 380$ °C) and ferroelectric with a high Curie temperature ($T_C = 810$ °C). And due to a residual moment from a canted spin structure, it exhibits weak ferromagnetism at room temperature [2]. Saturated ferroelectric hysteresis loops in BFO thin films at room temperature have been successfully observed and substrate-induced strains have been proven effective for enhancing the spontaneous polarization in the thin films [3]. As for BFO bulk ceramics, however, it had long been a great challenge to synthesize BFO ceramics with high phase purity and high resistivity. Remedies, such as leaching impurity phases with dilute nitric acid or forming solid solutions of BFO with other ABO_3 perovskite materials, had often been adopted to minimize secondary phases or increase the resistivity [4,5]. Recently, a rapid liquid phase sintering technique has been found useful for preparing single-phase BFO ceramics with high resistivity [6]. It was proposed that this rapid liquid phase sintering technique greatly suppresses the formation of Fe^{2+} and oxygen deficiency in BFO, so the leakage current has been greatly decreased. As BFO thin films and ceramics are becoming more and more promising for practical applications, the chemical stability of BFO should also be studied in time. For many electronic ceramic devices and components, the ambient-temperature reduction reaction of hydrogen from the electrolysis of water has been recognized as an important origin for degradation [7,8]. This degradation process is worthy of great attention since electroceramic components and devices always operate under some voltages while humidity is an essential environmental factor. For $Pt/SrBi_2Ta_2O_9/Pt$ thin film capacitors, it has been clearly demonstrated that one-half year maintenance under

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doi:10.1016/j.matlet.2007.02.001

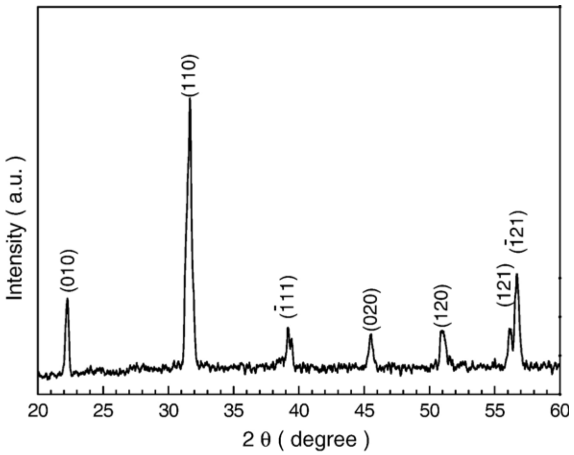

Fig. 1. X-ray diffraction pattern taken for a $BiFeO_3$ ceramic pellet prepared through a rapid liquid phase sintering technique.

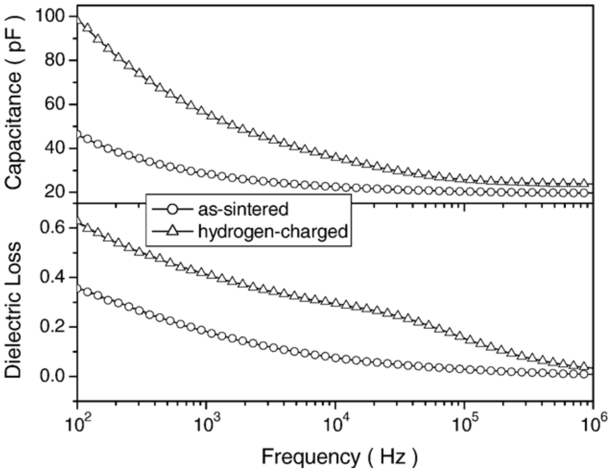

Fig. 3. Frequency spectra of capacitance and dielectric loss of a $BiFeO_3$ ceramic pellet measured as-sintered and after 3 h of electrochemical hydrogen charging, respectively.

typical atmospheric conditions (with relative humidity: 50–80%) will accumulate enough water for serious degradation [9]. Presently, we have studied the ambient-temperature reaction between BFO ceramics and hydrogen from the electrolysis of water. The influences of the reaction on the properties of BFO ceramics will be reported and the reaction mechanism will be discussed.

2. Experimental

Prepared by a rapid liquid phase sintering technique, BFO ceramic pellets with the size of 12 mm in diameter and 1.8 mm thick were used in our investigation. Silver electrodes of 3 mm in diameter were fired onto the centers of the two major surfaces of the pellets. Two different treatments were applied to the pellets for comparison. In the first treatment, some pellets were immersed in a 0.01 M NaOH solution for some time and then taken out, washed by de-ionized water and dried. In the second treatment, some other pellets were placed in a 0.01 M NaOH solution and DC voltages were applied between the silver electrodes of the pellets and a Pt electrode in the solution. The silver electrodes of the pellets acted as the cathode and hydrogen was evolved on them while oxygen was evolved on the Pt electrode when water was electrolyzed through the applied DC voltages. This treatment is referred to as “electrochemical hydrogen charging” hereafter. The solution was kept agitated by a magnetic agitator and the temperature was kept at 25 °C. The DC voltages were removed after some designated periods of time and the pellets were taken out, washed and dried. An Agilent 4294 A impedance analyzer was used to measure the frequency spectra of capacitance and dielectric loss of the pellets. The *I–V* characteristics of the pellets were recorded using a Keithley 6517 electrometer/high resistance meter. Both the dielectric and *I–V* measurements were conducted between the two silver electrodes of the pellets at room temperature (20 °C). Microstructural analyses were carried out by a scanning electron microscope Sirion FEG (Philips XL30) and an X-ray diffractometer (Philips PW 3719) with Cu K_α radiation was used for phase detection.

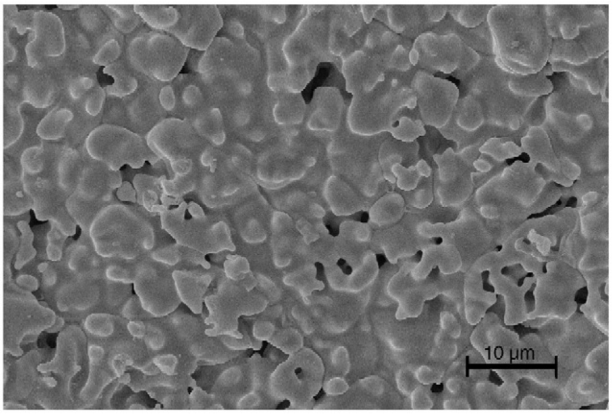

Fig. 2. SEM micrograph taken on the surface of a $BiFeO_3$ ceramic pellet prepared through a rapid liquid phase sintering technique.

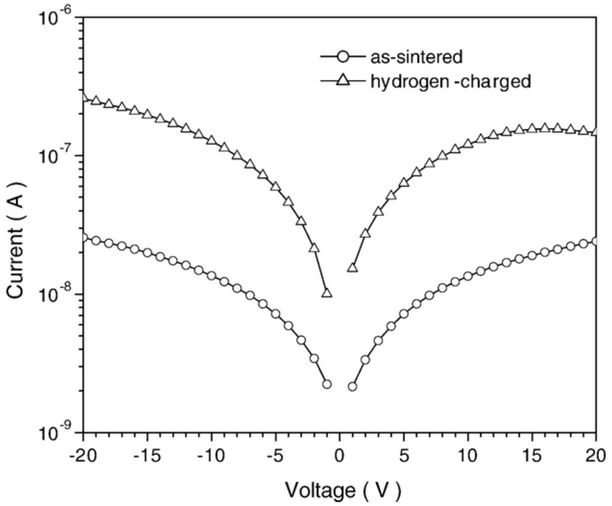

Fig. 4. *I–V* characteristics of a $BiFeO_3$ ceramic pellet measured as-sintered and after 3 h of electrochemical hydrogen charging, respectively.