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Chemical investigation of Fe^{3+}/Nb^{5+} -doped barium titanate ceramics

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Abstract

Renewed interest in the perovskite ferroelectric barium titanate (BaTiO₃) has been driven by the introduction of large recoverable electrostrain in doped BaTiO₃-based materials. Our previous work demonstrated that the potential for high-performance in Pb-free ferroelectrics based on BaTiO₃ was confirmed in Fe³⁺/Nb⁵⁺-doped BaTiO₃ systems. It is well documented that the electronic behavior of BaTiO₃ is intimately related to the chemical state of the constituents. However, information regarding the chemical states of the ions of the Fe³⁺/Nb⁵⁺-doped BaTiO₃ ceramics is currently unavailable. Consequently, this study describes the chemical state of sintered hybrid Fe³⁺/Nb⁵⁺-doped BaTiO₃ ceramics, compared with undoped BaTiO₃ ceramics derived from the same processing. Analysis by X-ray photoelectron spectroscopy (XPS) showed that the binding energy of Ti indicates the presence of more than one component of Ti within the doped BaTiO₃ ceramics, but only one component of Ti within the undoped BaTiO₃ ceramics. Unlike Ti, the XPS spectra indicates that more than one type of barium and oxygen species exist in both undoped and doped BaTiO₃ ceramics.

Keywords: D. Perovskite; Doped barium titanate; Chemistry state; XPS

1. Introduction

Barium titanates, BaTiO₃, are perovskite ferroelectric materials widely used in electronic applications, including capacitors, transducers, and semiconductors [1-3]. Doping BaTiO₃ with other metal oxides is generally found to be an effective method to modify electrical properties of these materials. Moreover, it is well established that the electrical properties of these ceramics also depend on the chemical states of the constituents and on the presence of contaminants [4,5].

According to the literature, X-ray photoelectron spectroscopy (XPS) has been occasionally used to investigate the chemical state of BaTiO₃ powders [6], BaTiO₃ ceramics [7,8], and doped BaTiO₃ ceramics [9]. Unfortunately, no work has been reported on the chemical state of Fe^{3+}/Nb^{5+} hybrid-doped barium titanate ceramics. Interestingly, members of our research team have reported the dielectric and ferroelectric properties of Fe^{3+}/Nb^{5+} hybrid-doped barium titanate ceramics and suggested that the change of chemical state of dopant occurred in the doped ceramics, which gave rise to changes in its dielectric and ferroelectric properties [10]. Here, we examine further the chemical constituents of the Fe^{3+}/Nb^{5+} hybrid-doped barium titanate ceramics in detail by using XPS. The ceramic samples investigated include: (a) undoped BaTiO₃, (b) BaTiO₃ doped with Fe^{3+} and Nb^{5+} having the formula $Ba(Ti_{0.98}Fe_{0.01}Nb_{0.01})O_3$, and (c) having the formula $Ba(Ti_{0.965}Fe_{0.01}Nb_{0.025})O_3$.

2. Methodology

The BaTiO₃ powders were prepared by a simple mixed oxide synthetic route using commercially available powders of BaCO₃ and TiO₂ (anatase form), (Fluka, > 99% purity) as starting materials. Undoped BaTiO₃ samples were sintered at 1400 °C for 4 h using the ball-milling method. The BaTiO₃ powders were mixed with Fe₂O₃ and

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Nb₂O₅ by the ball-milling method and then sintered at 1400 °C and 1450 °C for 4 h to form hybrid-doped BaTiO₃ ceramics with the formula Ba(Ti_{0.98}Fe_{0.01}Nb_{0.01})O₃ and Ba(Ti_{0.965}Fe_{0.01}Nb_{0.025})O₃, respectively. Phase formation and chemical composition of the ceramics were examined by using X-ray diffraction (XRD; Philips PW 1729 diffractometer), and an energy-dispersive X-ray (EDX) analyzer, respectively. X-ray photoelectron spectrawere collected using a PHI 5700 X-ray photoelectron spectrometer equipped with PHI 04091 neutralizer and a monochromatic Al K α X-ray source (hv = 1486.7 eV). After collection of the data, the binding energies were referenced by setting the C 1s binding energy to 284.8 eV. All peaks were fit with respect to spin-orbit splitting using standard curve-fitting software (Multipak V5.0A; Physical Electronics, Inc.).

3. Results and discussion

All undoped and doped BaTiO₃ samples were characterized with XRD to confirm a single-phase perovskite with tetragonal phase. Also, analysis by EDX showed that all chemical constituents of the ceramics were present in the sintered ceramics (data not shown). The Ba 3d XPS spectra of undoped BaTiO₃, Ba(Ti_{0.98}Fe_{0.01}Nb_{0.01})O₃, and $Ba(Ti_{0.965}Fe_{0.01}Nb_{0.025})O_3$ ceramics are shown in Fig. 1. After curve fitting, all peaks of the doped and undoped BaTiO₃ ceramics indicate two components (see inset in Fig. 1), one at \sim 778 eV and another at \sim 780 eV. The XPS spectra are similar to the spectra of BaTiO₃ reported by Mukhopadhyay and Chen [8] and Kumar et al. [9]. The first component at \sim 778 eVis assigned to Ba in the perovskite phase. The other peak at higher binding energy might arise from BaCO₃, which has been reported in $BaTiO_3$ powders by Miot et al. [7]. To verify the existence of BaCO₃, the C 1s spectra (data not shown) also show a



Fig. 1. XPS spectra showing the Ba 3d region for (a) undoped $BaTiO_3$, (b) $Ba(Ti_{0.98}Fe_{0.01}Nb_{0.01})O_3$, and (c) $Ba(Ti_{0.965}Fe_{0.01}Nb_{0.025})O_3$.

small peak at $\sim 288 \text{ eV}$, which can be attributed to CO_3^{2-} as described in the literature [7,11].

The Ti 2p XPS spectra are shown in Fig. 2. The Ti 2p spectra obtained from undoped BaTiO₃ (2(a)) and Ba(Ti_{0.98}Fe_{0.01}Nb_{0.01})O₃ (2(b)) ceramics are similar, exhibiting a $2p_{3/2}$ peak at ~457.5 eV and a $2p_{1/2}$ peak at \sim 463.5 eV. These results are similar to those observed for BaTiO₃ [9] and PbTiO₃ [12]. However, the Ti 2p spectra obtained from Ba(Ti_{0.965}Fe_{0.01}Nb_{0.025})O₃ (2(c)) show broad peaks with shoulders, especially the $2P_{3/2}$ peak. The peaks can be deconvoluted into two components (see inset in Fig. 2), one component at \sim 457.5 eV and another at lower binding energy, 456.0 eV. The component at higher binding energy can be attributed to Ti⁴⁺ in a perovskite structure [12,13], while the second component at lower binding energy might be attributed to Ti³⁺. According to the literature, if Ti³⁺ ions exist, the peak of Ti 2p should be broad, and the $2p_{3/2}$ peak of Ti^{3+} should appear at \sim 456 eV [13,14]. This might indicate that Ti⁴⁺ is substituted by Nb^{5+} in the BaTiO₃ lattice. The excess donor charge is compensated electronically by the reduction of Ti^{4+} into Ti^{3+} ion. However, we detected no Ti^{3+} ions in the Ti 2p spectra obtained from the Ba(Ti_{0.98-} Fe_{0.01}Nb_{0.01})O₃ ceramics, perhaps because the amount of Ti^{3+} was beneath the detection limit of the XPS technique.

The narrow-scan O 1s core level spectrum of undoped BaTiO₃ ceramics in Fig. 3(a) shows two peaks, which agrees with previous reports [7,9]. The first peak appears at \sim 529.5 eV, which is usually assigned to oxygen in the perovskite-base lattice [7,9]. The second peak appears at \sim 531.5 eV, which might be attributed to hydroxyl species and carbonate species. The O 1s spectrum of Ba(Ti_{0.98}. Fe_{0.01}Nb_{0.01})O₃ ceramics as shown in Fig. 3(b) is slightly different from those of undoped BaTiO₃. The different oxygen species might form due to the doping process; however, since the Fe and Nb spectra could not be



Fig. 2. XPS spectra showing the Ti 2p spectral region for (a) undoped $BaTiO_3$, (b) $Ba(Ti_{0.98}Fe_{0.01}Nb_{0.01})O_3$, and (c) $Ba(Ti_{0.965}Fe_{0.01}Nb_{0.025})O_3$.



Fig. 3. XPS spectra showing the O 1s spectral region for (a) undoped $BaTiO_3$, (b) $Ba(Ti_{0.98}Fe_{0.01}Nb_{0.01})O_3$ and (c) $Ba(Ti_{0.965}Fe_{0.01}Nb_{0.025})O_3$.



Fig. 4. XPS spectra showing the Nb 3d spectral region for $Ba(Ti_{0.965}Fe_{0.01} Nb_{0.025})O_3$.

detected in this sample, it is difficult to confirm this hypothesis. The O 1s spectrum of $Ba(Ti_{0.965}Fe_{0.01} Nb_{0.025})O_3$ ceramics (Fig. 3(c) and inset in Fig. 3) shows significant differences compared to those of undoped $BaTiO_3$ and $Ba(Ti_{0.98}Fe_{0.01}Nb_{0.01})O_3$ ceramics. Taking account to the differences in the corresponding Ti 2p and Nb 3d spectra, we believe that the new component of oxygen is generated by the doping process.

Fig. 4 shows the XPS spectral region for Nb 3d obtained from $Ba(Ti_{0.965}Fe_{0.01}Nb_{0.025})O_3$ ceramics. Attempts to detect the Nb 3d peak in samples of $Ba(Ti_{0.98}Fe_{0.01}Nb_{0.01})O_3$ were not successful, which is similar to our attempts to detect peaks for Fe 2p. The fact that we can detect no peaks for Nb 3d and Fe 2p is probably due to the low concentration of Fe and Nb in the samples. However, when we increase the amount of Nb, the broad and asymmetric Nb 3d peak was observed as shown in Fig. 4. After deconvolution of the peak, two components can identified (see inset in Fig. 4). The major component at binding energy $\sim 206.5 \text{ eV}$ can be assigned to Nb^{5+} in the perovskite structure [15], while the minor component at lower binding energy can be tentatively assigned to Nb⁴⁺ [16] or unreacted Nb₂O₅. Unruan et al. [10] reported changes in the dielectric and ferroelectric properties of Fe³⁺/Nb⁵⁺ hybrid-doped barium titanate ceramics, and proposed that Fe³⁺/Fe²⁺ and Nb⁵⁺/Nb⁴⁺ exist in the Fe^{3+}/Nb^{5+} hybrid-doped barium titanate ceramics. Our results in the present study might confirm the presence of Nb^{5+}/Nb^{4+} in doped barium titanate ceramics.

4. Conclusions

The chemical state of Ba, Ti, and oxygen in undoped BaTiO₃, Ba(Ti_{0.98}Fe_{0.01}Nb_{0.01})O₃ and Ba(Ti_{0.965}Fe_{0.01}Nb_{0.025})O₃ ceramics was examined using X-ray photoelectron spectroscopy. The studies showed that the chemical states of Ti and oxygen are altered by doping BaTiO₃ with Fe³⁺ and Nb⁵⁺, while the chemical state of Ba remains unchanged. However, the change could be detected only for the Ba(Ti_{0.965}Fe_{0.01}Nb_{0.025})O₃ ceramics. Also, BaCO₃ species were present in all of the samples.

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