Experiment and first principles investigation on the hydrogen-hindered phase transition of ferroelectric ceramics

H. Y. Huang, W. Y. Chu, Y. J. Su, J. X. Li, and L. J. Qiao[a)]
Laboratory of Environmental Fracture (Ministry of Education), Department of Materials Physics, University of Science and Technology Beijing, Beijing 100083, China

S. Q. Shi
Department of Mechanical Engineering, the Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong, China

In this letter, hydrogen-hindered phase transition of ferroelectric ceramics from cubic to tetragonal has been studied by experiment and first principles calculation. The calculation shows that for hydrogenated tetragonal $PbTiO_3$, double-lowest-energy sites of Ti along the c axis exist no longer and the only lowest energy site locates at the center of the cell. The calculation can explain the experiment that hydrogen charged above its Curie temperature can hinder phase transition of lead zirconate titanate from cubic paraelectricity to tetragonal ferroelectricity. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2358289]

Ferroelectric ceramics have been widely used in smart devices such as actuators, sensors, micropositioners, and transformers.[1] It is well known that hydrogen generated during forming gas annealing or in electroplating process may cause severe degradation in resistivity and ferroelectricity.[2–10] Up to now, however, there is no report about the effect of hydrogen on phase transition of ferroelectric ceramics. After forming gas annealing above its Curie temperature the polarization-voltage hysteresis loop of PZT film disappeared gradually.[9,10] No hysteresis implies that it is a cubic paraelectricity. Therefore, it seems that hydrogen entered above its Curie temperature can hinder the phase transition of the PZT film from cubic paraelectricity to tetragonal ferroelectricity, although nobody in Refs. 9 and 10 mentioned this point of view.

First principles investigations have obtained lots of significant results in ferroelectricity and ferroelectric transition for perovskite-based ferroelectric ceramics.[11–14] The goal of this letter was to investigate the effect of hydrogen on phase transition of ferroelectric ceramics through experiment and first principles calculation.

A commercial soft lead zirconate titanate ceramic $Pb(Zr_{0.52}Ti_{0.48})O_3$ (PZT-5H) was used. The description of specimen, charging process, and measurement of hydrogen concentration have been reported elsewhere.[15,16]

X-ray diffraction (XRD) and heating differential scanning calorimetry (DSC) patterns of PZT-5H in different charging conditions are shown in Figs. 1(a) and 1(b), respectively. The appearance of double peaks in curves A, B, C, and E in Fig. 1(a) corresponds to tetragonal phase and no double peaks in curve D corresponds to cubic phase. The ratios of c to a axis calculated based on curves A–E in Fig. 1(a) were 1.0114, 1.0128, 1.0113, 1.0000, and 1.0077, respectively. The calculation of c/a also proved that curve D corresponds to cubic phase and the others correspond to tetragonal phase. Figure 1(b) indicates that there is an endothermic transition from tetragonal ferroelectricity to cubic

paraelectricity at its Curie temperature of 300 °C for the samples uncharged and charged below the Curie temperature, as shown by curves A, B, and C in Fig. 1(b). For the sample charged in H_2 at 450 °C, however, there is no endothermic peak from 25 to 450 °C, as shown by curve D in Fig. 1(b). After outgassing at 800 °C, however, the endothermic peak appears again at the Curie temperature of 300 °C, as shown by curve E in Fig. 1(b). These results indicate that the lattice parameters and the tetragonal structure of the PZT-5H do not change after charging at the temperature below the Curie temperature. However, if the charging temperature is higher than the Curie temperature, the PZT-5H will be a cubic paraelectricity instead of tetragonal ferroelectricity after cooling to room temperature. After outgassing at 800 °C, the tetragonal ferroelectricity is restored. Therefore, hydrogen charged above its Curie temperature can hinder the phase transition from cubic to tetragonal during cooling to room temperature.

First principles plane-wave pseudopotential density functional theory as implemented in the CASTEP code within the local-density approximation was applied.[17] All calculations were carried out in $PbTiO_3$ structure instead of PZT structure to make it easier to discuss. A hydrogen atom was
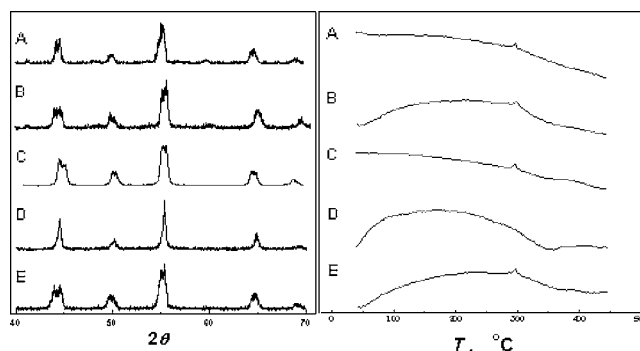

FIG. 1. XRD (a) and heating DSC curve (b) patterns of PZT-5H in different charging conditions. A, hydrogen-free; B, charging at 400 mA/cm^2 in solution at 20 °C, charging in H_2^- at 250 °C; D, charging in H_2 with P_{H_2} =0.4 MPa at 450 °C; and E, outgassing at 800 °C after charging in H_2 at 450 °C.

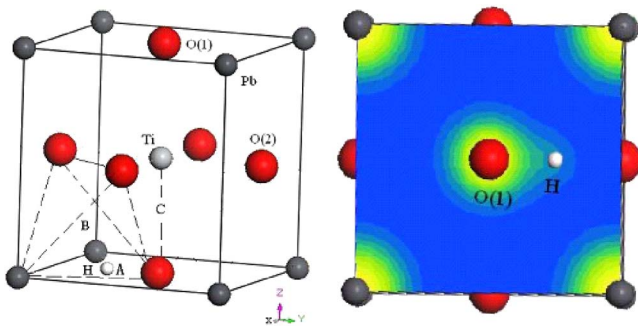[a)]Author to whom correspondence should be addressed; FAX: 86-10-6233-2345; electronic mail: lqiao@ustb.edu.cn

      © 2006 American Institute of Physics

FIG. 2. (Color online) Unit cell of tetragonal PbTiO₃ containing one hydrogen atom (a) and electronic clouds of *XOY* plane (b).

put into the perovskite-type unit of cubic and tetragonal PbTiO₃ and then its possible locations were looked for. Figure 2(a) is a tetragonal PbTiO₃ with one H in the unit cell and *A*, *B*, and *C* are three possible sites H occupied. Calculation showed that the minimum values of total energies corresponding to site *A* at (0.5, 0.25, 0.05), tetrahedral interstitial site *B* at (0.25, 0.25, 0.25), and site *C* between Ti and apical O(1) ion at (0.5, 0.5, 0.25) were −4601.73, −4601.04, and −4600.15 eV, respectively. When hydrogen occupied site *A*, *B*, or *C*, the distances between H and O(1) were 0.1016 nm, 0.1485 nm, and 0.1529 nm, respectively. Hydrogen should occupy site A, the total energy is the lowest and the distance between H and O(1) has a smallest value, compared to sites *B* and *C*, which are the possible sites proposed by Aggarwal *et al.*[9] The distance 0.1016 nm means that a strong interaction between H and O(1) exists, which can result in the overlap of the electronic clouds between H and O(1), as shown in Fig. 3(b). The calculation is consistent with the experimental results,[9,10] i.e., existing O–H bonds in PZT ceramics. Calculation showed that the electron overlap populations between O–Ti were 0.98 for hydrogen-free PbTiO₃ and 0.70 for hydrogenated PbTiO₃, respectively. Hydrogen decreases the electron overlap population between O–Ti means that hydrogen weakens the interaction between O–Ti. It has been pointed out that the stronger the hybridization between the two atoms, the larger tendency to form
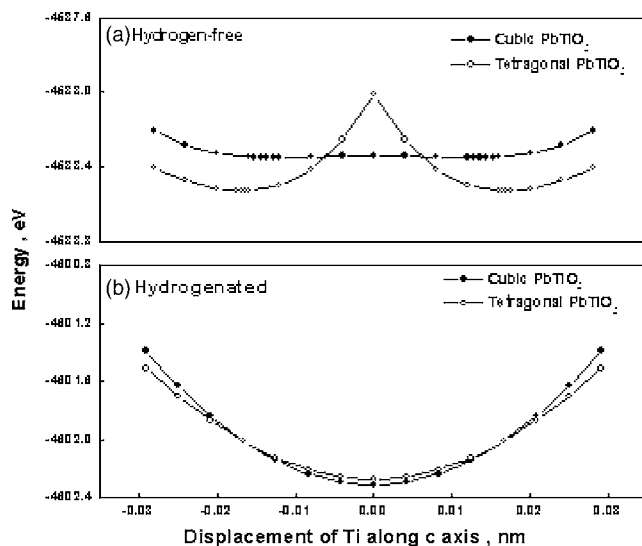
bond or interaction between two atoms.[18,19] Therefore, hydrogen decreases the overlap population between O–Ti and weakens the hybridization between O–Ti, resulting in the decrease of stability of tetragonal ferroelectric phase.

The variation of the total energy with the displacement of Ti along the *c* axis for hydrogen-free and hydrogenated PbTiO₃ is shown in Fig. 3. Fig. 3(a) indicates that for hydrogen-free PbTiO₃ with the tetragonal structure, there are two lowest energy sites for Ti in the *c* axis which are ±0.016 nm from the center of the unit cell. The calculation result is consistent with the experimental value of ±0.017 nm.[20] Figure 3(b), however, shows that for the hydrogenated tetragonal structure, the double-lowest-energy sites of Ti along the *c* axis disappear and the lowest energy site is located at the center of the cell. Therefore, when hydrogen enters into the cubic PbTiO₃ above its Curie temperature, the cubic structure continues to be a stable structure during cooling because for Ti there is no lower energy site than the center of the cell. As a result, ferroelectric tetragonal structure in PbTiO₃ charged above the Curie temperature will not appear during cooling to room temperature because of no displacement of Ti along the *c* axis. The calculation can explain the experiment that hydrogen charged above its Curie temperature will hinder phase transition of PZT-5H from cubic paraelectricity to tetragonal ferroelectricity.

Figure 1, however, also indicates that PZT keeps a tetragonal structure after charging at the temperature below the Curie temperature. The reason is the existence of energy barrier from tetragonal to cubic which composed of elastic energy, depoling energy, and static electric energy. Besides the insufficient thermal energy, hydrogen entered into tetragonal PZT during charging below the Curie temperature cannot provide an additive energy to overcome the energy barrier, and then the tetragonal structure cannot transform to cubic structure during charging below the Curie temperature.

In summary, the first principles calculation shows that for hydrogenated tetragonal PbTiO₃, the double-lowest-energy sites of Ti along the *c* axis exist no longer and the only lowest energy site locates at the center of the cell. Therefore, for a cubic PbTiO₃ charged above its Curie temperature, Ti cannot move along the *c* axis to be a tetragonal structure during cooling to room temperature. The calculation can explain the experiment that hydrogen charged above its Curie temperature can hinder phase transition of lead zirconate titanate from cubic paraelectricity to tetragonal ferroelectricity.

FIG. 3. Total energy vs displacement of Ti along the *c* axis, the original is the center of the cell. (a) Hydrogen-free PbTiO₃ and (b) hydrogenated PbTiO₃.

[1] K. Uchino, Acta Mater. **46**, 3745 (1998).
[2] J. P. Han and T. P. Ma, Appl. Phys. Lett. **71**, 1267 (1997).
[3] Nobuyuki Ikarashi, Appl. Phys. Lett. **73**, 1955 (1998).
[4] T. Tamura, K. Matsuura, H. Ashida, K. Kondo, and S. Otani, Appl. Phys. Lett. **74**, 3395 (1999).
[5] S. Aggarwal, S. R. Perusse, B. Nagaraj, and R. Ramesh, Appl. Phys. Lett. **74**, 3023 (1999).
[6] J. T. Evans, L. L. Boyer, G. Velasquez, R. Ramesh, S. Aggavwal, and V. Keramidas, Jpn. J. Appl. Phys., Part 1 **38**, 5361 (1999).
[7] N. R. Rajopadhye, S. S. V. Bhoraskar, and A. P. B. Sinha, J. Mater. Sci. **23**, 2631 (1988).
[8] W. P. Chen, L. T. Li, Y. Wang, and Z. L. Gui, J. Mater. Res. **13**, 1110 (1998).
[9] S. Aggarwal, S. R. Perusse, C. W. Tipton, R. Ramesh, H. D. Drew, T. Venkatesan, D. B. Romero, V. B. Podobedov, and A. Weber, Appl. Phys.

Lett. **73**, 1973 (1998).

[10] Heung Jin Joo, Sang Hern Lee, Jong Pil Kim, Min Ki Ryu, and Min Su Jang, Ferroelectrics **272**, 149 (2002).

[11] R. E. Cohen and H. Krakauer, Ferroelectrics **136**, 65 (1992).

[12] R. E. Cohen, Nature (London) **358**, 136 (1992).

[13] R. E. Cohen and H. Krakauer Phys. Rev. B **B42**, 6416 (1990).

[14] P. Ghosez, X. Gonze, and J. P. Michenaud, Ferroelectrics **220**, 1 (1999).

[15] Y. Wang W. Y. Chu, L. J. Qiao, and Y. J. Su, Mater. Sci. Eng., B **98**, 1 (2002).

[16] X. Peng, Y. J. Su, K. W. Gao, L. J. Qiao, and W. Y. Chu, Mater. Lett. **58**, 2073 (2004).

[17] M. D. Segall, P. J. D. Lindan, M. J. Probert, C. J. Pickard, P. J. Hasnip, S. J. Clark, and M. C. Payne, J. Phys.: Condens. Matter **14**, 2717 (2002).

[18] M. D. Segall, R. Shah, C. J. Pickard, and M. C. Payne, Phys. Rev. B **54**, 317 (1996).

[19] Y. Shimakawa, Y. Kubo, Y. Tauchi, H. Asano, T. Kamiyama, F. Izumi, and Z. Hiroi, Appl. Phys. Lett. **79**, 2791 (2001).

[20] D. Shirane, R. Pepinsky, and B. C. Frazer, Phys. Rev. **97**, 1179 (1955).