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Experiments and first principles calculations on the effects of hydrogen on the optical properties of ferroelectric materials

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Abstract The effects of hydrogen on the optical properties of lead zirconate titanate (PZT) ceramics and $BaTiO_3$ single crystals have been investigated. The experimental results showed that the color of $BaTiO_3$ single crystals changed from light to dark after charging of hydrogen in NaOH solution at room temperature and in H_2 gas at high temperature, and then, restored to light color after outgassing in the air, which were the same as PZT-5H ceramics reported earlier. Measurement of the absorbance indicated that hydrogen increased the absorbance within the visible spectrum for both PZT ceramics and $BaTiO_3$ single crystals. The first principles calculations for $Pb(Zr_{0.5}Ti_{0.5})O_3$ and $BaTiO_3$ showed that hydrogen increased the absorbance within the infrared and visible spectral region and the absorbance increased with the rise of hydrogen concentration. Density of states (DOS) researches indicated that hydrogen changed the DOS of the outer shell electrons, which caused the change of absorbance spectrum.

Introduction

In the rapidly developing field of photonics, there is an increasing demand for new devices that are capable of processing large quantities of optical information. Perovskite ferroelectric materials, such as lead zirconate titanate (PZT), and barium titanate ($BaTiO_3$), exhibit a combination of the properties that make them attractive for variety of photonic applications. Both ferroelectric materials were used to turn the optical energy and thermal energy to electric energy because of their pyroelectric properties, which was applied to the infrared imager. Hydrogen can enter into the ferroelectric ceramics, such as PZT and PMN-based relaxed ferroelectrics, during electrodepositing or annealing in the forming gas and cause color change and severe degradation in resistivity and ferroelectric properties [1–9]. In the reports by Huang et al. [1], Chen et al. [4], Evans et al. [10] and Rajopadhye et al. [11], the degradation in resistivity and ferroelectric properties were investigated in detail. For more and more comprehensive applications of ferroelectric materials in optical devices, that hydrogen can change the color of ferroelectric ceramics must be noted. This phenomenon has been reported in literature [1–4], but there was little approach in mechanism. First principles calculations have obtained many significant results on the optical properties of ferroelectric materials [10–16]. Stashans and Rivera [12] studied the geometry and electronic properties of the interstitial H atom in the tetragonal $PbTiO_3$ crystal using quantum chemical method. The results showed that H atom in the H-Doped $PbTiO_3$ bound to one of the O atoms and formed O–H groups and changed the electronic structure, which the optical properties of materials strongly depended on. Stashans and Rivera's results are consistent with our previous report [17]. The goal of this paper is to study the effect of hydrogen on the absorbance and its relation to the color change, by experiments for PZT-5H ceramics and $BaTiO_3$ single crystals, and by first principles calculations for $Pb(Zr_{0.5}Ti_{0.5})O_3$ and $BaTiO_3$ single crystals.

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Experiment procedure

Commercial PZT-5H, i.e., $Pb(Zr_{0.52}Ti_{0.48})O_3$ and $BaTiO_3$ single crystals were used in present experiments. Nickel electroplated PZT-5H samples were charged in the 0.2 mol/L NaOH + 0.25 g/L As_2O_3 solution at 20 °C with 10 mA/cm^2 for 45 h, and in pure H_2 gas (0.4 MPa) at 450 °C for 20 h. Two surfaces of 5 mm × 5 mm of one $BaTiO_3$ single crystals with the thickness of 1 mm were spread with silver electrodes and charged in 0.2 mol/L NaOH + 0.25 g/L As_2O_3 solution at 20 °C with 10 mA/cm^2 for 168 h [18, 19]. The other piece of $BaTiO_3$ single crystal was charged in pure H_2 gas (0.4 MPa) at 600 °C for 50 h. The colors of the PZT-5H ceramics changed from yellow to black after charging, and restored to yellow after outgassing in the air at 800 °C for 2 h, as shown in Ref. [1]. For the $BaTiO_3$ single crystals, the colors changed from light color to dark one after charging, and restored to light color after outgassing in the air at 400 °C for 6 h, as shown in Fig. 1.

The effects of hydrogen on the absorbance within the visible spectrum for PZT-5H ceramics and $BaTiO_3$ single crystals are shown in Fig. 2a and b, respectively. For both ferroelectric materials, the specimens charged in the solution and in H_2 gas have the same absorbance curves. Figure 2 indicated that hydrogen enhance the absorbance within the visible spectrum, which means hydrogen can cause these ferroelectric materials to change from a light color to a dark one.

Theoretical approach

First principles density functional theory calculations were conducted using the CASTEP code, aided by the Materials Studio graphical front–end interface [20]. Exchange correlation interactions were described by the generalized gradient approximation (GGA) in Perdew-Bruke-Ernzerholf (PBE) form [21]. The Ultra-soft pseudopotential of Vanderbilt type [22] was used for the treatment of core electrons. For all systems, we used a kinetic cutoff energy of 380 eV. A 6 × 6×6 mesh of special *k*-points in the irreducible Brillouin zone was employed for *k*-space integrations. The locations of hydrogen in $BaTiO_3$ and $Pb(Zr_{0.5}Ti_{0.5})O_3$ are shown in Fig. 3a and b, respectively. Our previous work showed the most stable position for H was ($0.5a$, $0.25a$, $0.05c$), where a and c are lattice constants of the tetragonal structure [13]. When H atom locates at the most stable position, the lattice constants of $BaTiO_3$ change from $a = b = 3.992$ Å, $c = 4.036$ Å to $a = 4.075$ Å, $b = 4.069$ Å, $c = 4.128$ Å, while that of $Pb(Zr_{0.5}Ti_{0.5})O_3$ from $a = b = 3.902$ Å, $c = 8.312$ Å to $a = 4.107$ Å, $b = 4.089$ Å, $c = 8.419$ Å. For $BaTiO_3$, the displacement between Ti atom and O plane cross the polarization direction decreases from 0.115 to 0.055 Å, the dipole moment of the cell decrease then lead to the falling polarization. For $Pb(Zr_{0.5}Ti_{0.5})O_3$, not only the displacement of the atoms but also the c/a decrease to reduce the polarization.

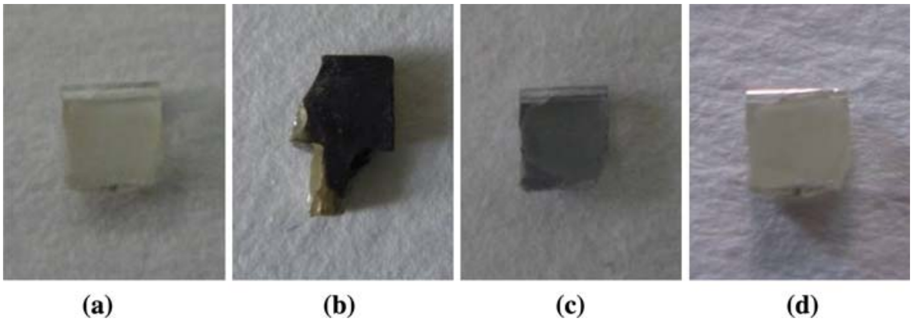

(a) (b) (c) (d)

Fig. 1 The color change of $BaTiO_3$ single crystal after charging and outgassing **a** hydrogen-free; **b** charging in the solution with 10 mA/cm^2 at 20 °C for 168 h; **c** charging in H_2 gas of 0.4 MPa at 600 °C for 50 h; **d** outgassing in air at 400 °C for 6 h

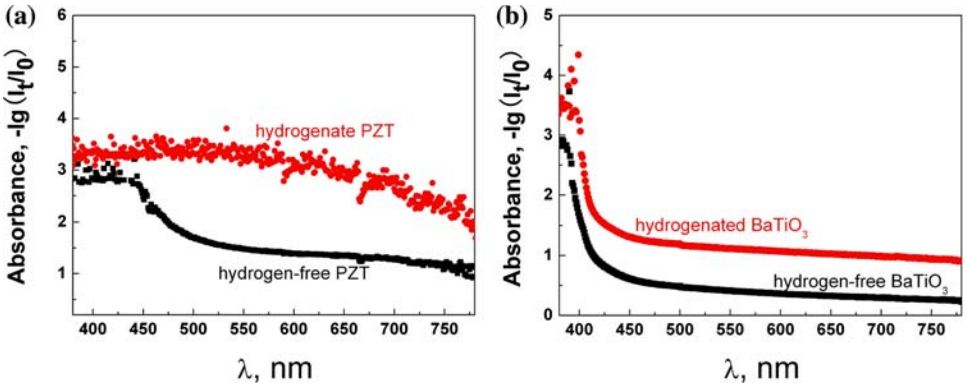


Fig. 2 Experiments demonstrated that hydrogen increased the absorbance within the visible spectrum for **a** PZT-5H ceramics **b** $BaTiO_3$ single crystals

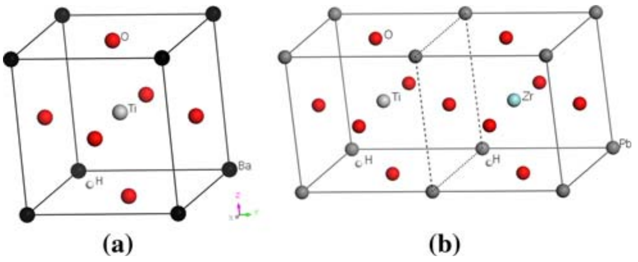


Fig. 3 Unit cells of **a** $BaTiO_3$ + H and **b** $Pb(Zr_{0.5}Ti_{0.5})O_3$ + H, *z* is the polarization direction

The absorbance can be directly obtained based on the CASTEP code [13–16]. For the insulating systems, most of the difference between Kohn–Sham eigenvalues and the true excitation energies can be accounted for by a rigid shift (known as scissors operator) of the conduction band upwards with respect to the valence band [16, 23]. The scissors approximation operator applied in the calculation for $BaTiO_3$ is 1.28 eV [15], and 1.55 eV was used for $Pb(Zr_{0.5}Ti_{0.5})O_3$. The calculation results show that hydrogen enhances the absorbance within visible and the infrared spectral region (λ = 380–1000 nm) for $Pb(Zr_{0.5}Ti_{0.5})O_3$ and $BaTiO_3$, as shown in Fig. 4. The increased absorbance in visible region means the samples absorb more visible light and the color should be changed to dark, which is consistent with experiments. The supercells of $[Pb(Zr_{0.5}Ti_{0.5})O_3]_8H$ and $[BaTiO_3]_8H$ were used for first principles calculations to vary the hydrogen concentration. The results indicate lower hydrogen concentration causes the absorbance to decrease, as shown with triangle symbol in Fig. 4. The absorbances in visible spectrum for both materials increase with the rise of hydrogen concentration.

The density of states (DOS) is calculated for hydrogen-free and hydrogenated tetragonal $Pb(Zr_{0.5}Ti_{0.5})O_3$ and $BaTiO_3$, respectively, as shown in Fig. 5. Figure 5a indicates that after scissors operator, the widths of the forbidden band are 3.20 and 3.15 eV for hydrogen-free $Pb(Zr_{0.5}Ti_{0.5})O_3$ and $BaTiO_3$, respectively. Only the visible light with energy greater than 3.20 and 3.15 eV, can be absorbed by hydrogen-free $Pb(Zr_{0.5}Ti_{0.5})O_3$ and $BaTiO_3$, respectively. Figure 5b shows that hydrogen causes DOS curves to move toward the direction of low-energy. As a result, one part of the bands used to be empty is below the Fermi energy. The continuous distribution of the state density near the Fermi energy makes all visible light absorbable. In the visible and infrared spectral region, the absorbance is due to the excitation of the outer shell electrons [16]. The partial density of states (PDOS) of Ti *d*, O *p*, Ba *s*, Pb *p*, Zr *d* for hydrogen-free and hydrogenated $Pb(Zr_{0.5}Ti_{0.5})O_3$ and $BaTiO_3$ are also calculated and showed in Fig. 6. From Fig. 6, hydrogen shifted the PDOS of the outer shell electrons toward the low-energy, which is

Fig. 4 First principles calculations demonstrate that hydrogen increases the absorbance within the visible and infrared spectrum for **a** $Pb(Zr_{0.5}Ti_{0.5})O_3$, **b** $BaTiO_3$. *Triangle* symbols correspond to the results of $[Pb(Zr_{0.5}Ti_{0.5})O_3]_8H$ and $[BaTiO_3]_8H$, respectively

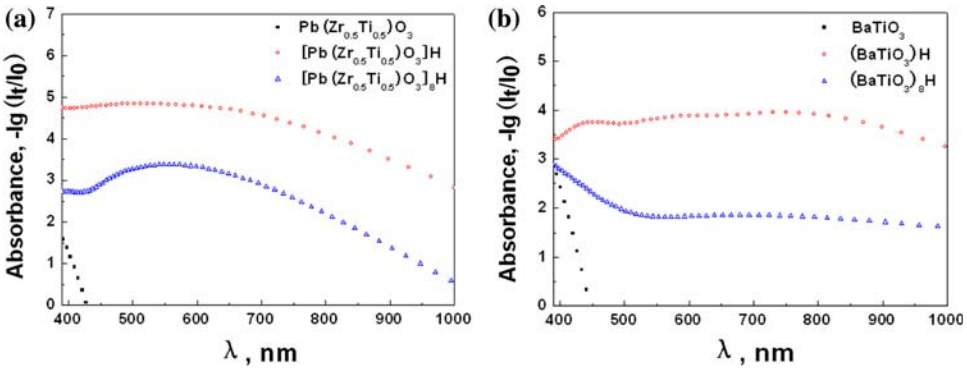
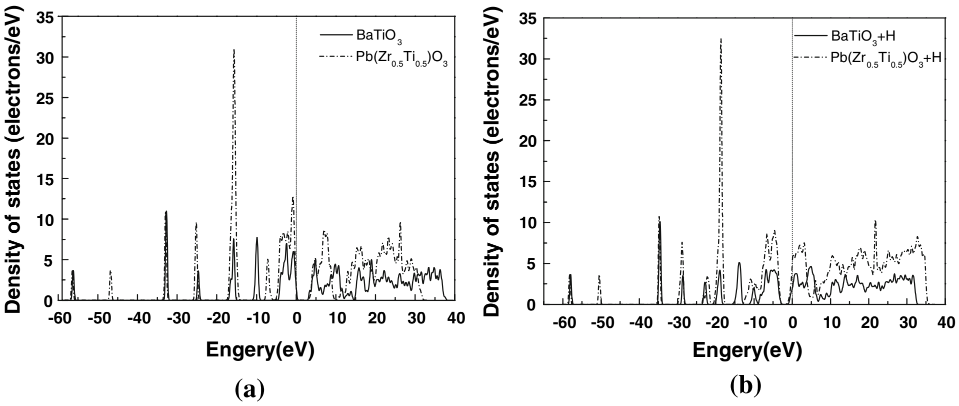


Fig. 5 DOS of **a** hydrogen-free and **b** hydrogenated $Pb(Zr_{0.5}Ti_{0.5})O_3$ and $BaTiO_3$



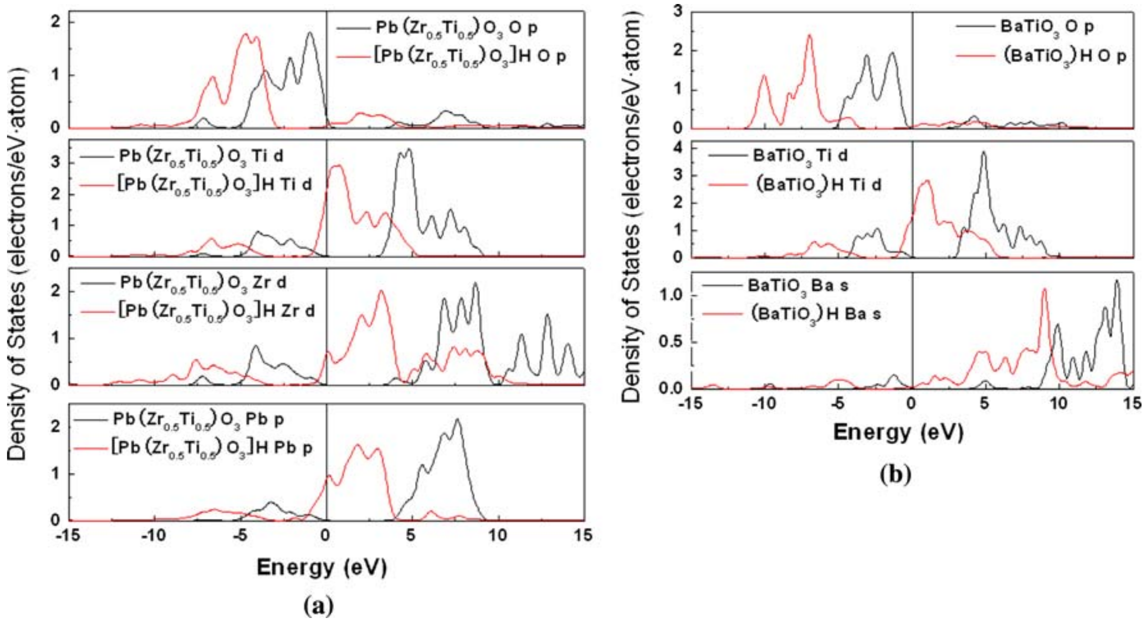

(a)
(b)

Fig. 6 PDOS of **a** hydrogen-free and **b** hydrogenated $Pb(Zr_{0.5}Ti_{0.5})O_3$ and $BaTiO_3$

the reason for the change of the absorbance in visible and infrared spectral region.

Discussion

The optical spectra of $BaTiO_3$ are assigned to interband contribution from O 2*p* valence bands to Ti 3*d* conduction bands in the low-energy region and from near valence band semicore levels Ba 5*p* and O 2*s* to conduction band in the high-energy region [15]. PDOS research shows that hydrogen changes the PDOS of the outer shell electrons moving to the low-energy, which induces increased absorbance in visible and infrared spectral region. As shown in Fig. 2, hydrogen enhances the absorbance within the visible spectrum, which means hydrogen can cause these ferroelectric materials to change from a light color to a dark one.

For ferroelectric materials, the cause of hydrogen-increased absorbance is identical to that of hydrogen-increased conductivity or hydrogen-induced semiconductor transformation [1]. Chen et al. proposed hydrogen during charging in the NaOH solution at room temperature could undergo reduction of

$$2\mathrm{H} + \mathrm{O}^{2-} \rightarrow \mathrm{H_2O} + V_{\mathrm{O}}^{*} \tag{1}$$

and electrons were generated from the ionization of oxygen vacancies V_{O}^{*}, resulting in the color change and transformation from insulator to semiconductor [4]. Rajopadhye et al. considered that some Pb^{2+} on the surface layer, during charging at high temperature, is reduced into metallic lead based on the following equation:

$$2\mathrm{H} + \mathrm{PbO} \rightarrow \mathrm{H_2O} + \mathrm{Pb} \tag{2}$$

resulting in color change and an increase in the conductivity [11]. The above reaction can only occur on the surface, therefore, the color change relate to the oxygen ions in the ceramics diffusing from the interior to the surface. Otherwise, the mechanism of oxygen loss, thereby creating free electrons, is also dependent upon the diffusion of oxygen. According to the following diffusion equation of oxygen in $BaTiO_3$ [24]:

$$D(\mathrm{cm^2/s}) = 2.9 \times 10^{-10} \exp[(-5250 \pm 1500)/T] \tag{3}$$

the maximum diffusion coefficient of oxygen at 20 °C is $D_{\mathrm{O}} = 1.1 \times 10^{-15}\,\mathrm{cm^2/s}$, and the maximum diffusion distance of oxygen during charging at 20 °C for 10 and 45 h is $X_{\mathrm{O}} = 4\sqrt{Dt} =$ 0.25 and 0.53 μm, respectively. The depths of the color change zone of PZT-5H ceramics are 440 and 900 μm, respectively, after charging at 20 °C for 10 and 45 h [1]. These depths are about 2×10^3 times larger than the diffusion distance of oxygen. Only atomic hydrogen has so large a diffusion coefficient, which is about $D_{\mathrm{H}} = X^2/16t = 4.9 \times 10^{-8}\,\mathrm{cm^2/s}$, based on the experimental results [1]. Therefore, the color change during charging at room or high temperature could be due to hydrogen diffused into the specimens, which generates extra electrons through ionization. The hydrogen positive ion binds to one of the O atoms and the electrons generated from ionization of hydrogen cause the density of states of ferroelectric materials to change, resulting in increased absorbance within visible spectrum.

Concluding remarks

We investigated the effect of hydrogen on the optical properties of PZT ceramics and $BaTiO_3$ single crystals. The experimental results showed that the colors of PZT-5H ceramics changed from yellow to black and that of $BaTiO_3$ single crystals changed from light color to dark one after charging of hydrogen in NaOH solution at room temperature and in H_2 gas at high temperature. The change of color can restore by outgassing in the air. Measurement of the absorbance indicated that hydrogen increased the absorbance within the visible spectrum for both PZT ceramics and $BaTiO_3$ single crystals. According to the results of first principles calculations, we can conclude the effect of hydrogen on optical properties of ferroelectric material into diffusion of hydrogen into the specimens, and ionization to generate extra electrons which cause the density of states of ferroelectric materials to change, resulting in increasing absorbance within visible spectral region. Hydrogen also can increase the absorbance within the infrared region. The absorbance for both materials in visible and infrared spectral region increases with the rise of hydrogen concentration.

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References

1. Huang HY, Chu WY, Su YJ, Gao KW, Li JX, Qiao LJ (2007) J Am Ceram Soc 90:2062
2. Aggarwal S, Perusse SR, Tipton CW, Ramesh R, Drew HD, Venkatesan T et al (1998) Appl Phys Lett 73:1973
3. Joo HJ, Lee SH, Kim JP, Ryu MK, Jang MS (2002) Ferroelectrics 272:149
4. Chen WP, Li LT, Wang Y, Gui ZL (1998) J Mater Res 13:1110
5. Han JP, Ma TP (1997) Appl Phys Lett 71:1267
6. Ikarashi N (1998) Appl Phys Lett 73:1955
7. Tamura T, Matsuura K, Ashida H, Kondo K, Otani S (1999) Appl Phys Lett 74:3395
8. Aggarwal S, Perusse SR, Nagaraj B, Ramesh R (1999) Appl Phys Lett 74:3023
9. Cao JL, Li LT, Wang YL, Zhao JQ, Gui ZL (2001) Mater Res Bull 36:2103
10. Evans JT, Boyer LL, Velasquez G, Ramesh R, Aggavwal S, Keramidas V (1999) Jpn J Appl Phys 389B:5361
11. Rajopadhye NR, Bhoraskar SSV, Sinha APB (1998) J Mater Sci 23:2631. doi:10.1007/BF01111925
12. Stashans A, Rivera R (2007) Int J Quantum Chem 108:1508
13. Samantaray CB, Sim H, Hwang H (2005) Appl Surf Sci 250:146
14. Samantaray CB, Sim S, Hwang H (2005) Microelectron J 36:725
15. Cai MQ, Yin Z, Zhang MS (2003) Appl Phys Lett 83:2805
16. Hosseini SM, Movlarooy T, Kompany A (2007) Phys B 391:316
17. Huang HY, Chu WY, Su YJ, Li JX, Qiao LJ (2006) Appl Phys Lett 89:142904
18. Su YJ, Wang Y, Chu WY, Gao KW, Qiao LJ (2004) Acta Mater 52:3753
19. Wang F, Su YJ, He JY, Qiao LJ, Chu WY (2006) Scr Mater 54:201
20. Segall MD, Lindan PJD, Probert MJ, Pickard CJ, Hasnip PJ, Clark SJ et al (2002) J Phys Condens Matter 14:2717
21. Perdew JP, Burke K, Ernzerhof M (1996) Phys Rev Lett 77:3865
22. Vanderbilt D (1990) Phys Rev B 41:7892
23. Godby RW (1992) Top Appl Phys 69:51
24. Karasnc S, Yamamura H, Haneda H (1980) J Chem Phys 73:1890