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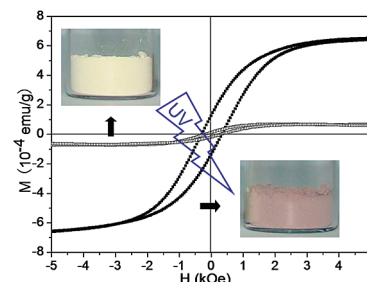
UV-Irradiation-Enhanced Ferromagnetism in BaTiO₃

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ABSTRACT Defect-induced ferromagnetism in nanoparticles has recently attracted extensive attention. We report here that (111) twinned BaTiO₃ crystallites synthesized through a modified hydrothermal method can exhibit ferromagnetic properties. The unexpected ferromagnetism is verified to originate from the point defects. We also find that UV irradiation can significantly enhance the ferromagnetism through creating more lattice defects. The photochromic effect is also observed and discussed.

SECTION Electron Transport, Optical and Electronic Devices, Hard Matter



Multiferroic materials have recently attracted extensive attention due to their potential applications in magnetoelectric coupling devices.¹ However, traditional ferroelectric materials such as barium titanate (BaTiO₃) usually have empty d orbitals and are therefore not ferromagnetic.^{2,3} An alternative strategy is to fabricate multiferroic composite structures of separate magnetic and ferroelectric components to achieve magnetoelectric coupling.⁴ Recently, it was reported that some oxide nanoparticles could become ferromagnetic if their defect structures are properly controlled. A general explanation is that point defects such as surface oxygen vacancies^{5,6} and cation vacancies^{7,8} provide traps for unpaired electrons, which are responsible for the observed ferromagnetic properties.^{9,10} Can this mechanism be utilized to introduce ferromagnetism into traditional ferroelectrics?

The studies on light-induced defects are of great interest. It is well-known that oxygen vacancies and Ti³⁺ cations can be created on the surfaces of titanates such as TiO₂ and SrTiO₃ by using ultraviolet (UV) irradiation above the band gap (E_g), which results in unusual properties, that is, hydrophilicity^{11,12} and photoluminescence.¹³ Although oxygen vacancies in perovskites have been extensively studied, existing studies usually focus on their effects on ferroelectric degradation and fatigue.^{14,15} In the present work, BaTiO₃ crystallites containing multiple (111) twins are successfully fabricated. Unique properties are expected to be induced from the particular twin structures. The defect structures of (111) twinned BaTiO₃ induced by UV irradiation were studied and discussed. We found for the first time that the ferromagnetic properties can be observed in (111) twinned BaTiO₃ crystallites and enhanced through a simple UV irradiation approach.

Figure 1 shows the XRD pattern of the as-synthesized sample. It is confirmed that the final product is tetragonal BaTiO₃ ($P4/mmm$, JCPD 79-2264). The field emission scanning electron microscopy (FESEM) image shown in the inset of Figure 1 indicates that the particle size of the BaTiO₃ powders can reach several tens of micrometers. The crystallites are

cubic in shape and exhibit penetrated morphologies containing multiple (111) twins. This phenomenon has been well-documented for cubic crystals and can be explained by the twin-plane re-entrant edges (TPREs) mechanism.¹⁶ The TPREs mechanism enables preferential nucleation and growth from the (111) twin planes of BaTiO₃ crystallites. The multiple (111) twins may originate from the amorphous TiO₂ clusters which contain face-sharing Ti–O octahedra. Due to stress concentration induced by the oxygen-deficient (111) twin planes, more lattice defects are expected.¹⁷

As shown in Figure 2, the photochromic effect is evident. The color of the (111) twinned BaTiO₃ powders changes from pale yellow to dark brown after the UV irradiation. Figure 2 shows the UV–vis absorption spectra of (111) twinned BaTiO₃ crystallites obtained before and after UV irradiation. The red shift of the absorption edge indicates the presence of defect energy levels. For both samples, their optical absorption edges are located at ~ 430 nm (2.9 eV), which is smaller than regular BaTiO₃ ($E_g = 3.2$ eV).¹⁸ Before UV irradiation, the sample has an absorption tail near 2.5 eV. After UV irradiation, a distinct optical absorption behavior can be clearly identified (Figure 2b). It has been widely accepted that oxygen vacancies create additional energy levels within the forbidden energy gap of titanates, which are usually 0.2–0.3 eV below the conduction band edge.^{19,20} As a result, the red shift of the measured absorption curves is caused by a combination of multiple absorption processes. This observation is similar to that of the vacuum-sintering reduced SrTiO₃,²¹ where energy levels associated with oxygen vacancies can extend the absorption edge over a spectral region of hundreds of nanometers. The red shift of the absorption edges after UV irradiation suggests that additional energy levels have been created within the forbidden energy gap, as suggested by Cronemeyer in ref 19 for rutile TiO₂. As a result, we believe

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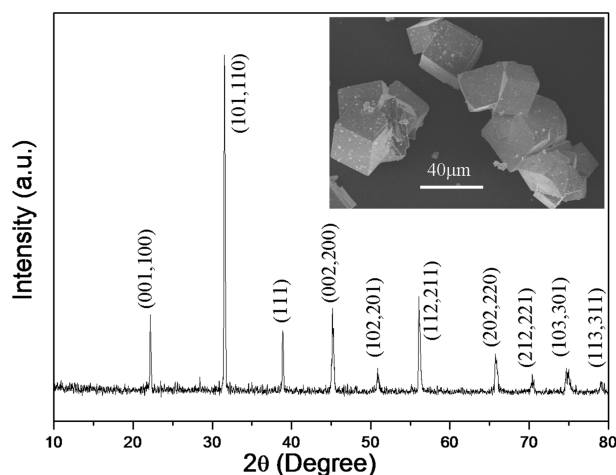


Figure 1. The XRD pattern of the as-synthesized BaTiO₃ crystallites. The inset is the corresponding SEM image.

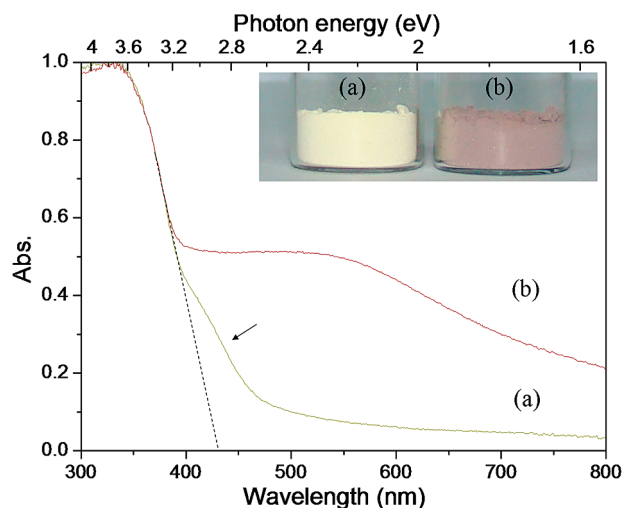


Figure 2. UV-vis absorption spectra of the BaTiO₃ crystallites before (a) and after (b) UV irradiation. The inset shows a digital image of the corresponding samples.

that defect levels created by UV irradiation are responsible for the observed photochromic effect. However, our experiments also show that, under the same experimental conditions, this photochromic behavior cannot be observed on commercial (Alfa Aesar, 99%) and traditional hydrothermal BaTiO₃ powders synthesized via the method reported in ref 22.

Figure 3 shows the XPS spectra of Ti-2p electrons before and after UV irradiation. A mixed Gaussian-Lorentzian simulation method with the same full width at half-maximum was used for the curve-fitting process. Figure 3a shows that the Ti-2p_{3/2} peak of the as-synthesized BaTiO₃ is located at ~458 eV, consistent with that of bulk BaTiO₃.²³ However, a shoulder peak appears at a position ~1.3 eV lower than that of the Ti⁴⁺ cations, suggesting the presence of Ti³⁺ cations.²⁴ Figure 3b shows Ti-2p_{3/2} photoemission peak of the BaTiO₃ sample after UV irradiation. It can be seen that the positions of the Ti-2p photoemission peaks do not change. However, the intensity of the Ti³⁺ peak is increased. The integrated

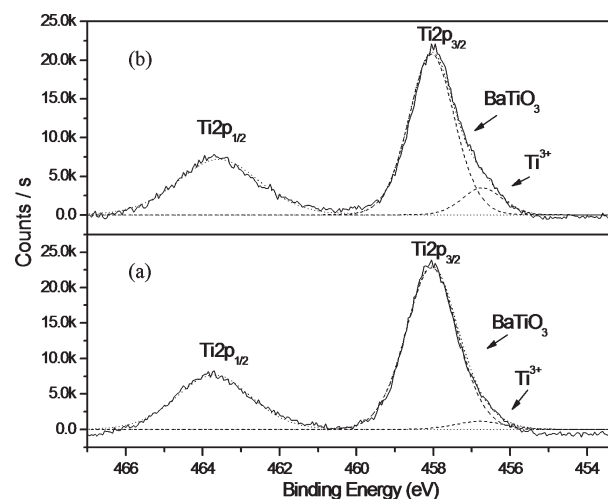


Figure 3. XPS spectra of the as-synthesized BaTiO₃ sample (a) and the UV irradiated sample (b).

intensity ratio between Ti³⁺ and Ti⁴⁺ cations at the near-surface region is changed from ~0.05 to ~0.15. The mechanism governing the formation of Ti³⁺ cations is discussed as follows. It is clear that large numbers of lattice defects already existed in the as-synthesized BaTiO₃ crystallites and increased the absorption cross section (Figure 2a). It means that more photons could be absorbed under UV irradiation. The valence band of BaTiO₃ is dominated by the O-2p state, whereas the conduction band is the Ti-3d state.¹⁸ A recent theoretical study suggested that BaTiO₃ lattices with oxygen vacancies at the surface region are more stable than that of perfect ones.⁹ As a result, electrons in O-2p orbits could be excited by UV photons to Ti-3d orbits, which may finally lead to the emergence of neighboring bridge oxygen ions and form gaseous oxygen and oxygen vacancies.^{12,15} Once the excited electrons leave the valence band, they could be captured by Ti⁴⁺ to form Ti³⁺ centers. In addition, electrons could also be trapped by oxygen vacancies to form F centers, which usually show strong absorption in the visible region.¹¹ Besides, the Ti³⁺-V_O^{••} complex formed at the surface area creates additional energy levels, which may also extend UV-vis absorption band to the low-energy region (Figure 2a).^{25,26}

The defect-induced unexpected ferromagnetism is measured at room temperature. Figure 4 shows the magnetization (*M*) versus applied magnetic field (*H*) curves before and after the UV irradiation. Experimental errors²⁷ were carefully avoided during the sample preparation and magnetism measurement. Both of the samples exhibit well-defined hysteresis loops, indicating ferromagnetism. The green sample presents very weak ferromagnetism, with a saturation magnetization of ~7 × 10⁻⁵ emu/g. The saturation magnetization for the UV-irradiated BaTiO₃ crystallites is substantially enhanced and becomes ~6.7 × 10⁻⁴ emu/g, which agrees with the increase of oxygen vacancies and Ti³⁺ cations caused by UV photons. However, the coercive field does not change obviously and remains to be ~305 Oe. This observation implies that the appearance of ferromagnetism in (111) twinned BaTiO₃ crystallites is strongly associated with the existence and accumulation of point defects. The inset of Figure 4 is the

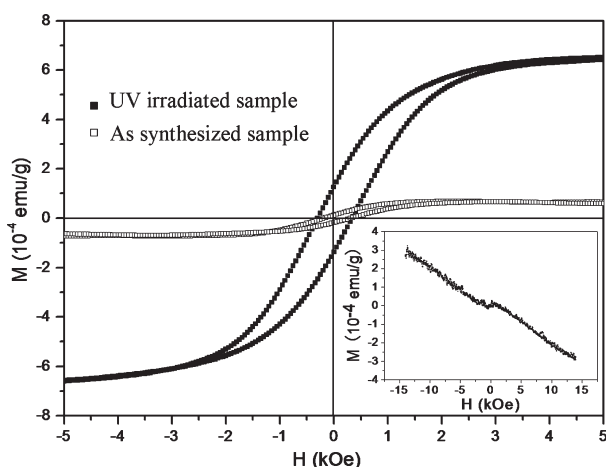


Figure 4. Room-temperature M – H curves of the UV-irradiated BaTiO_3 sample and the as-synthesized sample. The inset is the M – H curve of the sintered bulk sample.

M – H curve of the sintered bulk sample, which clearly shows the diamagnetic behavior. Similar observations have been reported for nanosized oxides particles^{5,6} due to the ferromagnetism origin of defects at the near-surface region, whose density could be greatly reduced by thermal treatment.

In summary, (111) twinned BaTiO_3 crystallites were synthesized through a modified hydrothermal method. The existing defect structures may assist the formation of more complex lattice defects under UV irradiation. It is confirmed that ferromagnetic properties in BaTiO_3 , a model ferroelectric material traditionally believed to be diamagnetic, could be significantly enhanced by regulating the defect structures. It is suggested that defect engineering could be a useful tool for the preparation and modification of ordinary ferroelectric materials to obtain ferromagnetic properties.

Experimental Methods

The (111) twinned BaTiO_3 crystallites were synthesized through a modified hydrothermal approach.^{28,29} First, 0.5 mmol of anatase powders were mixed with 9 g of composite hydroxides ($\text{NaOH/KOH} = 0.515:0.485$) in a 25 mL Teflon-lined autoclave. After the autoclave was sealed and heated at 180 °C for 5 h, 0.6 mmol of BaCl_2 and 2 mL of deionized water were added into the autoclave. The autoclave was sealed and heat treated again at 180 °C for 5 days. The product was collected and washed thoroughly with deionized water until a pH value of 7 was reached. Then, the powders were annealed at 200 °C overnight. The bulk sample was prepared by pressing the powders into a pellet followed by sintering at 1350 °C for 10 h. The UV irradiation was performed at atmospheric conditions with a low-pressure mercury lamp (20 W). The structure of the as-synthesized BaTiO_3 was measured by using an X-ray diffractometer (XRD, Bruker D8 Advance) with $\text{Cu K}\alpha$ radiation. The UV–vis absorption spectra were obtained by using a UV/vis spectrophotometer equipped with an integrating sphere (Shimadzu UV-2550). The surface structure was investigated with X-ray photoelectron spectroscopy (XPS, ESCALAB 250) by using $\text{Al K}\alpha$

excitation. The magnetic measurements were performed by using an alternating gradient magnetometer (AGM, MicroMag TM 2900) at room temperature.

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