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Raman study of barium titanate with oxygen vacancies

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ABSTRACT

Barium titanate ($BaTiO_3$) crystal samples with different distribution of oxygen vacancies were prepared through different thermal treatment processes. The influences of oxygen vacancies on the Raman spectra and X-ray photoelectron spectroscopy (XPS) spectra of $BaTiO_3$ single crystals were studied comparatively. Raman measurements of fast-cooled $BaTiO_3$, which annealed in vacuum and then cooled in air showed many different spectroscopic results comparing with as-received $BaTiO_3$ sample. Raman measurements of slow-cooled $BaTiO_3$, which annealed in vacuum and then cooled in tube furnace exhibited few spectroscopic differences. XPS measurements of as-received $BaTiO_3$ sample and fast-cooled $BaTiO_3$ sample confirmed that this discrepancy resulted from the surface phase of oxygen vacancy in $BaTiO_3$.

1. Introduction

For decades, barium titanate ($BaTiO_3$) has been extensively investigated due to its extensive applications in multilayer ceramic capacitors (MLCCs), sensors and high-density memory devices [1]. When used as capacitors, it exhibits degradation due to the electromigration of oxygen vacancies in $BaTiO_3$ [2]. Because of the close relationship between the dielectric property and lattice dynamical properties of $BaTiO_3$, many efforts have been devoted to understanding the lattice dynamics and role of oxygen vacancies in titanates [3–7]. Gong et al. showed that oxygen vacancies can change the crystal structure of $SrTiO_3$ crystal at appropriate cooling rate [8]. Bäuerle et al. and Crandles et al. demonstrated the influences of oxygen vacancies on lattice vibrations through the Raman spectroscopy and inelastic neutron scattering [9,10].

Recently Ren and Otsuka reported an universal property of point defects: symmetry of point defects follow crystal symmetry in the state of equilibrium [11,12]. They demonstrated that there was a time lag while point defects are moving, which relates to diffusion of atoms. This would lead to different distribution of point defects from the distribution in the equilibrium state and suggests that the distribution of oxygen vacancies can influence the lattice dynamics of $BaTiO_3$. In order to verify this effect, we studied the lattice dynamics of $BaTiO_3$ crystals with different oxygen vacancy distributions. Our results demonstrate that introduction of oxygen vacancies into $BaTiO_3$ crystal leads to significant changes of its Raman spectra. Moreover, the influence of oxygen vacancies distribution on the lattice dynamics of $BaTiO_3$ is further studied and interpreted as the contribution of surface phase of $BaTiO_3$.

2. Experimental

$BaTiO_3$ single crystal samples were purchased from Institute of Physics, Chinese Academy of Science, and used as received. In order to investigate the influence of oxygen vacancy distribution on lattice dynamical properties of $BaTiO_3$, two samples (Sample A and Sample B) were treated by annealing at 800 °C for 5 h in vacuum tube furnace. Sample A was cooled down to room temperature (RT) in vacuum for 24 hours, whereas sample B was cooled down to RT in air for ~2 hours.

Raman spectroscopy (RS: Renishaw inVia) measurements were taken under backscattering geometry utilizing a Leica microscope system equipped with 50x objectives. Unpolarized Raman spectra of samples at RT were measured from 100 to 900 cm^{-1} with 514.5 nm laser as excitation source. X-ray photoelectron spectroscopy (XPS: Thermo VG ESCALab 250) measurements were taken using a monochromated Mg K_α (1235.6 eV) X-ray source under a chamber pressure of $\sim 10^{-9}$ mbar. The surfaces of samples were cleaned by argon ion irradiation for 60 s. The Ba3d, Ti2p and O1s core level binding energy measurements were calibrated with

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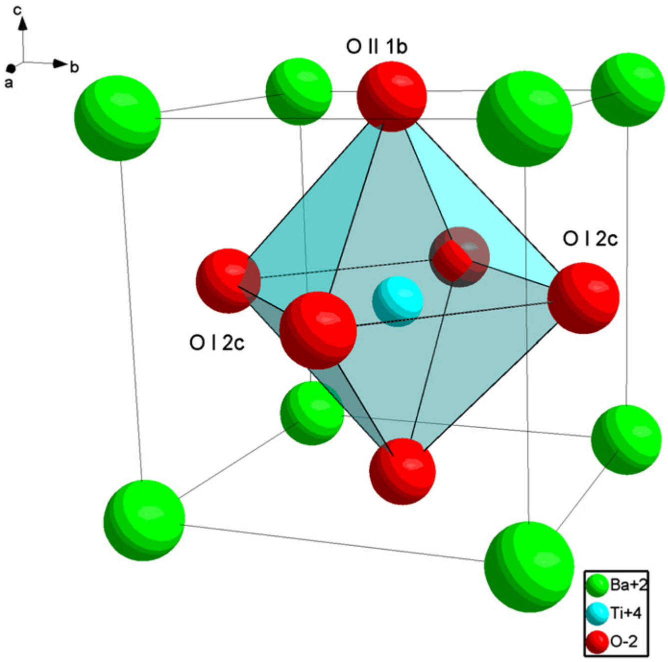

Fig. 1. Schematic representation of $BaTiO_3$ unit cell.

reference to the C1s peak at 284.5 eV. The spectral resolution of the Raman and the XPS measurements was 0.1 cm^{-1} and 0.1 eV, respectively.

3. Results and discussion

$BaTiO_3$ is known to undergo a ferroelectric transition at ~120 °C while its formula unit remains unchanged (equal to 1) per unit cell. Above transition temperature, $BaTiO_3$ has cubic (O_h^1 or $Pm3m$) symmetry with all oxygen atoms at 3c sites (Wyckoff notation), which have 4/mmm symmetry. Below transition temperature, $BaTiO_3$ has tetragonal (C_{4V}^1or $P4mm$) symmetry with two non-equivalent oxygen sites denoted as O_I and O_{II}, as shown in Fig. 1. O_I stands for 2c sites (Wyckoff notation) featuring 2 mm symmetry and O_{II} stands for 1b sites (Wyckoff notation) featuring 4 mm symmetry. The optical phonons of cubic-phase $BaTiO_3$ transform according to the triply degenerate irreducible representations $3F_{1u}\oplus F_{2u}$ of the O_h point group [3]. For ferroelectric-phase $BaTiO_3$ with tetragonal symmetry, each F_{1u} mode splits into A_1 and E irreducible representations, while each F_{2u} mode splits into B_1 and E representations [3,13]. The presence of long-range electrostatic forces further splits each of the A_1 and E modes into TO and LO modes.

Raman spectra of as-received $BaTiO_3$ crystal and Sample A are shown comparatively in Fig. 2. The Raman spectrum of as-received $BaTiO_3$ crystal shows a dip near 186 cm^{-1} [A_1(LO)], a broad peak centering near 265 cm^{-1} [A_1(TO)], a sharp peak at 305 cm^{-1} [B_1], an asymmetric broad band near 520 cm^{-1} [A_1, E(TO)] and a broad weak peak at about 720 cm^{-1} [A_1, E(LO)] [3,5]. These spectral features agree well with previous investigations [5,14] except that as-received $BaTiO_3$ sample has a shoulder at the low-frequency side of 520 cm^{-1} band. Compared with as-received $BaTiO_3$, the Raman spectrum of Sample A shows slight variation in intensity and locations of peaks, which suggests that the oxygen vacancies undergo few changes after cooling in furnace tube.

For comparison, Raman spectra of as-received $BaTiO_3$ crystal and Sample B are shown comparatively in Fig. 3. The Raman spectrum of Sample B has following notable features: (i) There occurs a new broad band ranging from 200 to 250 cm^{-1}; (ii) Almost all the peaks shift slightly, compared with those from as-received $BaTiO_3$ crystal; (iii) The low frequency shoulder at about 470 cm^{-1} becomes more distinct; (iv) Intensities of all the Raman lines increase, such as the feature at 474 and 720 cm^{-1}.

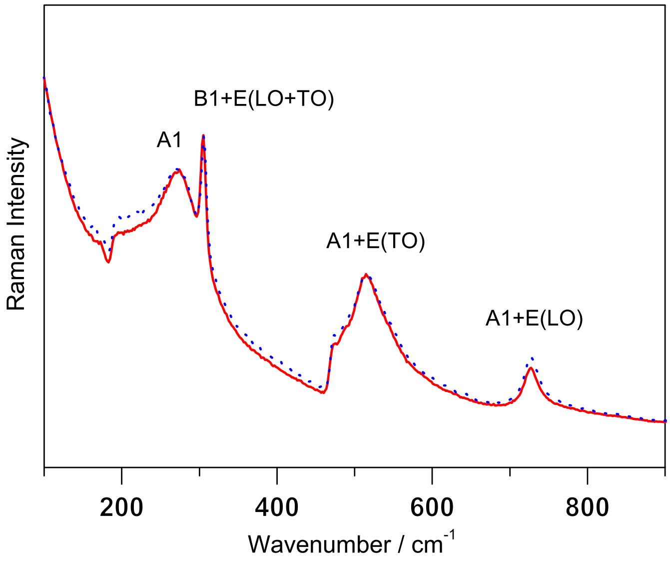

Fig. 2. Comparison of the room temperature un-polarized Raman spectra between as-received $BaTiO_3$ crystal (solid line) and Sample A (dotted line).

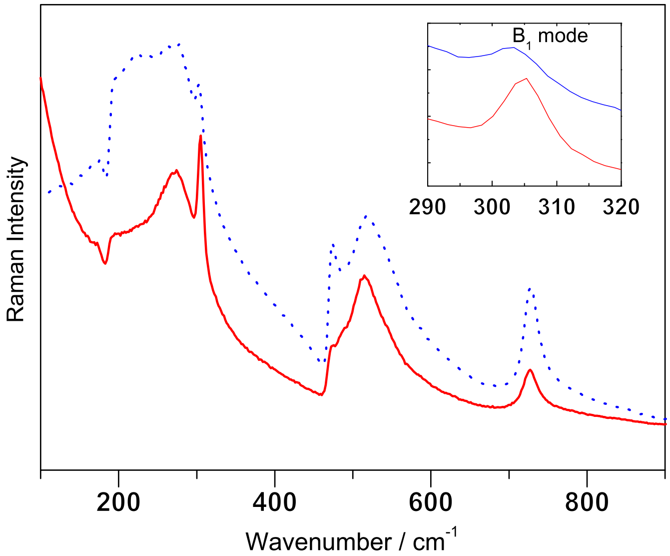

Fig. 3. Comparison of the room temperature un-polarized Raman spectra between as-received $BaTiO_3$ crystal (solid line) and Sample B (dotted line).

Since both sample A and sample B underwent the same anneal treatment in vacuum, this change of the Raman spectrum in Sample B implies different oxygen vacancies distributions in these samples while cooling it. Szot et al. pointed out that a high concentration of oxygen deficiencies can form within the surface region when $SrTiO_3$ single crystal is reduced in low partial pressure of oxygen ambience at 800 °C [15]. Kan et al. demonstrated that Ar^+ irradiation could introduce oxygen deficiencies into the surface of $SrTiO_3$ crystal [16]. Considering the new features, which exist in our Raman spectra, we hypothesize that our sample would have similar structure at the surface region and these new features in annealed samples result from the contribution of surface phase of $BaTiO_3$ sample.

Our results also indicate that the contribution of surface structure was influenced by different thermal treatment. These