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Defect induced ferromagnetism in h-BaTiO$_3$ synthesized from t-BaTiO$_3$ by microwave heating

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ABSTRACT

Structure modification of tetragonal BaTiO$_3$ (t-BaTiO$_3$) and corresponding phase transition by microwave heating were investigated. The sample compound was heated by 1.8 kW power and 2.45 GHz frequency microwave irradiation under N$_2$ atmosphere in a short experimental duration of 14 min. The maximum temperature of the surface of the sample was 1115 °C. The structure of the microwave irradiated BaTiO$_3$ was then analyzed by employing X-ray diffraction (XRD), Rietveld refinement analysis, Raman spectroscopy, and field emission scanning electron microscopy techniques. From XRD and Rietveld refinement analysis, the microwave irradiated BaTiO$_3$ sample was composed of hexagonal 89%, cubic 5% and tetragonal 6%. Due to the direct internal heating mechanism of microwaves, the core temperature of the sample might be higher than the phase transition temperature. The magnetic behavior of the sample was investigated using a vibrating sample magnetometer. The results indicated that the microwave irradiated BaTiO$_3$ exhibited mixed magnetism: ferromagnetic nature at low applied magnetic fields and diamagnetic nature at high applied magnetic fields.

1. Introduction

Barium titanate (BaTiO$_3$) is a fascinating material due to its unique properties such as ferroelectricity, piezoelectricity, and high dielectric constant [1–4]. It has a perovskite structure with ABO$_3$ stoichiometry in an octahedral arrangement [2]. In this structure, a small cation B (Ti^{4+} ions) is positioned at the center of an octahedron of oxygen and a large cation A (Ba^{2+} ions) is placed at the corners of the unit cell [5]. Over a range of temperatures, this perovskite undergoes a number of phase transitions, such as, cubic-tetragonal transition at around 120 °C, tetragonal-orthorhombic transition at around 0 °C, and orthorhombic-rhombohedral transition at around −90 °C [2,6]. The perovskite phase can also undergo a high temperature (~1460 °C) transition into a polymorph with hexagonal stacking [2]. This structure is a combination of cubic (c) and hexagonal (h) close packed BaO$_3$ layers based on a (cch)$_2$ sequence and is classified as a 6H-type hexagonal perovskite [4]. t-BaTiO$_3$ and doped t-BaTiO$_3$ are the most studied materials due to their technological applications. On the other hand, very little knowledge exists about the high temperature hexagonal polymorph of BaTiO$_3$ (h-BaTiO$_3$).

Ferroelectricity in t-BaTiO$_3$ arises from the off-centering of the B cations (Ti^{4+}) with respect to a centrosymmetric cubic perovskite crystal [7]. It is well known that the off-centering of the B cation (Ti^{4+}) originates from its d^0 electronic state [7]. The BaTiO$_3$ components, viz. Ba^{2+}, Ti^{4+}, and O$_{2-}$ ions have fully filled sub-shells and spin-paired electrons [5]. On the other hand, magnetism that arises from the local magnetic moments is associated with the occupation of the d-states at the B-site. In h-BaTiO$_3$, the origin of the magnetism is mainly associated with the Ti^{3+} ions and the O^{2-} vacancies at the grain boundaries [5,7]. h-BaTiO$_3$ was generally regarded as an ordinary dielectric. However, it was revealed that h-BaTiO$_3$ exhibits a ferroelectric transition at −199 °C (74 K) and another structural phase transition at −51 °C (222 K) [1,8]. The unique nature of h-BaTiO$_3$ encouraged us to synthesize them and to study their structural and magnetic behavior at room temperature.

The h-BaTiO$_3$ exists only at temperatures above 1460 °C and is unstable at room temperature [9]. h-BaTiO$_3$ can be stabilized at room temperature by heating under reducing conditions, resulting in the partial reduction of Ti^{4+} to Ti^{3+} ions and the creation of vacancies at the O(1) site in the hexagonal layers [1,9]. Sinclair et al. [10] synthesized the hexagonal polymorph of undoped BaTiO$_3$ by heating high purity t-BaTiO$_3$ powder in a graphite vacuum-furnace at high temperatures such as 1300, 1370, 1440 or 1510 °C for 10 h.

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Watanabe et al. [11] synthesized (001)-oriented h-$BaTiO_3$ by slip-casting in a strong magnetic field and by reduction a commercially available $BaTiO_3$ in H_2 atmosphere at 1500 °C for 1 h. Andrade et al. [1] used a sol-gel method to prepare h-$BaTiO_3$ thin films on borosilicate plate substrates. Above methods generally take a long processing time at high temperatures and have difficulties in controlling the local ionic structure. In order to overcome the difficulties in the synthesis of h-$BaTiO_3$using the conventional methods, we synthesized h-$BaTiO_3$ using a microwave heating technique based on the microwave absorption property of t-$BaTiO_3$.

2. Experimental technique

Fig. 1 shows the schematic illustration of the experimental apparatus. h-$BaTiO_3$ was synthesized from t-$BaTiO_3$ (99% purity, <1.28 μm, major impurities: SO_3 (0.051%), P_2O_5 (0.0325%), SrO (0.0299%), CaO 0.0227), (Alfa Asear, South Korea) in a microwave furnace (UM-03, Unicera, South Korea), a frequency of 2.45 GHz and a maximum power of 2 kW. Pellets with 10 mm diameter and 5.8 mm height of t-$BaTiO_3$ (each weighing 1.43 g) were prepared by applying a hydraulic pressure of 1-ton (250 MPa). In order to avoid microwave energy losses due to the binder, pellets were prepared without binder. Seven pellets were arranged in an alumina tray, which was placed at the center of the furnace, and 4 blocks of SiC plates ($35 \times 25 \times 3$ mm^3) were placed around the alumina tray. The experiments were carried out at a microwave power of 1.8 kW under an N_2 gas atmosphere with a flow rate of 200 ml/min. High purity (6N purity) N_2 gas prevents the transformation of h-$BaTiO_3$ to t-$BaTiO_3$ by the reaction with trace of oxygen. During the experiments, the temperature was measured using a B-type thermocouple placed on the top surface of the sample pellets. To avoid the interference of the microwaves with the monitored temperature, the thermocouple was protected by a double alumina lance (inner surface was Pt-coated). Although it was speculated that the core temperature of the pellets might be higher compared to the top surface of the pellets due to the direct internal heating mechanism of microwaves, it was impossible to investigate the temperature inside the pellets.

After the experiments, the samples were characterized by different techniques. The structural details were investigated using an X-ray diffraction (XRD) instrument (D/MAX-2500V, Regaku) with Cu Kα radiation of wavelength 0.15406 nm and step size of 0.01°/sec in the 2θ range of 20–70°. The morphologies of the samples were investigated using a field emission scanning electron microscope (FESEM, Hitachi, S-4300 model). The green density of the $BaTiO_3$ pellet was measured by Archimedean method at room temperature while using ethyl alcohol as the immersion liquid. The Raman spectra were recorded using Horiba LabRam Aramis IR2 spectrometer with the 532 nm line of Nd-YAG laser as the source. The magnetic properties of the samples were investigated at room temperature using a vibrating sample magnetometer (VSM, EV9-380V, MicroSenSe) in the field range of −15 kOe to + 15 kOe.

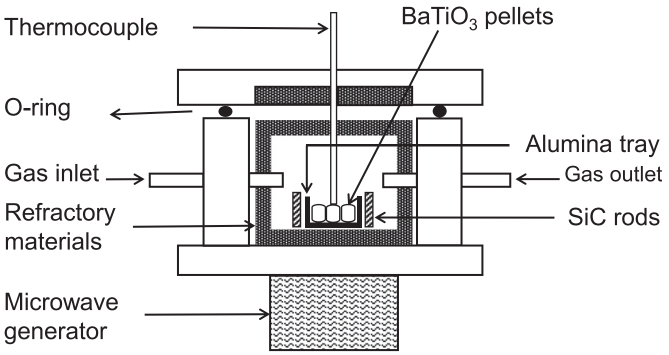

Fig. 1. Schematic diagram of the microwave furnace and the arrangement of pellets inside the furnace.

3. Results and discussion

3.1. Microwave heating behavior of $BaTiO_3$

When the microwave is irradiated to a dielectric material, it couples with the microwave, absorbing the electromagnetic energy volumetrically, transforming it into heat [12]. In this process, the dielectric loss factor determines the heating behavior of the material. At room temperature, t-$BaTiO_3$ does not absorb microwave irradiation due to the low value of its dielectric loss factor [12], which can be increased at higher temperatures. Therefore, SiC is widely adopted in microwave heating process as a heating accessory. In this study, SiC was applied as a heating accessory as well. Fig. 2 shows the heating and cooling behaviors of t-$BaTiO_3$ with and without SiC heating accessory, which are shown by solid and dashed lines, respectively. Without the heating accessory, a maximum temperature of 165 °C was obtained after 16 min microwave heating. However, with the help of SiC heating accessory, rapid heating (thermal runaway) at a low temperature region was observed [12,13]. When the temperature was higher than 830 °C, the heating rate suddenly increased. This behavior is possibly related to the change in the microwave absorption ability of t-$BaTiO_3$ with temperature. The power (P) absorbed by a dielectric material is calculated using Eq. (1) [14].

$$\begin{aligned} \text{Power, } P &= \text{Conductivity loss} + \text{Dielectric loss} + \text{Magnetic loss} \\ &= \frac{1}{2}\sigma\left|E^2\right| + \omega\varepsilon_0\varepsilon_r''|E|^2 + \omega\mu_0\mu_r''|H|^2 \end{aligned} \tag{1}$$

where σ is the electrical conductivity, $|E|$ and $|H|$ are the amplitudes of the electric and the magnetic fields, ω is the applied microwave frequency, ε_0 and μ_0 are the permittivity and permeability of free space, respectively and ε_r'' and μ_r'' are the imaginary parts of the relative permittivity and permeability of the material, respectively. At lower temperatures (below the critical temperature) t-$BaTiO_3$ exhibits diamagnetic nature, therefore, the microwave energy loss due to the magnetic components of $BaTiO_3$ is negligible [15]. Hence,

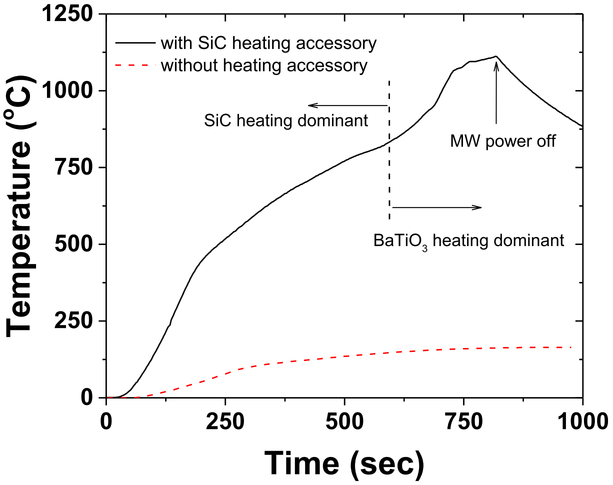

Fig. 2. Variation of the temperature of $BaTiO_3$ pellets with and without SiC heating accessory.