Journal of Solid State Chemistry 197 (2013) 242–247

Contents lists available at SciVerse ScienceDirect

Journal of Solid State Chemistry

journal homepage: www.elsevier.com/locate/jssc

Crystal structures and microwave dielectric properties of Zn,W co-substituted $BaTiO_3$ perovskite ceramics

Cailan Tian, Zhenxing Yue*, Yuanyuan Zhou, Longtu Li

State Key Laboratory of New Ceramics and Fine Processing, Department of Materials Science and Engineering, Tsinghua University, Beijing 100084, China

ARTICLE INFO

Article history:
Received 28 May 2012
Received in revised form
21 August 2012
Accepted 27 August 2012
Available online 6 September 2012

Keywords:
Microwave dielectric ceramic
Hexagonal
Perovskite
$BaTiO_3$

ABSTRACT

Zn,W co-substituted $BaTiO_3$ perovskite ceramics with compositions of $Ba[Ti_{1-x}(Zn_{1/2}W_{1/2})_x]O_3$ (x=0.40–1.00) were synthesized by the conventional solid-state reaction method and studied by X-ray diffraction and dielectric measurements. Their structures transferred from cubic (x=0.40) with space group $Pm\overline{3}m$ to hexagonal (x=0.55–0.60) with $P6_3/mmc$, and then to cubic double pervoskite (x=1.00) with $Fm\overline{3}m$. The refinement results of sample (x=0.60) revealed that the negative and positive charge centers are not consistent with each other in the face-sharing oxygen octahedra. Compared with the cubic perovskites, the hexagonal ones had the increased quality factor ($Q\times f$), the decreased dielectric constant (ε_r), and especially the near-zero temperature coefficient of resonant frequency (τ_f), whose absolute values were less than 5 ppm/°C. The relationships between structures and properties were discussed.

1. Introduction

Microwave dielectric ceramics are widely used as filters, oscillators, and dielectric resonators. Recently, they have attracted considerable attentions for the rapidly developing of the mobile and satellite telecommunication [1–4]. High dielectric constant (ε_r), high quality factor ($Q\times f$) and near-zero temperature coefficient of resonant frequency (τ_f) are required to satisfy the device minimization, frequency selectivity and stabilization [2,3]. As microwave dielectric ceramics, cubic perovskites have been extensively studied and well understood. It is found that the τ_f values of simple cubic perovskites were usually large, but that of hexagonal ones were usually small [5,6].

However, the hexagonal perovskite is a high temperature stable phase, which is less common than the cubic one in nature. For instance, pure $BaTiO_3$ is stabilized as tetragonal phase at room temperature and transfers into cubic phase at ~130 °C (Curie-Temperature, T_c), and then it can be stabilized as hexagonal phase from 1460 °C until melting. In fact, partial face-sharing octahedra exist in the hexagonal structure is the main difference to the cubic one, in which all of the octahedra are connected by corners [7,8]. There is unfavorable electrostatic repulsion associated with the much shorter B–B distance between adjacent face-sharing octahedra [6]. This is assumed to be the reason why the hexagonal phase is unstable at room temperature. And the stable mechanism of the hexagonal phase is still not clear. Nevertheless, some hexagonal perovskites can be stabilized at room temperature by some routes [9–13], such as sintering under reduced atmosphere, quenching from high sintering temperature, and chemical doping with acceptors. The above routes usually introduced a number of oxygen vacancies into the crystal lattice, which may be favorable to the formation of the hexagonal phase.

Because the microwave dielectric ceramics are sensitive to the oxygen vacancies, some new routes without introducing a number of oxygen vacancies are still needed to be explored. It is noticed that Takahashi et al. [14] had synthesized hexagonal perovskite in the $xBa(Mg_{1/2}W_{1/2})O_3$-$(1-x)BaTiO_3$ system, in which Ti^{4+} cations were co-substituted by Mg^{2+} and W^{6+} cations. It should be noted that the average valence state of Mg^{2+} and W^{6+} is +4, which is equal to that of Ti^{4+}. Thus, a number of oxygen vacancies were considered not to be introduced into crystal lattice. Moreover, Joby et al. [15] had also synthesized $Ba_3FeTiSbO_9$ and $Ba_3GaTiSbO_9$ hexagonal perovskites in the $Ba_3M^{III}TiM^{V}O_9$ (M^{III}=Fe, Ga, Y, Lu, M^{V}=Nb, Ta, Sb) system. In our previous works [16,17], hexagonal perovskites in $Ba[Ti_{1-x}(Ni_{1/2}W_{1/2})_x]O_3$ and $Ba[Ti_{1-x}(Co_{1/2}W_{1/2})_x]O_3$ systems had also been synthesized. Therefore, the above route seemed to be effective in stabilizing the hexagonal perovskite.

Interestingly, some structural transitions between cubic and hexagonal perovskites with the co-substituting amounts were observed. For example, with increasing x, the structures of $Ba[Ti_{1-x}(Co_{1/2}W_{1/2})_x]O_3$ ceramics [17] transferred from cubic to hexagonal and then to cubic double perovskites. But the chemical composition regions of signal hexagonal phase varied largely in

---

* Corresponding author. Fax: +86 010 62772556.
E-mail address: yuezhx@tsinghua.edu.cn (Z. Yue).

0022-4596/$ - see front matter © 2012 Elsevier Inc. All rights reserved.
http://dx.doi.org/10.1016/j.jssc.2012.08.054

different systems. For example, the chemical composition region was about 10% for the system containing Ni [16], whereas it was only 1% for that of Co [17]. Nowadays, the relationships among chemical compositions–structures–microwave dielectric properties are still not clear. In this work, a Zn,W co-substituted $BaTiO_3$ route was adopted, the perovskite ceramics with compositions of $Ba[Ti_{1-x}(Zn_{1/2}W_{1/2})_x]O_3$ were synthesized. The crystal structure, microwave dielectric properties and their relationships were discussed.

2. Experimental procedure

Zn,W co-substituted $BaTiO_3$ perovskite ceramics with nominal compositions of $Ba[Ti_{1-x}(Zn_{1/2}W_{1/2})_x]O_3$ were synthesized by the conventional solid-state reaction method. High-purity grade $BaCO_3$, ZnO, TiO_2, and WO_3 powders (Bei Hua Fine Chemicals Co. Ltd., Beijing, China) were used as the starting materials. The powders were weighed in required molar ratios and milled for 4 h using a planetary mill, then dried and screened. The obtained powders were calcined at 1200 °C for 4 h. After milling, a small amount of polyvinyl alcohol solution (5 wt%) was added as binder. Then the powders were pressed into cylinders with diameters of 10 mm and heights about 6 mm under applied pressures of 200 MPa. Finally, the samples were preheated at 600 °C to expel the binder and then sintered at temperature from 1300 to 1425 °C for 4 h in air.

The bulk densities of the sintered ceramics were measured by the Archimedes method. The phases of ceramics were determined by X-ray diffraction (XRD, Rigaku D/Max-2500, Tokyo, Japan). Rietveld refinement of the crystal structure in a selected case was carried out by the Fullprof program [18]. For structure refinement, XRD data were collected over the 2θ range 10°–140°, with a step size of 0.01° and count-time of 0.5 s per step. The pattern was typically refined for the background, zero, scale factor, unit cell parameters, pseudo-Voigt profile function (U, V, W, X, and Y), isothermal temperature factors (Biso), and site occupancies. The microstructures of the sintered ceramics were examined under scanning electron microscopy (SEM, JEOL JSM-6301F, Tokyo, Japan). The microwave dielectric properties of the samples were investigated by a HP8720ES network analyzer (Hewlett–Packard, Santa Rosa, CA). The dielectric constant was measured using the Hakki–Coleman post-resonator method [19] by exciting the TE_{011} resonant mode of the dielectric resonators using the electric probe of an antenna as suggested by Courtney [20]. The unloaded quality factors were measured using the TE_{011} mode in the cavity method [21]. All measurements were made in the frequency range of 5–10 GHz at room temperature. The τ_f values were measured in the temperature range of 25–80 °C.

3. Results and discussion

Typical XRD patterns for $Ba[Ti_{1-x}(Zn_{1/2}W_{1/2})_x]O_3$ (x=0.40–1.00) ceramics sintered at 1420 °C are shown in Fig. 1. These XRD patterns can be indexed on cubic, hexagonal, and cubic double structures, with the space group $Pm\overline{3}m$, $P6_3/mmc$, and $Fm\overline{3}m$, respectively. For the XRD pattern at x=0.40, the peaks without splitting indicate that it is the cubic phase. The pattern at x=1.00 can be indexed on cubic double perovskite, because of the appearance of noticeable super lattice peaks indexed as (311), and (331) at about 2θ=37° and 49°, respectively [17,22,23]. For the pattern at x=0.60, a hexagonal structure is identified according to a PDF card of 89-8119. The sample at x=0.70 is a mixture composed of cubic and hexagonal perovskite phases. The cubic and hexagonal structures can be distinguished by the characteristic peaks at about 2θ=31°. For the splitting peaks, the one at a lower degree represents the hexagonal structure, and the other at a higher degree represents the cubic or cubic double structure. Moreover, the relative amount of hexagonal and cubic phases could be estimated by the relative intensity of the splitting peaks. Except for the major phases, a small amount of $BaWO_4$ presents as a secondary phase in these ceramic samples. The above results prove that the crystal structures of the ceramics were largely dependent on the chemical composition. With increasing x, their structures transferred from cubic (x=0.40) to hexagonal (x=0.55–0.60), and then to cubic double (x=1.00) perovskite.

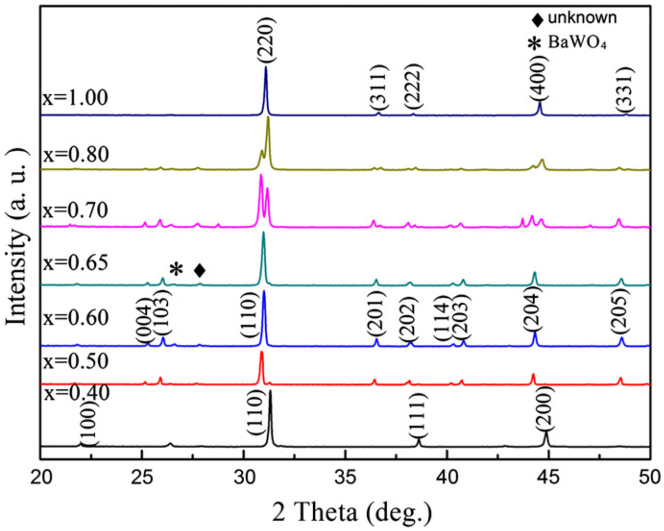

Fig. 1. Typical XRD patterns for $Ba[Ti_{1-x}(Zn_{1/2}W_{1/2})_x]O_3$ (x=0.40–1.00) ceramics sintered at 1420 °C.

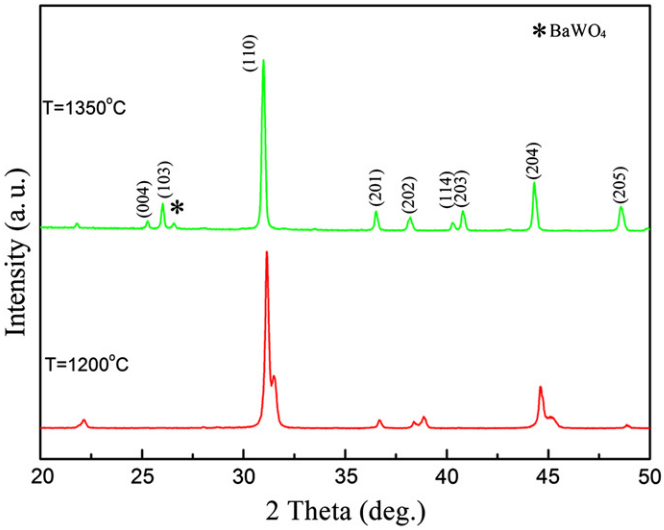

Fig. 2. XRD patterns for $Ba[Ti_{1-x}(Zn_{1/2}W_{1/2})_x]O_3$ (x=0.60) powders synthesized at 1200 °C and ceramics sintered at 1350 °C.

A cubic–hexagonal phase transition was also observed as a function of the sintering temperature. The XRD patterns of $Ba[Ti_{1-x}(Zn_{1/2}W_{1/2})_x]O_3$ (x=0.60) are shown in Fig. 2. The pattern of powder calcined at 1200 °C is indexed on cubic and hexagonal structures, which is observed clearly by the splitting of the peaks at about 2θ=31°. And for the ceramic sintered at 1350 °C, its pattern can be indexed on hexagonal structure. It is concluded that the sintering temperature had a profound effect on the