Contents lists available at ScienceDirect

Journal of the European Ceramic Society

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

Original Article

Effect of temperature and stoichiometry on the long-range 1:2 cation order in $BaZn_{1/3}Ta_{2/3}O_3$

Taras Kolodiazhnyi[a,*], Jintara Padchasri[b], Rattikorn Yimnirum[b]

[a] National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan
[b] School of Physics, Institute of Science and NANOTEC-SUT COE on Advanced Functional Nanomaterials, Suranaree University of Technology, Nakhon Ratchasima 30000, Thailand

ARTICLE INFO

Keywords:
Complex perovskites
Non-stoichiometry
Phase transitions
Microwave dielectric resonators

ABSTRACT

We report on the compositional stability range, the degree of atomic order and Raman and optical spectra of the off-stoichiometric $BaZn_{1/3}Ta_{2/3}O_3$ (BZT) within the BaO–ZnO–Ta_2O_5 ternary diagram. Almost all off-stoichiometric BZT compositions equilibrated at 1200 °C show significant degree of the long-range 1:2 cation order ranging from 60% to 80%. Ceramics equilibrated at 1550 °C and annealed at 1450 °C show strong effect of composition on the 1:2 order. The regions where an 1:2 atomic order is robust to the deviation from stoichiometry include the off-stoichiometric compositions along the BZT–$Ba_4Ta_2O_9$, BZT–$Ba_3Ta_2O_8$, BZT–$BaTa_2O_6$, BZT–Ta_2O_5, BZT–$ZnTa_2O_6$ and BZT–$Zn_4Ta_2O_9$ (pseudo) tie lines. At the same time ceramics formulated along the BZT–BaO, BZT–ZnO, BZT–$BaZnO_2$, BZT–Ba_2ZnO_3 tie lines and BZT–'Ba_3ZnO_4' pseudo tie line show complete disorder. There is a very close correlation between the degree of the 1:2 order on one hand and the unit cell volume and lattice distortion on the other hand. The ordered BZT show contraction of the unit cell whereas disordered ceramics show expansion of the unit cell in the off-stoichiometric region. The pronounced signatures of the order-disorder phase transition in the Raman and optical spectra are discussed.

1. Introduction

The problem of 1:2 *B*-site cation order–disorder transition in perovskite $Ba(B'_{1/3}B''_{2/3})O_3$, where B' and B'' are di- and penta-valent cations, respectively, has been studied by both theoretical [1–5] and experimental [6–14] methods. Electrostatic (Coulomb) force that drives the *B*-site cation ordering in $Ba(B'_{1/3}B''_{2/3})O_3$ is proportional to $1/\varepsilon$, where ε is the static dielectric constant [1]. As such, the $Ba(B'_{1/3}B''_{2/3})O_3$ niobates that have higher ε disorder more easily than tantalates, whereas the high-ε $Pb(B'_{1/3}B''_{2/3})O_3$ perovskites do not show 1:2 order at all.

Beside the exposure to high-temperature there are other ways to disorder the $Ba(B'_{1/3}B''_{2/3})O_3$ perovskites. The 1:2 *B*-site order in $Ba(B'_{1/3}B''_{2/3})O_3$ can be destroyed by partial substitution with alio-valent cations. For example, $(1-x)BaMg_{1/3}Ta_{2/3}O_3$-$xBaSnO_3$, $(1-x)BaMg_{1/3}Nb_{2/3}O_3$-$xBaSnO_3$ and $(1-y)BaMg_{1/3}Ta_{2/3}O_3$-$yBaTiO_3$ alloys disorder at $x \geq 0.1$ and $y \geq 0.15$, respectively [8,15,16]. Similarly, in the $(1\text{-}x)BaZn_{1/3}Ta_{2/3}O_3$-$xBaZrO_3$ the disorder sets on at $x \approx 0.04$ [17]. The 1:2 order in the $(1\text{-}x)BaZn_{1/3}Ta_{2/3}O_3$-$xSrGa_{1/2}Ta_{1/2}O_3$ solid solution disappears at $x \geq 0.1$ [18], whereas in the $(1\text{-}x)$ $BaZn_{1/3}Ta_{2/3}O_3$-$xZrO_2$ ceramics the 1:2 cation order is destroyed at $x \geq 0.015$ [19]. The Raman spectra and powder X-ray diffraction of $(1\text{-}x)BaZn_{1/3}Ta_{2/3}O_3$-$xBaGa_{1/2}Ta_{1/2}O_3$ ceramics sintered between 1450–1600 °C show complete disorder for $x = 0.05$ [20].

Cation disorder in $Ba(B'_{1/3}B''_{2/3})O_3$ can also be induced by intrinsic point defects formed as a result of the deviation from ideal stoichiometry. According to Koga et al. [10,11], partial disorder has been found in $BaZn_{1/3}Ta_{2/3}O_3$ with a small deviation towards the Ba-rich composition. Similar trend was found by Surendran et al. [9] for Ba-rich $BaMg_{1/3}Ta_{2/3}O_3$ perovskite. Later on, Wu and Davies reported complete disorder in Ba-rich and Nb-deficient $BaZn_{1/3}Nb_{2/3}O_3$ ceramics [21], whereas Belous et al. [13], Ovchar et al. [12] and Sayyadi-Shahraki et al. [14] have found similar trends in $BaMg_{1/3}Nb_{2/3}O_3$ and $BaCo_{1/3}Nb_{2/3}O_3$ perovskites. Partial disorder in Ba-rich $BaMg_{1/3}Ta_{2/3}O_3$ has been reported in Ref. [22].

It is widely accepted that the 1:2 *B*-site order in $Ba(B'_{1/3}B''_{2/3})O_3$ ceramics critically affects the microwave dielectric loss [23–25]. Therefore, understanding the factors and mechanisms that drive the order-disorder phase transition is important from both the academic and industrial perspectives. There are very few studies of the off-stoichiometric $BaZn_{1/3}Ta_{2/3}O_3$, hereafter abbreviated as BZT. According to the subsolidus BaO–ZnO–Ta_2O_5 phase diagram reported by Vanderah

---

[*] Corresponding author.
E-mail address: kolodiazhnyi.taras@nims.go.jp (T. Kolodiazhnyi).

https://doi.org/10.1016/j.jeurceramsoc.2017.11.048
Received 1 October 2017; Received in revised form 15 November 2017; Accepted 22 November 2017
0955-2219/

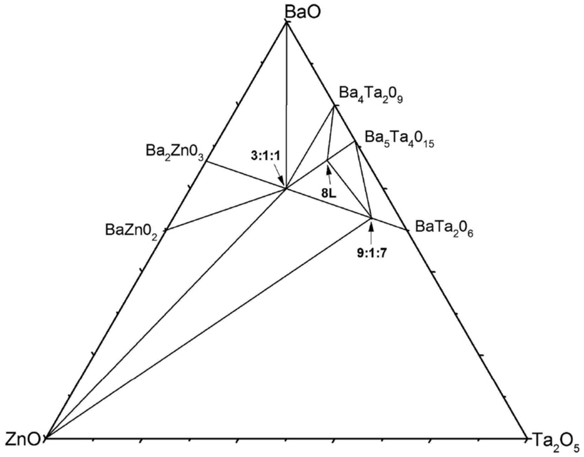

Fig. 1. Part of the BaO–ZnO–Ta_2O_5 subsolidus phase diagram. Pseudo-ternary phases: $Ba_3ZnTa_2O_9$, $Ba_8ZnTa_6O_{24}$ and $Ba_9ZnTa_{14}O_{45}$ are labeled as 3:1:1, 8 L and 9:1:7, respectively. The Ta_2O_5-rich part of the phase diagram is omitted for clarity.

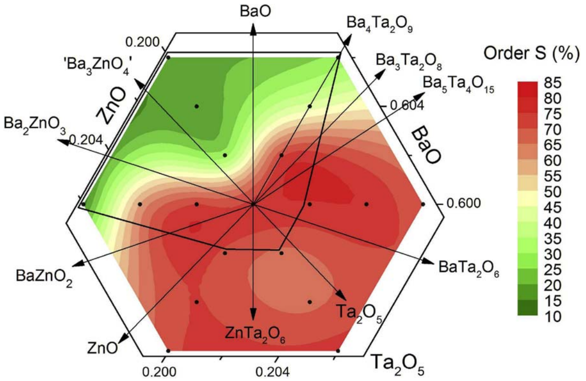

Fig. 2. Enlarged part of Fig. 1 in the vicinity of the BZT composition that shows the order parameter of the off-stoichiometric BZT equilibrated at 1400 °C for 100 h adapted from Koga et al. [10]. The black line polygon outlines the single-phase region. The axis numbers are the mole fractions of the corresponding oxides labeled in large font.

et al. [26], BZT forms seven tie lines with pseudo-binary and pseudo-ternary compounds (Fig. 1). These include: BZT – $Ba_9ZnTa_{14}O_{45}$, BZT – $Ba_8ZnTa_6O_{24}$, BZT – $Ba_4Ta_2O_9$, BZT – BaO, BZT – Ba_2ZnO_3, BZT – $BaZnO_2$ and BZT – ZnO. The pseudo-ternary phase with approximate composition of $Ba_9ZnTa_{14}O_{45}$ belongs to the tetragonal tungsten bronze (TTB) structure first reported by Kryshtop et al. [27], whereas the $Ba_8ZnTa_6O_{24}$ is a hexagonal 8-layer perovskite first reported by Tolmer and Desgardin [28] and solved by Moussa et al. [29]. Furthermore, we cannot rule out two more BZT tie lines with metastable $Ba_3Ta_2O_8$ and $Ba_6Ta_2O_{11}$ phases reported by Kovba et al. [30,31] although the existence of the latter phases has been questioned by Vanderah et al. [32]. The most detailed study of the BZT off-stoichiometry and the 1:2 order disorder was reported by Koga et al. [10] for ceramics sintered at 1400 °C. Their data adapted from Ref. [10] are shown in Fig. 2. While the high degree of the 1:2 order in the Ta-rich and Ba-deficient regions of the off-stoichiometric BZT can be understood in terms of the point defect model of Wu and Davies [21], the existence of the long range 1:2 cation order in the Ba-deficient and Zn-rich regions (Fig. 2) are at odds with the order–disorder interpretation proposed in Ref. [21]. Given the industrial importance of these ceramics [23], we felt it necessary to explore the order-disorder phase transition in the off-stoichiometric BZT in more detail.

2. Experimental

Around 95 chemical compositions with different xBaO–yZnO–$z$$Ta_2O_5$ ratios were prepared from well-dried $BaCO_3$ (99.9%, Wako Chemicals), ZnO (99.9%, Wako Chemicals) and Ta_2O_5 (99.9%, Kanto Kagaku Reagents). The powders were mixed in ethanol with zirconia balls on rollers at 80 rpm for 20 h. After drying at 60 °C the powders were screened through the 100-mesh nylon sieve and compressed into pucks of 25 mm diameter under 500 kg/cm^2 pressure in tungsten carbide (WC) pressing die. The pucks were calcined in air at 1200 °C for 5 h in 99.6% pure alumina crucibles covered with alumina lids. Care was taken to avoid cross-contamination of the pucks and to minimize the loss of ZnO during heat-treatment. After calcination, the powders were re-milled at the same conditions, mixed with polyvinyl alcohol binder, screened through the 100-mesh nylon sieve and compacted into pellets of 7 mm diameter and 3 mm thickness under uniaxial 1000 kg/cm^2 pressure in WC pressing die. The compacted pellets were heat treated under two different conditions: (i) 1200 °C for 5 h and (ii) 1550 °C for 10 h followed by anneal at 1450 °C for 20 h. Finally both sets of samples were cooled down to room temperature at 1000 °C/h.

Phase purity and lattice parameters of the ceramic specimens were analyzed by powder X-ray diffraction (PXRD) (Miniflex 600 diffractometer with Cu K_α X-ray source, Rigaku, Japan). To minimize the second phases that form on the surface of the ceramic pucks, prior to X-ray diffraction, the outer surface of the sintered ceramics was ground with abrasive paper. This usually helped to reduce the surface second phase contamination in the powder X-ray diffraction patterns. The structural parameters were obtained from Rietveld refinement of the X-ray data by using JANA2006 program [33]. Lattice parameters and Wyckoff site and atomic fractional coordinates were initiated by using the BZT structural data from Ref. [34] The diffraction profiles were refined in the range of $10^\circ < 2\theta < 140^\circ$. During refinement, atomic thermal factors, B, for weak X-ray scattering elements such as, O1(3e), O2(6i) and Zn(1b) were fixed, while the B factors for Ba1(1a), Ba2(2d) and Ta(2d) were relaxed and successfully refined to positive values. To estimate the degree of B-site cation disorder, the occupancies of the B-site cations were relaxed under constraint $g[\mathrm{Zn(1b)}] \times 1 + g[\mathrm{Zn(2d)}] \times 2 = 1$ and $g[\mathrm{Ta(1b)}] \times 1 + g[\mathrm{Ta(2d)}] \times 2 = 2$, where g is the fractional occupancy of the ion whose Wyckoff site is shown in brackets.

Although the above approach worked well for highly ordered BZT compositions, it was found that the majority of the non-stoichiometric BZT samples had significant degree of disorder with rather broad ± 1/3{hkl} supercell reflections due to the small size of the 1:2 ordered domains. These latter cases were rather difficult to refine using a single histogram approach because of the very different peak profiles for sub- and super-cell reflections. Similar problem has been also reported by Reaney et al. [34]. Therefore, in this study a 'brute force' method was used to achieve a more systematic estimate of the order parameter. The order parameter, S, was deduced from the ratio of the X-ray integrated intensity of the strongest supercell peak, (100), to the integrated intensity of the main peak of the BZT structure. The 1:2 order parameter is given by

$$S = \sqrt{\frac{(I_{100}/I_{110,012,102})_{\mathrm{obs}}}{(I_{100}/I_{110,012,102})_{\mathrm{calc}}}}, \tag{1}$$

where $(I_{100}/I_{110,012,102})_{\mathrm{obs}}$ is the ratio of the observed integrated intensity of the (100) supercell reflection to that of (110,012,102) main reflection, and $(I_{100}/I_{110,012,102})_{\mathrm{calc}} \approx 0.037$ is the calculated value for a completely ordered BZT structure.

Microstructure and phase assemblage of the polished ceramics were examined with Hitachi S-4800 scanning electron microscope equipped with energy dispersive X-ray spectrometer (HORIBA Emax) and YAG backscattered electron detector. Room temperature Raman spectra (Jobin Yvon/Horiba) of the fine-polished sample surface were measured in the backscattered geometry in the 30–1200 cm^{-1} frequency range with Ar–Kr 514.5 nm laser. Room temperature optical absorption