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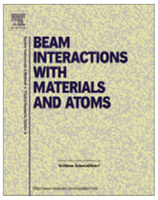

Structural study of Ca doped barium titanate

Jong-Seo Park, Yun-Hee Lee, Ki-Bok Kim, Yong-Il Kim *

Korea Research Institute of Standards and Science, P.O. Box 102, Yuseong, Daejeon 305340, Republic of Korea

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ABSTRACT

Both the combined structural refinement and the geometry energy calculation based on quantum mechanics were applied to determine the site preference and occupancies of Ca atom as a dopant in Ca-doped $BaTiO_3$ prepared by the hydrothermal process. Of possible models based on cation disorder and anion vacancy, the best structural refinement result was obtained from the model, in which Ca atoms co-substituted for Ba and Ti atoms, and vacancies of the two O sites were created for charge compensation due to the substitution of Ca^{2+} ions for Ti^{4+} ions. The model proposed by the combined structural refinement was verified by the virtual crystal approximation method dealing with the disorder of atoms based on the first principle calculation. The final weighted *R*-factor and the goodness-of-fit for both data was 6.78% and 1.42%. The occupancies of Ca atoms distributed over Ba and Ti sites were 0.086(2) at Ba site and 0.027(2) at Ti site, and the vacancies of O atoms at O(1) and O(2) sites were 0.011(2) and 0.019(2), respectively.

1. Introduction

Multi-layer ceramic capacitors (MLCCs) produced from $BaTiO_3$ powder have been widely used in the electronic industry for various applications like infrared detectors, piezoelectric transducers, waveguide modulators, gate dielectrics, ferroelectric memories and so on. These MLCCs based the X7R specification are required to extend their working range up to 150 °C because the present electronic devices become much smaller in size and higher in performances than ever before [1]. In order to attain these industrial requirements, many studies have been performed to find a way of extending working temperature of MLCC by doping of metal ions such as Co^{2+}, Fe^{3+} and Mn^{3+} into the $BaTiO_3$ host lattice [2]. In addition, it is well known that alkaline earth metals as dopants produce various physical properties of $BaTiO_3$-based materials, including ferroelectricity, conductivity, structural transformations and so forth [3]. Among these alkaline metals, the substitution of Ca and Sr atoms for every cation in $BaTiO_3$ have a significant effect on the Curie temperature (T_C) and electrical properties of $BaTiO_3$ with the solid solution limit of each site [4–6].

Although many reports have noted that Ca atoms possibly play a key role in the reduction of electrical resistance and the formation of other phases, most of the studies concerning the amount of Ca atoms substituting for cationic atoms have focused chemically on the quantities of Ca atoms in the compound. Determining the quantities of Ca atoms in the crystal lattice is an important thing because the amount of Ca atoms doped into the crystal lattice of $BaTiO_3$ is directly related in predicting the ferroelectric properties and modified electronic structure of $BaTiO_3$. Furthermore, the behavior of Ca atom as a dopant in the host lattice is important to understand the spontaneous polarization at room temperature. However, the studies on the behavior of Ca atoms in Ca-doped $BaTiO_3$ are lacking relative to the studies on preparation.

Therefore, this work has attempted to perform the combined structural refinement for Ca-doped $BaTiO_3$ system using X-ray and neutron powder diffraction in order to determine the preferential site of Ca atom and to quantify the amount of constituent atoms. Two kinds of diffraction data in this study were used to get complementary information on every atom in Ca-doped $BaTiO_3$ due to the different scattering properties of neutrons versus X-rays, even though the neutron diffraction is very similar to X-ray diffraction.

2. Experimental

The samples ($BaTiO_3$:Ca_x) were synthesized by a hydrolysis method using barium hydroxide monohydrate [$Ba(OH)_2 \cdot H_2O$, Aldrich, 98.0%), titanium isopropoxide [$Ti(OCH(CH_3)_2)_4$, Aldrich, 99.9%] and calcium chloride [$CaCl_2$, Aldrich, 99.9%] as precursors with *x* ranging from 0 to 0.15. And then, the washing, filtering, and drying process were carried out. Finally, the resultants were heat-treated at 1050 °C for 6 h in the air.

Neutron powder diffraction data were measured over scattering angles between 0° and 160° with a 2θ step of 0.05° using 1.8343 Å on the High Resolution Powder Diffractometer (HRPD) at Hanaro

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* Corresponding author. Tel.: +82 42 868 5448; fax: +82 42 869 5635.
E-mail address: yikim@kriss.re.kr (Y.-I. Kim).

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Center of the Korea Atomic Energy Research Institute (KAERI). X-ray diffraction data were obtained from the powder diffractometer (Dmax 2200, Rigaku, Japan) in the step scan mode ($15^\circ \leqslant 2\theta \leqslant 130^\circ$ at a 2θ step of 0.02°) using copper radiations with a graphite monochromator in the reflection geometry at room temperature. The structural refinement was carried out with the EXPGUI program, a graphical user interface for General Structure Analysis System (GSAS) [7,8]. The peak profile function was modeled using the convolution of the Thompson-Cox-Hastings pseudo-Voigt (pV-TCH) with the asymmetry function described by Finger et al. [9].

The geometry energy calculation was performed using the Cambridge Serial Total Energy Package (CASTEP) developed by Payne et al., which employs a plane wave basis set to treat valence electrons and pseudo-potentials to approximate the potential field of ion cores [10]. Ultra-soft pseudo-potentials and the Perdew–Burke–Emzerhof (PBE) generalized gradient approximation (GGA) functions were used for all calculations. The energy cutoff was set to be above 340 eV for every element [11,12].

3. Results and discussion

The X-ray diffraction patterns for Ca-doped $BaTiO_3$ ($BaTiO_3$:Ca_x, $x = 0$–0.15) samples were shown in Fig. 1. All samples, ($BaTiO_3$:Ca_x, $x = 0$–0.15), were indexed by the tetragonal crystal system of $BaTiO_3$ and the lattice parameters of these samples were slightly smaller than those of undoped $BaTiO_3$. However, the diffraction peaks corresponding to $CaTiO_3$ phase for the sample with 15 at.% Ca ($BaTiO_3$:Ca_x, $x = 0.15$) were observed. In addition, a peak splitting behavior of (0 0 2) and (2 0 0) reflections which typically indicate the tetragonal phase of $BaTiO_3$ converged into nearly one peak. These mean that the substitutional limit of Ca atom as a dopant in Ca-doped $BaTiO_3$ sample synthesized in this study is about 12 at.%. Consequently, the ($BaTiO_3$:Ca_x, $x = 0.12$) sample which was shown in the maximum substitutional limit of Ca atom was used to investigate the behavior of Ca atom as a dopant in Ca-doped $BaTiO_3$.

The initial structural refinement requires a crystal structural model that contains a reasonable approximation of the actual crystal structure. The initial crystal structural model of Ca-doped $BaTiO_3$ was constructed with crystallographic data based on the space group *P*4*mm* [13,14]. The crystal structure of $BaTiO_3$ composed of two cations and one anion may be viewed as $Ba^{n+}[TiO_3]^{n-}$ where the corner-shared linkage of TiO_6 octahedral forms a framework extending in an elongated octahedral configuration.

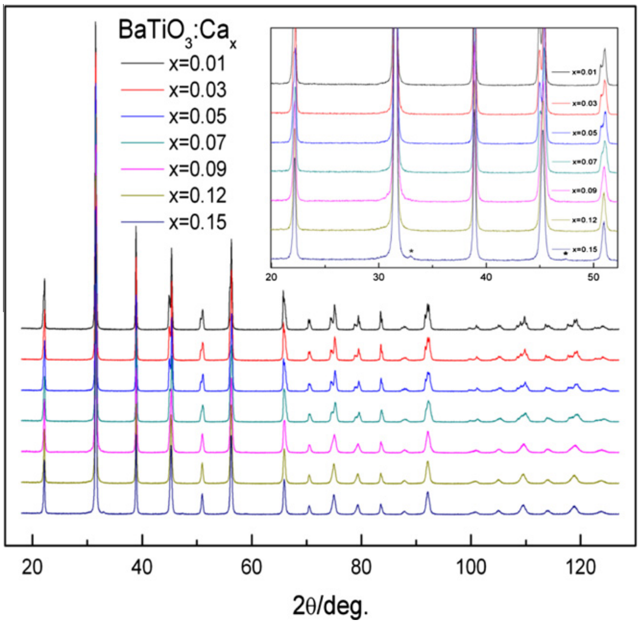

Fig. 1. X-ray diffraction patterns of Ca-doped $BaTiO_3$ ($BaTiO_3$:Ca_x, $x = 0$–0.15) samples at room temperature as a function of Ca contents.

Considering the crystal structure of $BaTiO_3$ mentioned above, order–disorder models between Ca and two atoms (Ba and/or Ti) in $BaTiO_3$ are possible when Ca atoms are doped into $BaTiO_3$. In addition, there are other possibilities of Ca atoms to partially occupy two cationic sites (Ba and Ti sites) in the $BaTiO_3$ lattice. If Ca atoms (Ca^{2+}) partially occupied at Ti site, it gives rise to form the oxygen vacancies at two oxygen sites [(O(1) and O(2)) for charge compensation.

Finally, there are seven kinds of models to be possible, assuming the substitution of Ca atoms for two cations (Ba and/or Ti) and the generation of oxygen vacancies at two different anionic sites [O(1) and O(2)]: the substitution of Ca atoms for only Ba atoms at 1*a* site (0, 0, 0) (B model), the substitution of Ca atoms for only Ti atoms at 1*b* site (1/2, 1/2, z) and the generation of oxygen vacancies at only O(1) site (1*b* site: 1/2, 1/2, z) (T-O1 model), the substitution of Ca atoms for only Ti atoms and the generation of oxygen vacancies at only O(2) site (2*c* site: 1/2, 0, z) (T-O2 model), the substitution of Ca atoms for only Ti atoms and the generation of oxygen vacancies at the two O sites (O(1) and O(2)) (T-O12 model), partially co-substitution of Ca atoms for two cations (Ba and Ti sites) and the generation of oxygen vacancies at only O1 site (BT-O1 model), partially co-substitution of Ca atoms for two cations (Ba and Ti sites) and the generation of oxygen vacancies at only O(2) site (BT-O2 model), and finally partially co-substitution of Ca atoms for two cations (Ba and Ti sites) and the generation of oxygen vacancies at all O sites (O(1) and O(2)) (BT-O12 model) (Table 1).

Table 1
Geometry energy calculation for possible order–disorder models of Ca atoms in Ca-doped $BaTiO_3$ system.

Model	Atomic site	Mixture atom (%)	Energy (eV)
B	1*a*[a]	Ba: 88, Ca: 12	-3.550194783×10^3
	1*b*[b]	Ti: 100	
	1*b*[c]	O: 100	
	2*c*[d]	O: 100	
T-O1	1*a*	Ba: 100	-3.552168544×10^3
	1*b*	Ti: 88, Ca: 12	
	1*b*	O: 88	
	2*c*	O:100	
T-O2	1*a*	Ba: 100	-3.552329413×10^3
	1*b*	Ti: 88, Ca: 12	
	1*b*	O1: 100	
	2*c*	O2: 94	
T-O12	1*a*	Ba: 100	$-3.5512701245 \times 10^3$
	1*b*	Ti: 88, Ca: 12	
	1*b*	O1: 94	
	2*c*	O2: 97	
BT-O1	1*a*	Ba: 94, Ca: 6	-3.551250523×10^3
	1*b*	Ti: 94, Ca: 6	
	1*b*	O1: 94	
	2*c*	O2: 100	
BT-O2	1*a*	Ba: 94, Ca: 6	-3.550203571×10^3
	1*b*	Ti: 94, Ca: 6	
	1*b*	O1: 100	
	2*c*	O2: 97	
BT-O12	1*a*	Ba: 94, Ca: 6	-3.549933760×10^3
	1*b*	Ti: 94, Ca: 6	
	1*b*	O1: 97	
	2*c*	O2: 98.5	

[a] 1*a* site (0, 0, 0).
[b] 1*b* site (1/2, 1/2, z).
[c] 1*b* site (1/2, 1/2, z).
[d] 2*c* site (1/2, 0, z).