สัญญาเลขที่ TRG5880225

รายงานวิจัยฉบับสมบูรณ์

ตำหนิแบบช่องว่างของไอออนบวกในแบเรียมไททาเนตเฟอร์โรอิเล็กทริกเซรามิก

Cation Vacancy Defect in Modified Barium Titanate Ferroelectric Ceramics

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Abstract

Project Code:	TRG5880225
Project Title:	Cation Vacancy Defect in Modified Barium Titanate Ferroelectric Ceramics
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Project Period:	2 years
Keywords:	Point Defect, Cation Vacancy, Lead-free, Ferroelectric

The development of advanced materials for electronic applications has been continuously undertaken due to the increasing demands of new devices with high performance and efficiency. Careful modification of the materials could result in improvement of the electrical properties. Defects are known to play an important role in governing the electrical properties of titanate-based perovskites. Improvement of dielectric properties and insulation resistance are important for the development of high-performance dielectric materials. Various techniques can be used in order to improve the performance of such materials. The effect of A-cation non-stoichiometry on the electrical properties of barium strontium titanate ceramics is an interesting topic of investigation. This study examined the stoichiometric, Ba-excess, Ba-deficient, Sr-excess and Sr-deficient compositions of $(Ba_{0.8}Sr_{0.2})TiO_3$ ceramics. A-cation non-stoichiometry of $(Ba_{0.80}Sr_{0.20})TiO_3$ ceramics affected dielectric properties differently. The Ba- and Sr-excess compositions decreased dielectric constant at T_{max} while still maintaining broad phase transition characteristics. In contrast, dielectric constant increased in the Ba- and Sr-deficient compositions. The characteristics of electrical conduction are different at high temperatures when Ba- and Sr-deficiency is introduced to the dielectrics. Ti^{4+} state for the Ba-deficient composition is maintained. However, Ti^{4+} state partially changes to Ti^{3+} state, giving rise in the polaron hopping conduction process for Sr-deficient composition. Therefore, this study shows that minor deviation of A-cation from stoichiometry can induce a different conduction process while maintaining the dielectric permittivity characteristics.

บทคัดย่อ

รหัสโครงการ: TRG5880225
ชื่อโครงการ: ตำหนิแบบช่องว่างของไอออนบวกในแบเรียมไททาเนตเฟอร์โรอิเล็กทริกเซรามิก
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ระยะเวลาโครงการ : 2 ปี
คำหลัก : ตำหนิแบบจุด, ช่องว่างของไอออนบวก, ไร้สารตะกั่ว, เฟอร์โรอิเล็กทริก

การพัฒนาวัสดุขั้นสูงสำหรับการใช้งานทางด้านอิเล็กทรอนิกส์ได้มีการดำเนินการมาอย่างเป็นเวลานาน เนื่องจากมีความต้องการใช้งานจากอุตสาหกรรมที่เกี่ยวข้องพร้อมกับอุปกรณ์ใหม่ที่ต้องการประสิทธิภาพที่สูง การปรับปรุงวัสดุอย่างระมัดระวังช่วยทำให้สมบัติทางไฟฟ้าพัฒนาดีขึ้นได้ ตำหนิเป็นตัวแปรหนึ่งที่สำคัญต่อการควบคุมสมบัติทางไฟฟ้าของวัสดุเพอร์รอฟสไกต์ฐานไททาเนต การพัฒนาสมบัติไดอิเล็กทริกและความต้านทานไฟฟ้าเป็นสิ่งที่สำคัญต่อการพัฒนาวัสดุไดอิเล็กทริกให้มีประสิทธิภาพสูง โดยเทคนิคในการพัฒนาสมบัติหรือประสิทธิภาพของวัสดุไดอิเล็กทริกให้ดีขึ้นนั้นมีหลากหลาย ซึ่งในงานวิจัยนี้สนใจที่จะศึกษาผลกระทบของปริมาณไอออนที่ตำแหน่งเอของวัสดุเพอร์รอฟสไกต์ต่อสมบัติทางไฟฟ้าของแบเรียมสตรอนเทียมไททาเนตเซรามิก โดยเฉพาะมีการควบคุมปริมาณของไอออนดังนี้ แบเรียมเกิน แบเรียมขาด สตรอนเทียมเกิน และสตรอนเทียมขาด ที่เป็นองค์ประกอบของสารประกอบ $(Ba_{0.8}Sr_{0.2})TiO_3$ ผลการทดลองพบว่าสมบัติไดอิเล็กทริกมีการเปลี่ยนแปลงแตกต่างกันเมื่อปริมาณแบเรียมหรือสตรอนเทียมไอออนเกินและขาด สารประกอบที่มีองค์ประกอบของแบเรียมไอออนหรือสตรอนเทียมไอออนที่เกินมีค่าคงที่ไดอิเล็กทริกสูงสุดลดลงและมีพีคลักษณะกว้าง ในทางตรงกันข้ามค่าคงที่ไดอิเล็กทริกมีค่าสูงขึ้นในสารประกอบที่มีองค์ประกอบของแบเรียมไอออนหรือสตรอนเทีนยมไอออนขาด เมื่อศึกษาสารประกอบที่มีองค์ประกอบของแบเรียมไอออนขาดหรือสตรอนเทียมไอออนขาดอย่างละเอียดพบว่าลักษณะเฉพาะของการนำไฟฟ้าที่อุณหภูมิสูงมีความแตกต่างกัน นอกจากนี้ยังพบว่าสถานะวาเลนซ์อิเล็กตรอนของไทเทเนียมไอออนมีความแตกต่างกันระหว่างสารประกอบที่มีแบเรียมไอออนขาดและสารประกอบที่มีสตรอนเทียมไอออนขาด Ti^{4+} บางส่วนได้เปลี่ยนเป็น Ti^{3+} ในสารประกอบที่มีสตรอนเทียมไอออนขาดเท่านั้น ซึ่งตำหนินี้เป็นส่วนสำคัญที่ทำให้เกิดกระบวนการนำไฟฟ้าแบบโพรารอน ดังนั้นจากงานวิจัยนี้แสดงให้เห็นว่าการที่องค์ประกอบทางเคมีของแบเรียมไอออนหรือสตรอนเทียมไอออนเปลี่ยนแปลงเพียงเล็กน้อยก็ส่งผลต่อการนำไฟฟ้าที่ต่างกันอย่างชัดเจนและสมบัติไดอิเล็กทริก

Executive Summary

Development of advanced technologies for electronic applications, particularly aiming to increase energy efficiency and sustainability, are increasing in demand for regular usage. A majority of this development involves improvement of material's properties. Researcher has been continuously studied and developed new electronic material. Ferroelectric ceramic is one of many materials that is of interest, for example, lead-based (e.g. $Pb(Mg_{1/3}Nb_{2/3})O_3$: PMN) and lead-free (e.g. $Ba(Zr,Ti)O_3$: BZT) materials. It is, however, known that the RoHS (Restriction of Hazardous Substances Directive) listed Lead (Pb) as one of the hazardous materials and is restricted for using in many electronic applications. Therefore, the development of lead-free materials has increased in attention and there is many more aspects of research to be explored. The electrical properties of relaxor ferroelectric ceramics, especially dielectric and ferroelectric behaviors, are improved from normal ferroelectric ceramic, which led to the usage of these materials in various applications such as capacitors and piezoelectric devices. A majority of researches focuses on fundamental understanding of relaxor behavior both experimentally and theoretically as well as device development based on these materials. In fabrication process, it is common to find defects in polycrystalline materials, which can be in a range of atomic-scale to micro-scale. These defects play major roles in controlling electrical properties of the ceramics. In some applications, defects can be advantage as to improve the properties of the devices. On the other hand, properties of devices can be deteriorated by the present of defects leading to electrical fatigue and failure of devices under extreme conditions. It is, therefore, important to understand how cation vacancy defect affects electrical properties of modified barium titanate ferroelectric ceramics. The effect of A-cation non-stoichiometry on the electrical properties of barium strontium titanate ceramics is an interesting topic of investigation. This study examined the stoichiometric, Ba-excess, Ba-deficient, Sr-excess and Sr-deficient compositions of $(Ba_{0.8}Sr_{0.2})TiO_3$ ceramics. A-cation non-stoichiometry of $(Ba_{0.80}Sr_{0.20})TiO_3$ ceramics affected dielectric properties differently. The Ba- and Sr-excess compositions decreased dielectric constant at T_{max} while still maintaining broad phase transition characteristics. In contrast, dielectric constant increased in the Ba- and Sr-deficient compositions. The characteristics of electrical conduction are different at high temperatures when Ba- and Sr-deficiency is introduced to the dielectrics. Ti^{4+} state for the Ba-deficient composition is maintained. However, Ti^{4+}

state partially changes to Ti^{3+} state, giving rise in the polaron hopping conduction process for Sr-deficient composition. Therefore, this study shows that minor deviation of A-cation from stoichiometry can induce a different conduction process while maintaining the dielectric permittivity characteristics.

Objectives

The main objectives for this study are listed below.

1. to determine characteristic of defect species in modified barium titanate ferroelectric ceramics.
2. to investigate effect of defect on electrical properties of modified barium titanate ferroelectric ceramics.
3. to develop fundamental understanding of defect behavior in ferroelectric ceramics.

Methodology

The methodology of this research consists of two main parts. First, fabrication of ceramic specimens in which defect will be introduced into the specimens by controlling stoichiometry of interested compositions. Second, defect characteristics and electrical properties will be characterized. Details of experimental design are given below.

1.1. Fabrication of ceramics

Modified barium titanate based on $(Ba_{1-x}Sr_x)TiO_3$ compositions, where x is 0.2, were fabricated via solid state reaction technique. The $BaCO_3$ (>99.0% purity), $SrCO_3$ (>99.0% purity) and TiO_2 (>99.0% purity) were used as precursors. Batch calculation for stoichiometric and non-stoichiometric compositions was carried out in which A-cation vacancy was the main focus. The $(Ba_{0.8-y}Sr_{0.2-z})TiO_3$ compositions where x = 0.2, y = 0, 0.01 and 0.02, and z = 0, 0.01 and 0.02 were fabricated. The $BaCO_3$, $SrCO_3$ and TiO_2 precursors were mixed and ground via ball milling technique. Calcination was undertaken by putting dried powders in alumina crucible and fire at 1100 °C for 4 hours with heating/cooling rate of 5 °C/min in air atmosphere. Ceramic disc with diameter of about 1 cm and thickness of about 1 mm were prepared by sintering green sample in electric furnace at 1400 – 1475 °C for 4 hours with heating/cooling rate of 5 °C/min in air atmosphere. Silver paste was applied on the polished surface of the sintered pellet before firing at 700 °C for 15 minutes.

1.2. Characterizations

Perovskite phase formation was investigated by using X-ray diffraction technique via a laboratory X-ray diffractometer (XRD) measuring at room temperature. Morphology and microstructure observations were conducted by using scanning electron microscope (SEM) in order to observe change, if any, due to the presence of defect.

Defect characteristics were characterized using X-ray photoelectron spectroscopy (XPS). This technique can detect changes in valence state of Ti cation that is associated with defect species presented in the specimen, for example, Ti^{3+}, singly ionized and doubly ionized oxygen vacancies, other impurities.

Electrical properties measurement was carried out on ceramic specimens. Dielectric properties of the specimen were measured by using LCR meter. The frequency dependence of permittivity and loss data were collected simultaneously while heating and cooling the specimen from room temperature to 200 °C. The impedance spectroscopy was used to measure dielectric relaxation phenomena in the temperature ranging from 400 to 600 °C.

Results and discussion

Part 1: Influence of A-cation non-stoichiometry on dielectric properties of $(Ba_{1-x}Sr_x)TiO_3$ *ceramics*

In this study, the A-cation non-stoichiometry $(Ba_{0.80}Sr_{0.20})TiO_3$ compositions were investigated. Four groups of composition were chosen, i.e., Ba-excess ($(Ba_{0.8+x}Sr_{0.2})TiO_3$), Ba-deficient ($(Ba_{0.8-x}Sr_{0.2})TiO_3$), Sr-excess ($(Ba_{0.8}Sr_{0.2+x})TiO_3$) and Sr-deficient ($(Ba_{0.8}Sr_{0.2-x})TiO_3$). The concentration of x was varied from 0 to 0.02 with 0.005 increment.

Perovskite phase was maintained in all compositions, as shown in figure 1. Peak shifting and peak broadening could not be observed within the resolution limit of laboratory X-ray diffractometer. All composition showed characteristics of tetragonal symmetry as seen from {002} peak broadening ($2\theta \approx 45°$). It suggested that average crystal structure was not affected by A-cation non-stoichiometry.

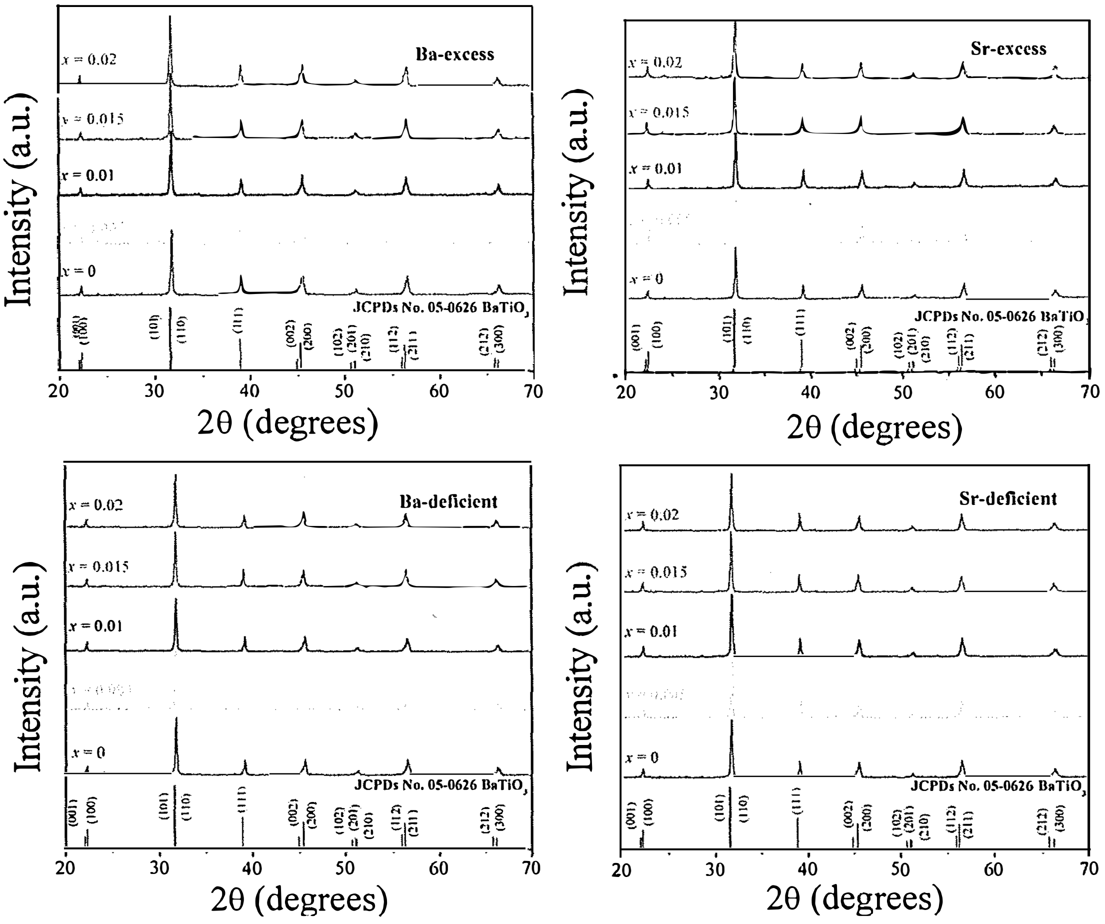

Figure 1. X-ray diffraction patterns of Ba-excess, Sr-excess, Ba-deficient and Sr-deficient $(Ba_{0.80}Sr_{0.20})TiO_3$ polycrystalline ceramics.

Temperature dependence of dielectric properties measured at 10 kHz of Ba-excess, Ba-deficient, Sr-excess and Sr-deficient $(Ba_{0.80}Sr_{0.20})TiO_3$ ceramics were illustrated in figure 2-5.

For Ba-excess $(Ba_{0.80+x}Sr_{0.20})TiO$ compositions, dielectric constant at room temperature was in the range of 2300-2700. The dielectric constant increased as temperature increased until it reached maximum values at T_{max} (a temperature at which dielectric constant is maximum). This broad peak was a characteristic of broad phase transition, which was expected for the $(Ba_{0.80}Sr_{0.20})TiO_3$ ceramics. A change in T_{max} A significant decrease of maximum dielectric constant at T_{max} when x increased was observed, as shown in figure 2.

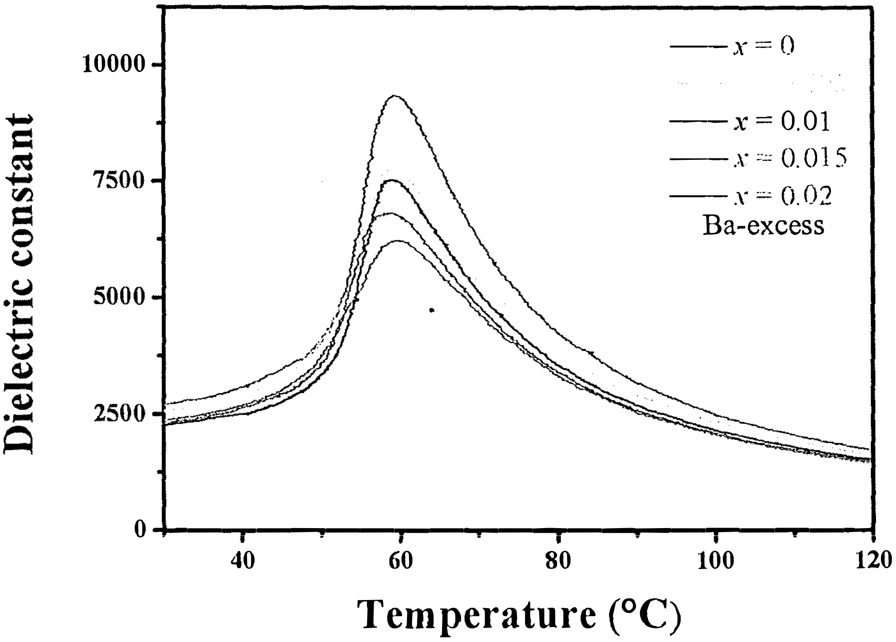

Figure 2. Temperature dependence of dielectric constant measured at 10 kHz of Ba-excess $(Ba_{0.80}Sr_{0.20})TiO_3$ ceramics

Figure 3 showed dielectric constant as a function of temperature of Ba-deficient $(Ba_{0.80-x}Sr_{0.20})TiO_3$ compositions. The dielectric peak maintained broad phase transition characteristics in all compositions. The dielectric constant at all temperatures increased with increasing x content. The T_{max} slightly shifted toward lower temperatures when x increased. However, at x = 0.02, the dielectric constant significantly increased to 22500 and 36000 at room temperature and T_{max}, respectively. This could be due to a high concentration of cation vacancy leading to high concentration of oxygen vacancy, which can lead to high dielectric constant and become conductive easily.

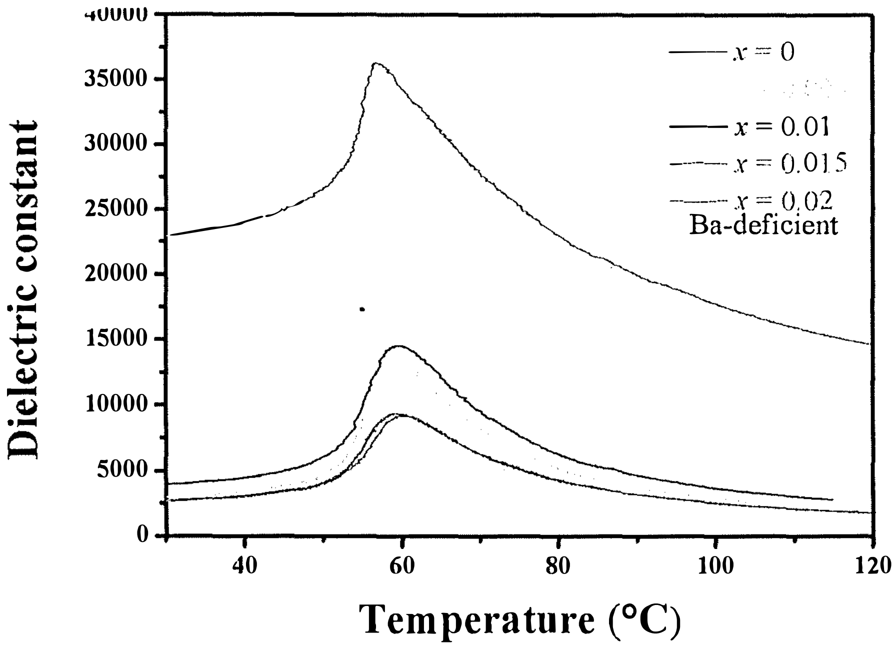

Figure 3. Temperature dependence of dielectric constant measured at 10 kHz of Ba-deficient $(Ba_{0.80}Sr_{0.20})TiO_3$ ceramics

Dielectric constant as a function of temperature of Sr-excess $(Ba_{0.80}Sr_{0.20+x})TiO_3$ ceramics of all compositions was shown in figure 4. Broad phase transition of dielectric characteristic was observed. Dielectric constant at T_{max} decreased as x increased. The T_{max} of compositions with $x > 0$ was lower than that of stoichiometric compositions. The maximum dielectric constant at T_{max} changed from 9200 to 7000 for $x = 0$ and $x = 0.02$, respectively. This could be due to the excess content of Sr that might lead to secondary phase, which cause reduction of dielectric constant. However, the secondary phase was not clearly shown from X-ray diffraction patterns, which could come from detection limit of the laboratory X-ray diffractometer.

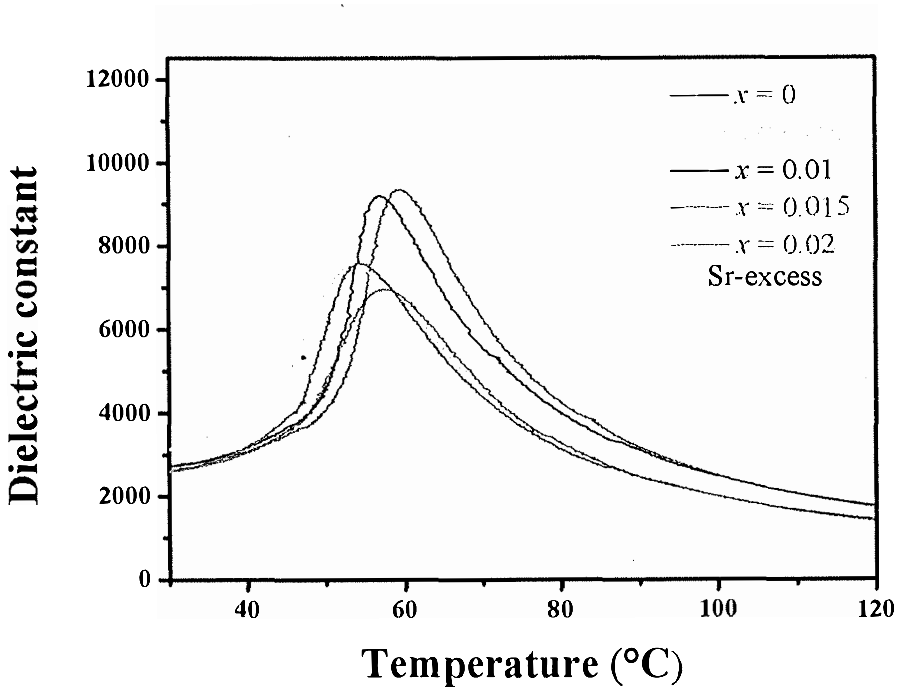

Figure 4. Temperature dependence of dielectric constant measured at 10 kHz of Sr-excess $(Ba_{0.80}Sr_{0.20})TiO_3$ ceramics

Temperature dependence of dielectric constant of Sr-deficient $(Ba_{0.80}Sr_{0.20-x})TiO_3$ ceramics were illustrated in figure 5. All compositions showed broad phase transition of dielectric characteristic. When x increased, T_{max} and dielectric constant at T_{max} increased. At T_{max}, dielectric constant of x = 0 – 0.015 were in the range of 9200 to 11000. However, the dielectric constant at T_{max} of 24000 was found for x = 0.02. Similar to Ba-deficient composition, this could be due to a high concentration of cation vacancy leading to high concentration of oxygen vacancy, which can lead to high dielectric constant and become conductive easily. Moreover, the T_{max} systematically increased as x increased.

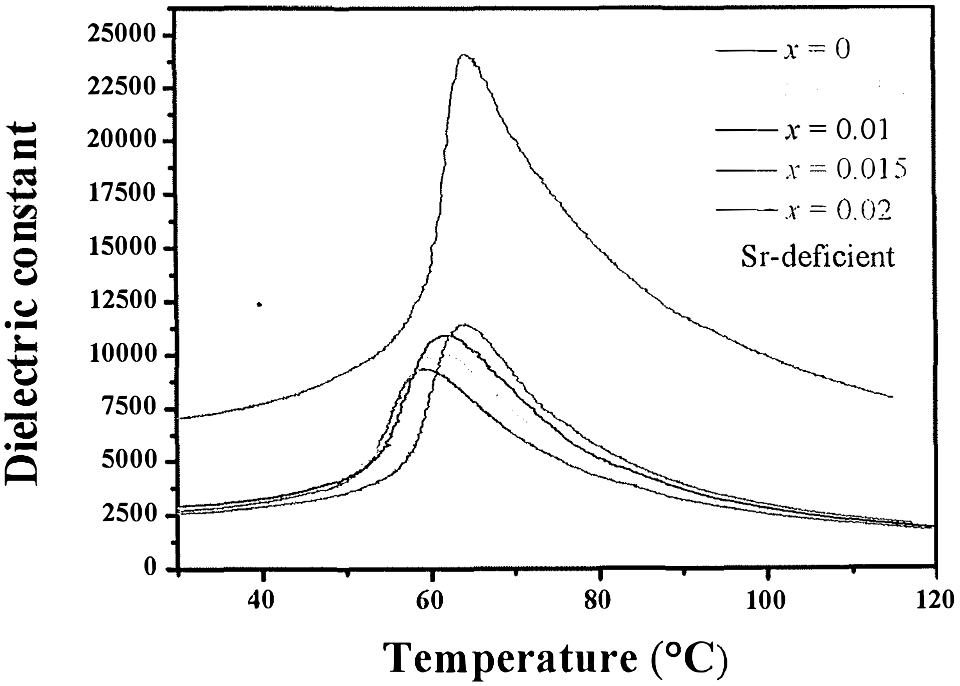

Figure 5. Temperature dependence of dielectric constant measured at 10 kHz of Sr-deficient $(Ba_{0.80}Sr_{0.20})TiO_3$ ceramics

A-cation non-stoichiometry of $(Ba_{0.80}Sr_{0.20})TiO_3$ ceramics affected dielectric properties differently. The Ba- and Sr-excess compositions generally decreased dielectric constant at T_{max} while still maintaining broad phase transition characteristics. In contrast, dielectric constant was found to increase in the Ba- and Sr-deficient compositions. The shift in T_{max} was higher in Sr-excess and Sr-deficient compositions as compare with that of Ba-excess and Ba-deficient compositions. Although the improvement of dielectric constant was observed in the Ba- and Sr-deficient compositions. However, the Ba- and Sr-deficient compositions with x = 0.02 exhibited dramatically increase in dielectric constant. The high concentration of A-cation vacancy induced oxygen vacancy to occur, thus, led to high dielectric constant accompanying with high conductive behavior. Thus, it was a major drawback for dielectric materials.

It was clearly seen that the A-cation deficient composition was a promising method to improve dielectric properties of $(Ba_{0.80}Sr_{0.20})TiO_3$ ceramics. It is of interest to gain more understanding of the effect of A-cation deficiency on electrical properties of the materials. Therefore, the stoichiometric, 0.01 mol Ba-deficient and 0.01 mol Sr-deficient

$(Ba_{0.80}Sr_{0.20})TiO_3$ ceramics were selected to study further, which was explained in details in next section.

Part 2: Effect of A-cation deficiency on electrical properties of $(Ba_{0.80}Sr_{0.20})TiO_3$ ceramics

In this study, Ba-deficient and Sr-deficient compositions were chosen for investigation. The electrical properties is the main focus in order to understand the roles of A-cation deficiency in $(Ba_{0.80}Sr_{0.20})TiO_3$ ceramics.

Stoichiometric composition of $(Ba_{0.80}Sr_{0.20})TiO_3$ polycrystalline ceramic was investigated by comparing to 0.01 mol Ba-deficient and 0.01 mol Sr-deficient compositions, i.e. $(Ba_{0.79}Sr_{0.20})TiO_{3-x}$ and $(Ba_{0.80}Sr_{0.19})TiO_{3-x}$, respectively. Perovskite phase was confirmed in all compositions, as shown in Figure 6. The shifting of peak was not observed within the resolution limit of a laboratory X-ray diffractometer, indicating that changes in long-range crystal structure were not observed. However, the secondary phase of unknown species was observed at 2θ of 24° and 28° for stoichiometric composition. The secondary phase, as shown in the XRD pattern, could not be identified with good accuracy. However, the peak at 2θ of 24° closely matched with the $BaCO_3$ phase. This implied that a small fraction of remaining $BaCO_3$ precursor was unreacted. For Ba-deficient and Sr-deficient compositions, peaks at 2θ of 24° were not observed, which indicated that A-site deficiency affected the formation of the secondary phase.

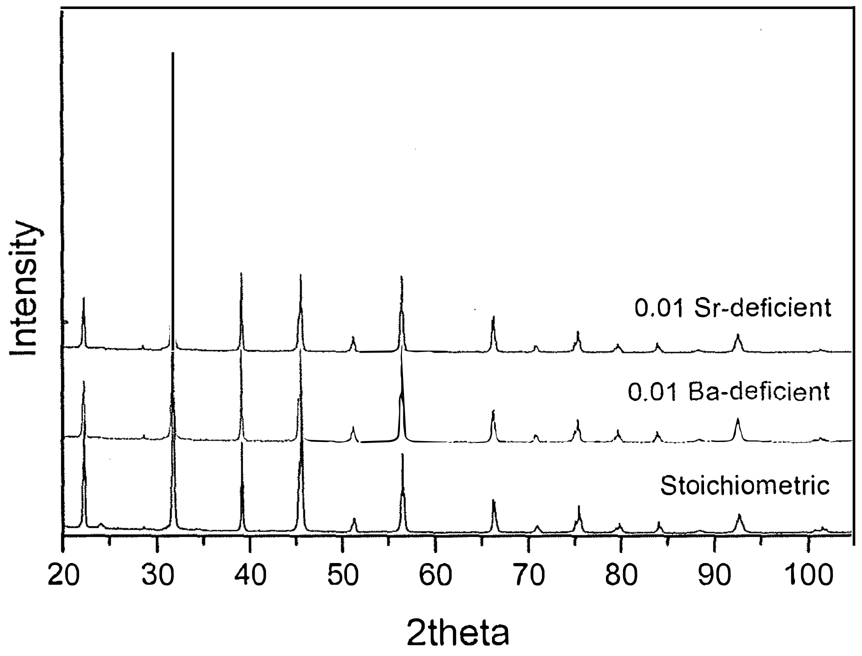

Figure 6. X-ray diffraction patterns of stoichiometric, 0.01 mol Ba-deficient, and 0.01 mol Sr-deficient compositions of $(Ba_{0.8}Sr_{0.2})TiO_3$ ceramics

Dielectric properties as a function of temperature are shown in Figure 7. The stoichiometric composition exhibited frequency-independent dielectric permittivity around the temperature T_{max} (58 °C), at which dielectric permittivity is maximum. At high temperature, frequency-dependent behavior of dielectric loss was observed for the stoichiometric composition. An increase of dielectric permittivity was clearly seen in the 0.01 mol Ba-deficient composition. Dielectric loss was found to be higher than that of the stoichiometric composition. Frequency dispersion of dielectric properties was observed, as seen at T_{max}. However, the T_{max} of the 0.01 mol Ba-deficient composition was found to be the same as that of the stoichiometric composition. Additionally, frequency dispersion of dielectric loss at high temperature could not be seen from the dielectric data. Dielectric permittivity with frequency-independent behavior was observed in the 0.01 mol Sr-deficient composition. Dielectric permittivity at T_{max} was comparable to that of the stoichiometric composition. T_{max} shifted to higher temperature as compared to that of the stoichiometric composition. However, a large increase of dielectric loss at high temperature (> 100 °C) was observed. Additionally, close inspection of the dielectric constant versus temperature curves of the Ba- and Sr-deficient compositions suggested that a step change in dielectric constant was observed as temperature increased to right below T_{max}, which could be interpreted as an intermediate phase. However, the dielectric anomaly was weak for the Ba-deficient composition. Moreover, this phenomenon was not observed in the stoichiometric compositions. Since A-cation vacancy (V_A) was introduced to the composition, the system was compensated by oxygen vacancy. Formation of (V_A-V_O) defect associate could be possible, which could induce the distortion of TiO_6 octahedra. Moreover, it is possible that the induced oxygen vacancy defect could reduce Ti^{4+} to Ti^{3+} forming defect complex (Ti^{3+}-V_O), which could also affect the distortion of unit cell, particularly octahedral distortion. Thus, the intermediate phase was observed. As temperature increases, the intermediate phase might change its configuration and TiO_6 octahedra becomes less distorted, resulting in a dielectric anomaly at temperature right below T_{max}.

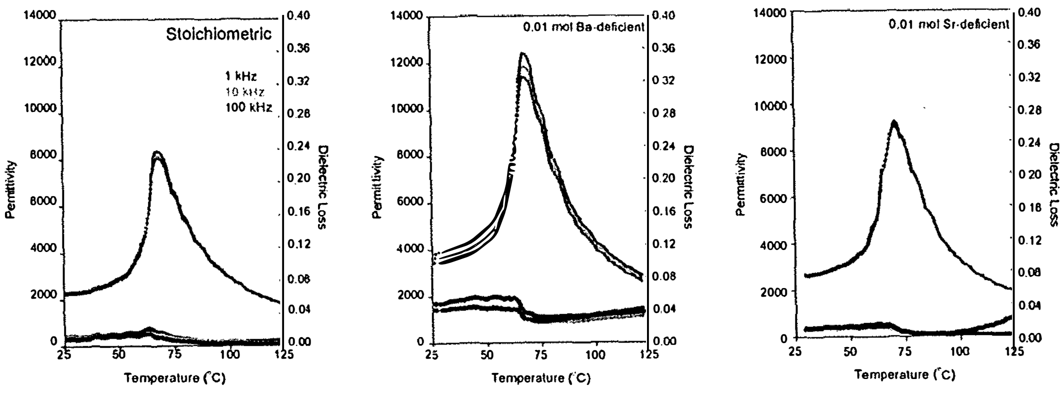

Figure 7. Temperature dependence of dielectric permittivity of stoichiometric, 0.01 mol Ba-deficient, and 0.01 mol Sr-deficient compositions of $(Ba_{0.8}Sr_{0.2})TiO_3$ ceramics

Not only is the behavior of dielectric permittivity as a function of temperature slightly changed, but the behavior of dielectric loss at high temperatures was also different when comparing between three compositions. The increase of dielectric loss at high temperatures suggested that resistive behavior at high temperature deteriorated, which could be due to a change in the conduction mechanism. Therefore, impedance measurements were undertaken at various temperatures ranging from 450 to 550 °C in order to understand conduction behavior at high temperature.

Figure 8 shows the impedance spectra of the stoichiometric, 0.01 mol Ba-deficient, and 0.01 Sr-deficient compositions measured at 500 °C in a frequency range of 10^2 - 10^6

Hz. Frequency dispersion of Z' and Z" was observed for the stoichiometric and 0.01 Ba-deficient compositions. However, dispersion could not be observed for the 0.01 Sr-deficient composition due to much lower resistance. Additionally, analysis of the Nyquist plot for impedance provided useful information about the transport phenomena and electrical characteristics. A suppressed-nonsymmetrical semicircle curve of the impedance was observed for the stoichiometric composition. This suggested that multiple conduction paths contributed to the overall conduction process of the sample. In other words, the heterogeneous conduction process existed. In comparison, the Nyquist plot of impedance for the 0.01 mol Ba-deficient showed the symmetric semicircle curve, which indicated that the conduction path could be supported by a homogeneous process. However, the suppressed semicircle curve was observed for the 0.01 Sr-deficient composition. Similar to the stoichiometric composition, the impedance spectra suggested that the conduction process was heterogeneous.

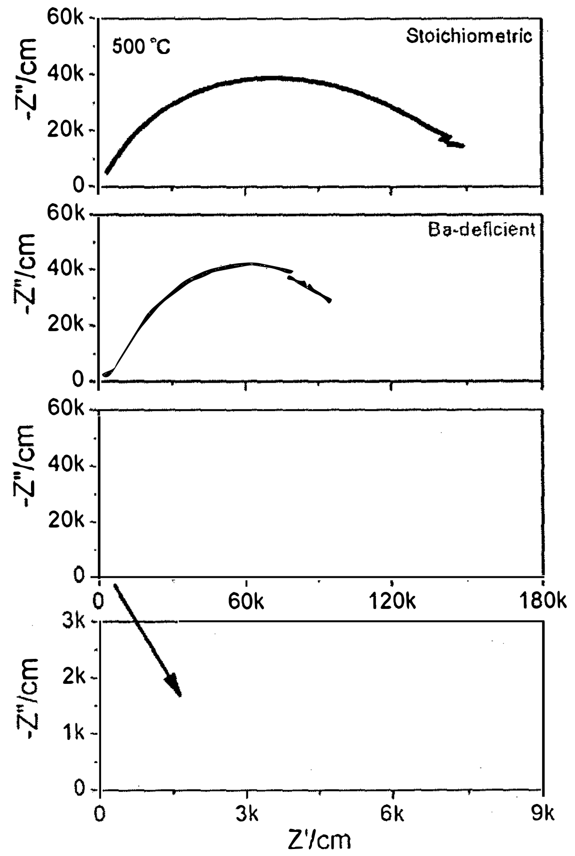

Figure 8. Impedance spectra for stoichiometric, 0.01 mol Ba-deficient, and 0.01 mol Sr-deficient compositions of $(Ba_{0.8}Sr_{0.2})TiO_3$ ceramics measured at 500 °C

It is important to note that the impedance data measured at 500 °C indicated that different compositions of A-cation deficiency affected the electrical characteristics significantly. Therefore, temperature dependence of the impedance data was further analyzed in order to enhance understanding of the conduction process for the samples. As shown in Figure 9, relaxation peaks in all compositions were observed. The shifting of peaks to higher frequency was found in all compositions as temperature increased. Broad and nonsymmetrical peaks of the semilog plot for Z" measured at a wide range of temperatures were observed for the stoichiometric composition. Sharp and symmetric peaks were observed at all measured temperatures for the 0.01 Ba-deficient composition. Broad and nonsymmetrical peaks were seen for the 0.01 Sr-deficient compositions. For the stoichiometric and 0.01 mol Ba-deficient compositions, the peak shape of the semi-log plot for -Z" versus frequency remained unchanged as temperature increased. This indicated that the conduction behavior was not changed. For the 0.01 mol Sr-deficient compositions, the broad and nonsymmetrical peaks changed as temperature increased, suggesting that the conduction process changed gradually.

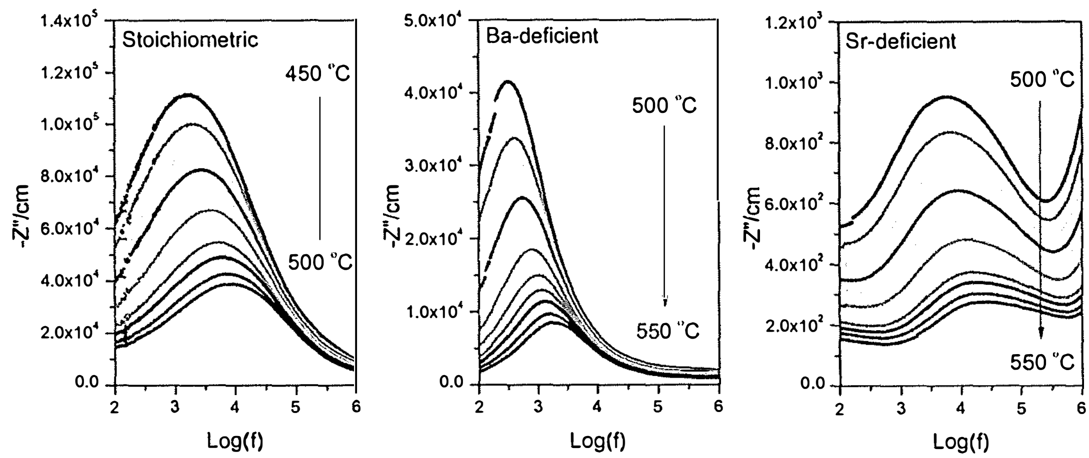

Figure 9. Frequency dependence of imaginary impedance (Z") measured at high temperatures for stoichiometric, 0.01 mol Ba-deficient, and 0.01 mol Sr-deficient compositions of $(Ba_{0.8}Sr_{0.2})TiO_3$ ceramics measured at 500 °C

Analysis of frequency dependence for the imaginary part of impedance (Z") at various temperatures using Arrhenius relationship provided additional information about the transport phenomena. The activation energy of conduction (E_a) could be obtained by fitting the linear regression for the logarithm of frequency, at which -Z" is maximum ($f_{Z"max}$) versus 1/T, as shown in Figure 10. The $f_{Z"max}$ was obtained using the peak-fitting method with a Gaussian model. Analysis of the stoichiometric and 0.01 Ba-deficient compositions could be obtained. The $f_{Z"max}$ of the 0.01 mol Sr-deficient composition could not be obtained with good accuracy. The peak shape was nonsymmetrical, which originated from the overlapping of multiple $f_{Z"max}$ peaks. Therefore, analysis of the Arrhenius plot for the 0.01 mol Sr-deficient composition was not included in this study. The activation energies of conduction at 0.57 and 0.86 eV were obtained for the stoichiometric and 0.01 mol Ba-deficient compositions, respectively. A significant increase in activation energy was observed when Ba-deficiency was introduced to the sample.

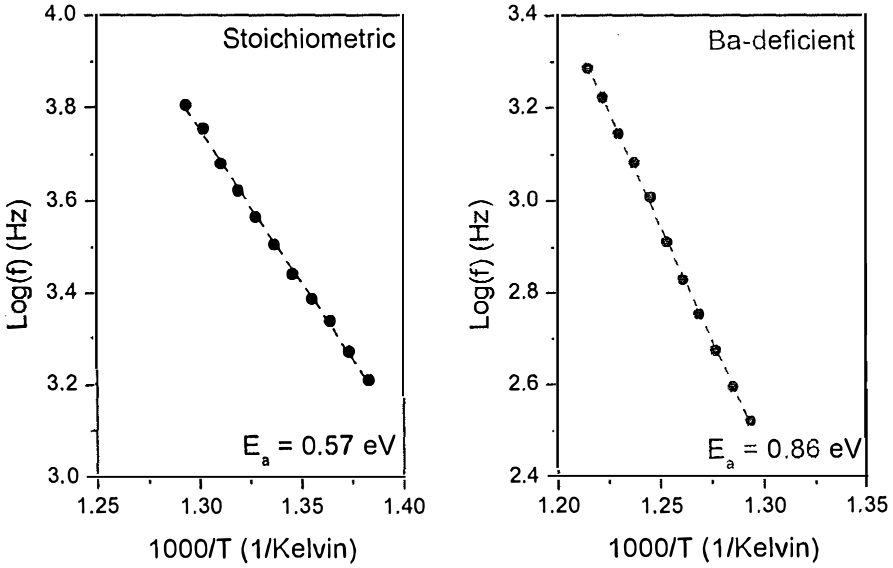

Figure 10. Arrhenius plot of data extracted from semi-log plot of Z" versus frequency for stoichiometric and 0.01 mol Ba-deficient compositions of $(Ba_{0.8}Sr_{0.2})TiO_3$ ceramics

To obtain further understanding of the origin of the change in conduction behavior, X-ray photoelectron spectroscopy (XPS) analysis was used. The spectra of Ti 2p species are illustrated in Figure 11. For all compositions, the binding energy for Ti 2p electrons are 458.1 and 465.8 eV for $2p_{3/2}$ and $2p_{1/2}$, respectively, indicating the presence of Ti^{4+} species. They are expected in titanate-based perovskite since Ti^{4+} specie occupied at BO_6 octahedra.[19,20] The results suggest that there was no change in Ti^{4+} valency when Ba-deficiency was introduced to the sample. However, lower binding energy of Ti 2p electrons at 457.6 and 463.1 eV for $2p_{3/2}$ and $2p_{1/2}$, respectively, were also observed in the Sr-deficient composition. The presence of this signal indicated that the Ti^{3+} specie was found. This indicated that the 0.01 mol Sr-deficient composition affected the stability of Ti^{4+} specie, i.e. the Ti^{4+} specie partially transformed into Ti^{3+} specie.

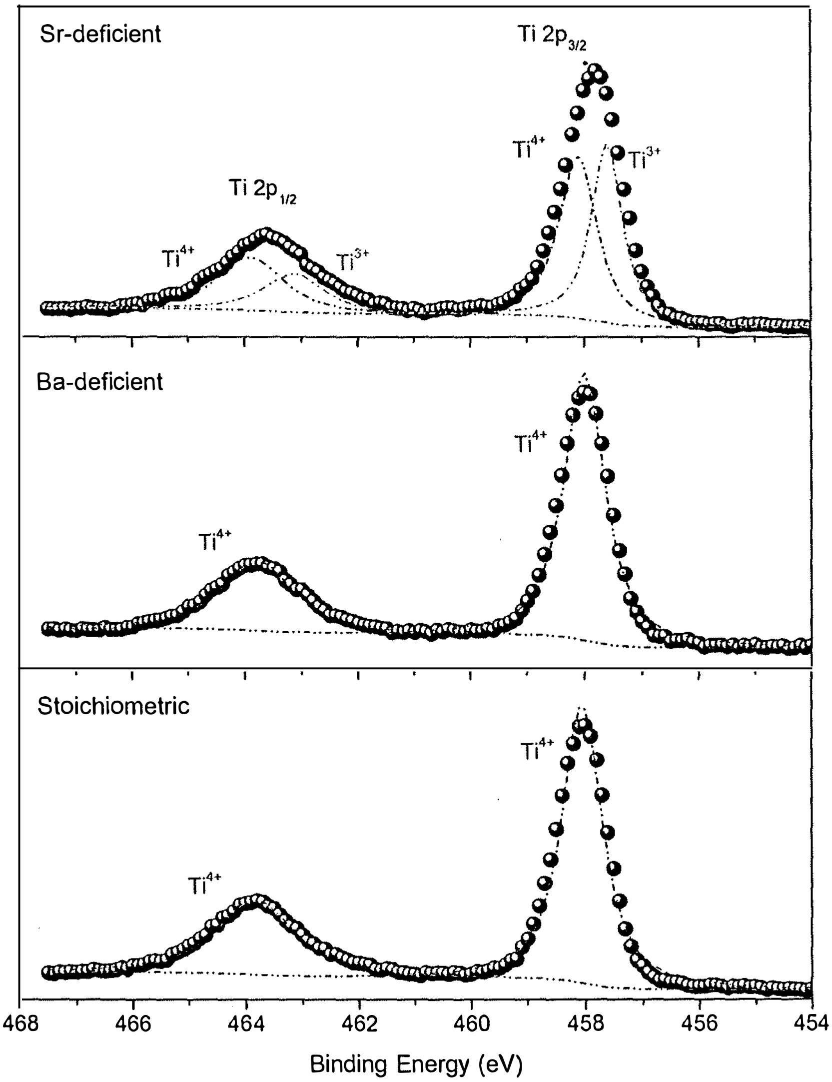

Figure 11. XPS spectra of Ti 2p species for stoichiometric, 0.01 mol Ba-deficient, and 0.01 mol Sr-deficient compositions of $(Ba_{0.8}Sr_{0.2})TiO_3$ ceramics

Based on the results obtained in this study, tentative defect models for the Ba- and Sr-deficient compositions were proposed. In $BaTiO_3$-based materials, oxygen vacancy is known to be a charge compensating defect for A-cation vacancy (V_A), forming (V_A-V_O) defect associates.[8, 21, 22] The presence of the (V_A-V_O) defect associates in $BaTiO_3$-based materials could modify electrical resistivity, as shown in related materials.[8] However, the Ti^{3+} defect specie was found in the Sr-deficient composition, which suggests the defect compensation mechanisms between Ba- and Sr-deficient compositions are different. A possible defect model that could explain this observation is (Ti^{3+}-V_O-V_A). The Ti^{3+} defect specie could be induced by ionized oxygen vacancy and acceptor-type defect (A-cation vacancy). The co-existence of two acceptor species for Ti^{3+} and Na(K) acceptor-type defects was previously reported by Scharfschwerdt *et al.*[23] The defect model of (Ti^{3+}-V_O-Na(K)) was observed in Na/K acceptor-doped $BaTiO_3$. Therefore, it might be possible that the distortion of TiO_6 octahedra near the A-cation vacancy site of Ba- and Sr-deficient compositions exhibited different characteristics. In other words, it preferred to form only stable (V_A-V_O) defect specie in the Ba-deficient composition, while it formed (V_A-V_O) and (Ti^{3+}-V_O-V_A) defect species in the Sr-deficient composition.

The presence of both Ti^{4+} and Ti^{3+} ions in the 0.01 mol Sr-deficient compositions could also be indicative of polaron hopping conduction mechanisms. In general, the activation energy of conduction found in a hopping mechanism is smaller than in an intrinsic mechanism. Thus, it could describe the observation of broad and nonsymmetrical relaxation peaks for Z" shown in Figure 9. Electrons could easily hop between Ti^{4+} and Ti^{3+} lattice sites. As temperature increases, polaron hopping could be easily activated. Therefore, the change in conduction mechanism was observed as shown previously.

Conclusion

Perovskite phase can be formed with or without A-cation non-stoichiometry. A-cation non-stoichiometry of $(Ba_{0.80}Sr_{0.20})TiO_3$ ceramics affected dielectric properties differently. The Ba- and Sr-excess compositions generally decreased dielectric constant at T_{max} while still maintaining broad phase transition characteristics. In contrast, dielectric constant was found to increase in the Ba- and Sr-deficient compositions. The shift in T_{max} was higher in Sr-excess and Sr-deficient compositions as compare with that of Ba-excess and Ba-deficient compositions. Although the improvement of dielectric constant was observed in the Ba- and Sr-deficient compositions. High temperature impedance spectra analysis reveals a different conduction process, in which homogeneous electrical characteristics exist in the stoichiometric and Ba-deficient compositions and heterogeneous electrical characteristics persist in the Sr-deficient composition. In addition, the Ti^{3+} ion accompanying Ti^{4+} ion in the Sr-deficient composition gives rise to the broad and asymmetric relaxation peak, indicating that the conduction process governs using polaron hopping mechanisms.

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   ชื่อผู้แต่ง: Natthaphon Raengthon, Gobwute Rujijanagul, David P. Cann
   ชื่อเรื่อง: Influence of A-site deficiency on electrical characteristics of barium strontium titanate perovskite dielectrics
   ชื่อวารสาร: Journal of Applied Physics
   ปี: 2018
   เล่มที่: 124
   เลขที่: 154105

2. การเสนอผลงานในที่ประชุมวิชาการ

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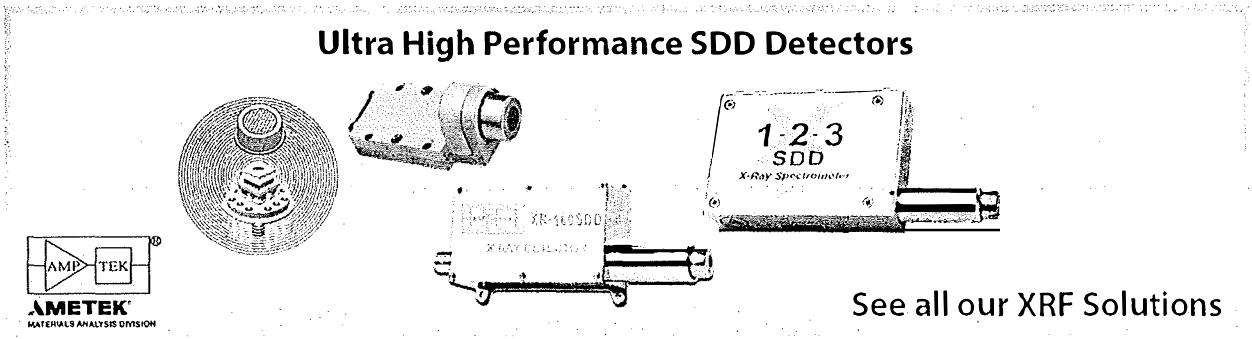
   สถานที่: international Convention Center Hiroshima, Japan
   ช่วงเวลา: May 27 – June 1, 2018
   ชื่อเรื่องที่นำเสนอ: Influence of Cation Non-Stoichiometry on Electrical Properties of Titanate-based Ceramics

Influence of A-site deficiency on electrical characteristics of barium strontium titanate perovskite dielectrics

Natthaphon Raengthon, Gobwute Rujijanagul, and David P. Cann

Citation: Journal of Applied Physics **124**, 154105 (2018); doi: 10.1063/1.5047503
View online: https://doi.org/10.1063/1.5047503
View Table of Contents: http://aip.scitation.org/toc/jap/124/15
Published by the American Institute of Physics



JOURNAL OF APPLIED PHYSICS 124, 154105 (2018)

Influence of A-site deficiency on electrical characteristics of barium strontium titanate perovskite dielectrics

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(Received 8 July 2018; accepted 29 September 2018; published online 17 October 2018)

Improvement of dielectric properties and insulation resistance are important for the development of high-performance dielectric materials. Various techniques can be used in order to improve the performance of such materials. The effect of A-cation deficiency on the electrical properties of barium strontium titanate ceramics is an interesting topic of investigation. Thus, this study examined the stoichiometric, 0.01 mol Ba-deficient, and 0.01 mol Sr-deficient compositions of $(Ba_{0.8}Sr_{0.2})TiO_3$ ceramics. Changes in the dielectric characteristics were observed in the 0.01 mol Ba-deficient and 0.01 mol Sr-deficient compositions. The characteristics of electrical conduction revealed by impedance analysis are different at high temperatures when Ba-deficiency and Sr-deficiency are introduced to the dielectrics. The Ti^{4+} state for the Ba-deficient composition is maintained. However, the Ti^{4+} state partially changes to the Ti^{3+} state, giving rise to the polaron hopping conduction process for Sr-deficient composition. Therefore, this study shows that a minor deviation of the A-cation from stoichiometry can induce a different conduction process while maintaining the dielectric permittivity characteristics. *Published by AIP Publishing.* https://doi.org/10.1063/1.5047503

INTRODUCTION

The development of advanced materials for electronic applications such as capacitors, sensors, transducers, photovoltaic devices, and catalysts has been continuously undertaken due to the increasing demands of new devices with high performance and efficiency. The careful modification of the materials could result in the improvement of the electrical properties. Defects are known to play an important role in governing the electrical properties of titanate-based perovskites. For example, bismuth sodium titanate perovskite, $(Bi_{0.50}Na_{0.50})TiO_3$: BNT, is well known as a promising candidate for lead-free piezoelectric. Large remnant polarization and large coercive field could be modified by doping or forming complex solid solutions with other perovskite end members.[1–4] The introduction of defects onto the A-site of BNT, such as Bi deficiency or divalent cation doping, revealed a high ionic conductivity characteristic.[5–7] High dielectric permittivity ceramics based on the $BaTiO_3$-$Bi(Zn_{1/2}Ti_{1/2})O_3$ system were obtained with the improvement of electrical properties at high temperature when A-site nonstoichiometry was introduced.[8,9] Barium strontium titanate $(Ba,Sr)TiO_3$ ceramics have also been investigated for more than a decade.[10,11] Substitution of the Ti cation with transition metal cations (Fe^{3+}, Mn^{3+}, Y^{3+}, and Ga^{3+}) resulted in changes of dielectric permittivity and reduction of the dielectric loss.[12] The first principles calculation of defects in titanate-based perovskite was used to obtain a better understanding of the materials.[13,14] Extensive studies of defect chemistry for titanate-based perovskite have been reported by showing the validity of comparable results from first principles calculation and experimental results.[15] In addition, defects in $Ba_{0.8}Sr_{0.2}TiO_3$ have played an important role in the improvement of electrostrain, which leads to defect-induced structural distortion.[16] Moreover, the effects of the A-cation/Ti ratio on the microwave tunability of $Ba_{0.6}Sr_{0.4}TiO_3$ ceramics have been studied.[17] It was reported that the A/B ratio affected dielectric permittivity, dielectric loss, and the tunability of materials. The improvement of microwave tunability occurred only when the A/B ratio was less than unity. Therefore, the cation nonstoichiometry in the $(Ba_{0.80}Sr_{0.20})TiO_3$ reconfigured domain enhanced microwave tunability.[18]

In this study, Ba-deficient and Sr-deficient compositions were chosen for investigation. The electrical properties are the main focus in order to understand the roles of A-cation deficiency in $(Ba_{0.80}Sr_{0.20})TiO_3$ ceramics.

EXPERIMENTAL METHOD

The precursors of $BaCO_3$ (>99.0% purity), $SrCO_3$ (>99.0% purity), and TiO_2 (>99.0% purity) were used to prepare barium strontium titanate, $(Ba_{0.80}Sr_{0.20})TiO_3$, ceramics via the solid-state reaction technique. Batch calculation was carried out for stoichiometric composition, 0.01 mol Ba-deficient composition, and 0.01 mol Sr-deficient composition,

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[a)] Author to whom correspondence should be addressed: Natthaphon.R@chula.ac.th i.e., $(Ba_{0.80}Sr_{0.20})TiO_3$, $(Ba_{0.79}Sr_{0.20})TiO_{3-x}$, and $(Ba_{0.80}Sr_{0.19})TiO_{3-x}$, respectively. The precursors were mixed and milled for 24 h using the ball-milling technique. After drying, the mixed powders were calcined at 1100 °C for 4 h. The calcined powders were ground to reduce particle size using the ball-milling technique for 24 h. The calcined powders were then mixed with 2 wt. % polyvinyl alcohol (PVA) solutions prior to being uniaxially pressed into the pellet shape. The green body was placed in an alumina crucible with embedded powders and sintered at 1475 °C for 4 h. Silver paste was applied on the polished surface of the sintered pellet before firing at 700 °C for 15 min. The temperature dependence of permittivity measured at 1 kHz, 10 kHz, and 100 kHz was investigated from 25 to 125 °C. Impedance spectroscopy was carried out at high temperature from 450 to 550 °C. X-ray photoelectron spectroscopy (XPS) was studied at room temperature on the well-packed powder of ground sintered samples.

RESULTS AND DISCUSSIONS

The stoichiometric composition of $(Ba_{0.80}Sr_{0.20})TiO_3$ polycrystalline ceramic was investigated by comparing to 0.01 mol Ba-deficient and 0.01 mol Sr-deficient compositions, i.e., $(Ba_{0.79}Sr_{0.20})TiO_{3-x}$ and $(Ba_{0.80}Sr_{0.19})TiO_{3-x}$, respectively. The perovskite phase was confirmed in all compositions, as shown in Fig. 1. The shifting of the peak was not observed within the resolution limit of a laboratory X-ray diffractometer, indicating that changes in the long-range crystal structure were not observed. However, the secondary phase of unknown species was observed at 2θ of 24° and 28° for stoichiometric composition. The secondary phase, as shown in the XRD pattern, could not be identified with a good accuracy. However, the peak at 2θ of 24° closely matched with the $BaCO_3$ phase. This implied that a small fraction of the remaining $BaCO_3$ precursor was unreacted. For Ba-deficient and Sr-deficient compositions, peaks at 2θ of 24° were not observed, which indicated that A-site deficiency affected the formation of the secondary phase.

Dielectric properties as a function of temperature are shown in Fig. 2. The stoichiometric composition exhibited frequency-independent dielectric permittivity around the temperature T_{max} (58 °C), at which the dielectric permittivity is maximum. At high temperature, frequency-dependent behavior of dielectric loss was observed for the stoichiometric composition. An increase of dielectric permittivity was clearly seen in the 0.01 mol Ba-deficient composition. The dielectric loss was found to be higher than that of the stoichiometric composition. Frequency dispersion of dielectric properties was observed, as seen at T_{max}. However, the T_{max} of the 0.01 mol Ba-deficient composition was found to be the same as that of the stoichiometric composition. Additionally, frequency dispersion of dielectric loss at high temperature could not be seen from the dielectric data. Dielectric permittivity with frequency-independent behavior was observed in the 0.01 mol Sr-deficient composition. Dielectric permittivity at T_{max} was comparable to that of the stoichiometric composition. T_{max} shifted to a higher temperature as compared to that of the stoichiometric composition. However, a large increase in the dielectric loss at high temperature (>100 °C) was observed. Additionally, close inspection of the dielectric constant versus temperature curves of the Ba- and Sr-deficient compositions suggested that a step change in the dielectric constant was observed as temperature increased to right below T_{max}, which could be interpreted as an intermediate phase. However, the dielectric anomaly was weak for the Ba-deficient composition. Moreover, this phenomenon was not observed in the stoichiometric compositions. Since A-cation vacancy (V_A) was introduced to the composition, the system was compensated by the oxygen vacancy. The formation of the (V_A-V_O) defect associate could be possible, which could induce the distortion of TiO_6 octahedra. Moreover, it is possible that the induced oxygen vacancy defect could reduce Ti^{4+} to Ti^{3+} forming the defect complex (Ti^{3+}-V_O), which could also affect the distortion of the unit cell, particularly octahedral distortion. Thus, the intermediate phase was observed. As temperature increases, the intermediate phase might change its configuration and TiO_6 octahedra become less distorted, resulting in a dielectric anomaly at the temperature right below T_{max}.

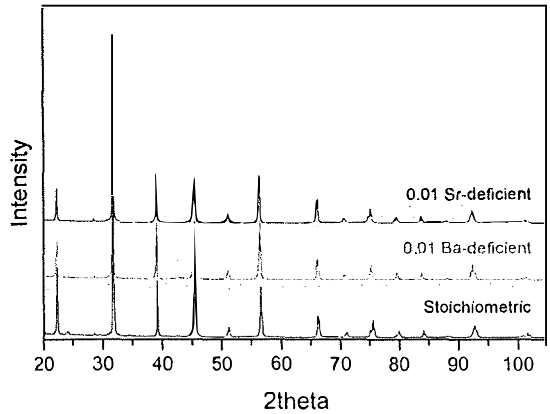

FIG. 1. X-ray diffraction patterns of stoichiometric, 0.01 mol Ba-deficient, and 0.01 mol Sr-deficient compositions of $(Ba_{0.8}Sr_{0.2})TiO_3$ ceramics.

Not only is the behavior of dielectric permittivity as a function of temperature slightly changed, but the behavior of dielectric loss at high temperatures was also different when comparing between three compositions. The increase in the dielectric loss at high temperatures suggested that resistive behavior at high temperature deteriorated, which could be due to a change in the conduction mechanism. Therefore, impedance measurements were undertaken at various temperatures ranging from 450 to 550 °C in order to understand conduction behavior at high temperature.

Figure 3 shows the impedance spectra of the stoichiometric, 0.01 mol Ba-deficient, and 0.01 Sr-deficient compositions measured at 500 °C in a frequency range of 10^2–10^6 Hz. Frequency dispersion of Z' and Z'' was observed for the stoichiometric and 0.01 Ba-deficient compositions. However, dispersion could not be observed for the 0.01 Sr-deficient composition due to much lower resistance. Additionally, the analysis of the Nyquist plot for impedance provided useful information about the transport phenomena and electrical characteristics. A suppressed-nonsymmetrical semicircle curve of

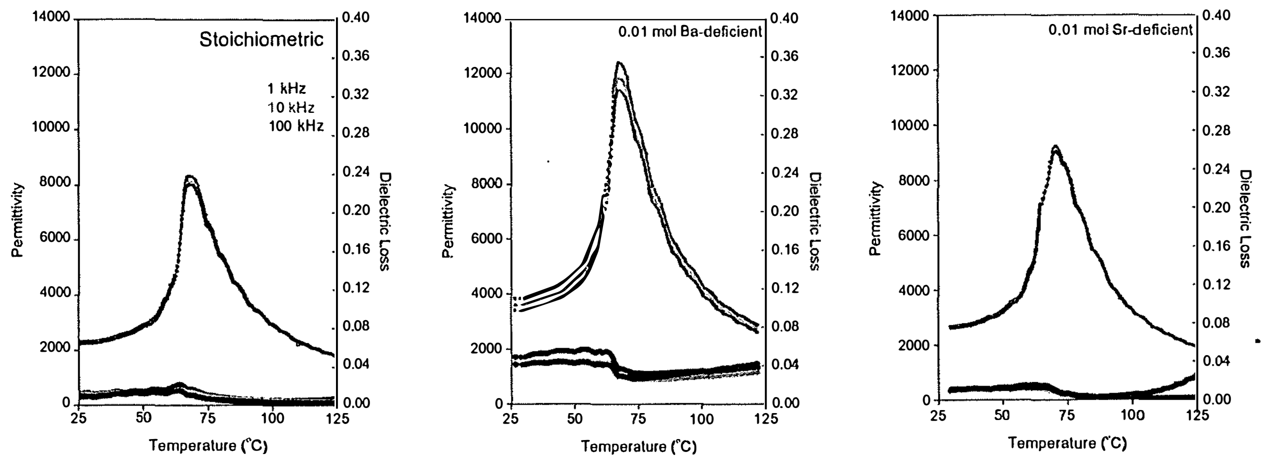

FIG. 2. Temperature dependence of dielectric permittivity of stoichiometric, 0.01 mol Ba-deficient, and 0.01 mol Sr-deficient compositions of $(Ba_{0.8}Sr_{0.2})TiO_3$ ceramics.

the impedance was observed for the stoichiometric composition. This suggested that multiple conduction paths contributed to the overall conduction process of the sample. In other words, the heterogeneous conduction process existed. In comparison, the Nyquist plot of impedance for the 0.01 mol Ba-deficient showed the symmetric semicircle curve, which indicated that the conduction path could be supported by a homogeneous process. However, the suppressed semicircle curve was observed for the 0.01 Sr-deficient composition. Similar to the stoichiometric composition, the impedance spectra suggested that the conduction process was heterogeneous.

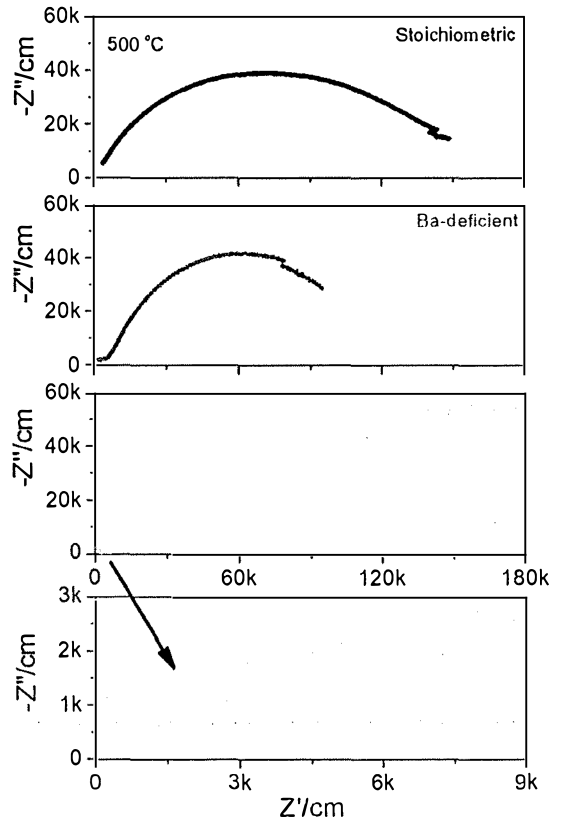

FIG. 3. Impedance spectra for stoichiometric, 0.01 mol Ba-deficient, and 0.01 mol Sr-deficient compositions of $(Ba_{0.8}Sr_{0.2})TiO_3$ ceramics measured at 500 °C.

It is important to note that the impedance data measured at 500 °C indicated that different compositions of A-cation deficiency affected the electrical characteristics significantly. Therefore, temperature dependence of the impedance data was further analyzed in order to enhance understanding of the conduction process for the samples. As shown in Fig. 4, relaxation peaks in all compositions were observed. The shifting of peaks to higher frequency was found in all compositions as temperature increased. Broad and nonsymmetrical peaks of the semilog plot for Z'' measured at a wide range of temperatures were observed for the stoichiometric composition. Sharp and symmetric peaks were observed at all measured temperatures for the 0.01 Ba-deficient composition. Broad and nonsymmetrical peaks were seen for the 0.01 Sr-deficient compositions. For the stoichiometric and 0.01 mol Ba-deficient compositions, the peak shape of the semi-log plot for $-Z''$ versus frequency remained unchanged as the temperature increased. This indicated that the conduction behavior was not changed. For the 0.01 mol Sr-deficient compositions, the broad and nonsymmetrical peaks changed as the temperature increased, suggesting that the conduction process changed gradually.

The analysis of frequency dependence for the imaginary part of impedance (Z'') at various temperatures using the Arrhenius relationship provided additional information about the transport phenomena. The activation energy of conduction (E_a) could be obtained by fitting the linear regression for the logarithm of frequency, at which $-Z''$ is maximum ($f_{Z''\max}$) versus $1/T$, as shown in Fig. 5. The $f_{Z''\max}$ was obtained using the peak-fitting method with a Gaussian model. The analysis of the stoichiometric and 0.01 Ba-deficient compositions could be obtained. The $f_{Z''\max}$ of the 0.01 mol Sr-deficient composition could not be obtained with a good accuracy. The peak shape was nonsymmetrical, which originated from the overlapping of multiple $f_{Z''\max}$ peaks. Therefore, the analysis of the Arrhenius plot for the 0.01 mol Sr-deficient

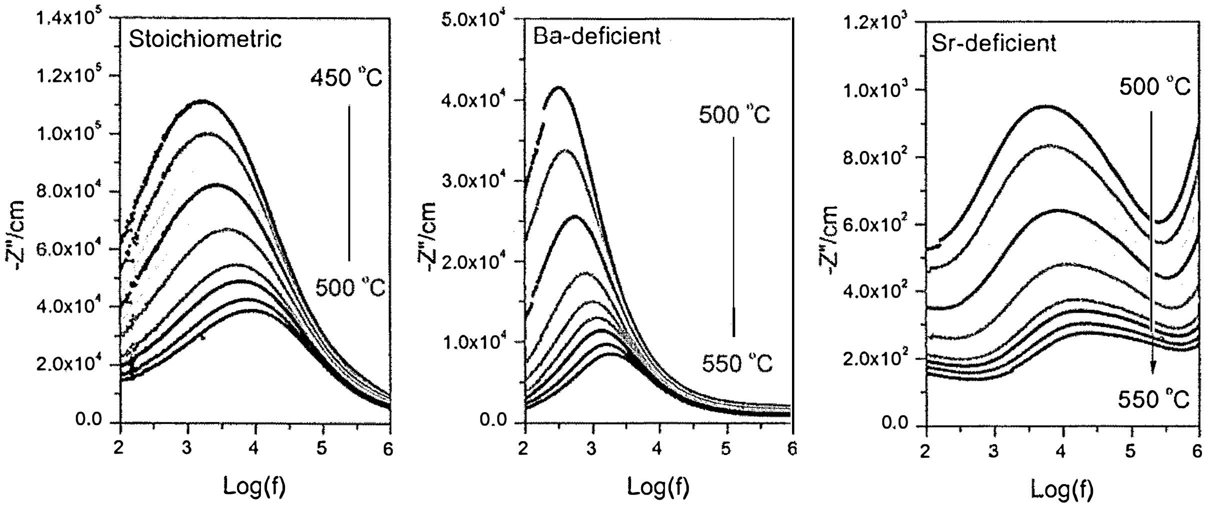

FIG. 4. Frequency dependence of imaginary impedance (Z'') measured at high temperatures for stoichiometric, 0.01 mol Ba-deficient, and 0.01 mol Sr-deficient compositions of $(Ba_{0.8}Sr_{0.2})TiO_3$ ceramics measured at 500 °C.

composition was not included in this study. The activation energies of conduction at 0.57 and 0.86 eV were obtained for the stoichiometric and 0.01 mol Ba-deficient compositions, respectively. A significant increase in activation energy was observed when Ba-deficiency was introduced to the sample.

For further understanding of the origin of the change in conduction behavior, X-ray photoelectron spectroscopy (XPS) analysis was used. The spectra of Ti 2p species are illustrated in Fig. 6. For all compositions, the binding energies for Ti 2p electrons are 458.1 and 465.8 eV for $2p_{3/2}$ and $2p_{1/2}$, respectively, indicating the presence of Ti^{4+} species. They are expected in titanate-based perovskite since Ti^{4+} species occupied at BO_6 octahedra.[19,20] The results suggest that there was no change in the Ti^{4+} valency when Ba-deficiency was introduced to the sample. However, the lower binding energy of Ti 2p electrons at 457.6 and 463.1 eV for $2p_{3/2}$ and $2p_{1/2}$, respectively, was also observed in the Sr-deficient composition. The presence of this signal indicated that the Ti^{3+} species was found. This indicated that the 0.01 mol Sr-deficient composition affected the stability of Ti^{4+} species, i.e., the Ti^{4+} species partially transformed into Ti^{3+} species.

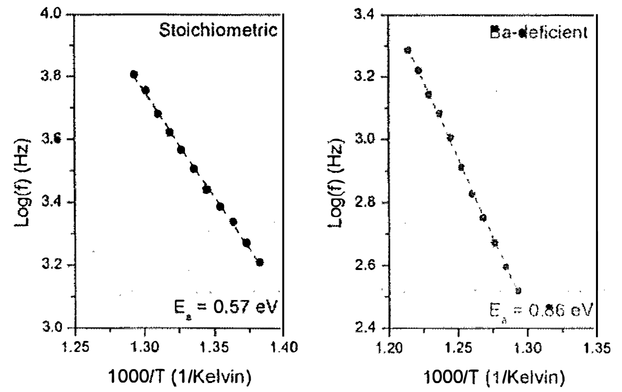

FIG. 5. The Arrhenius plot of data extracted from semi-log plot of Z'' versus frequency for stoichiometric and 0.01 mol Ba-deficient compositions of $(Ba_{0.8}Sr_{0.2})TiO_3$ ceramics.

Based on the results obtained in this study, tentative defect models for the Ba- and Sr-deficient compositions were proposed. In $BaTiO_3$-based materials, the oxygen vacancy is known to be a charge compensating defect for the A-cation vacancy (V_A), forming the (V_A-V_O) defect associates.[8,21,22] The presence of the (V_A-V_O) defect associates in $BaTiO_3$-based materials could modify electrical resistivity, as shown in related materials.[8] However, the Ti^{3+} defect species

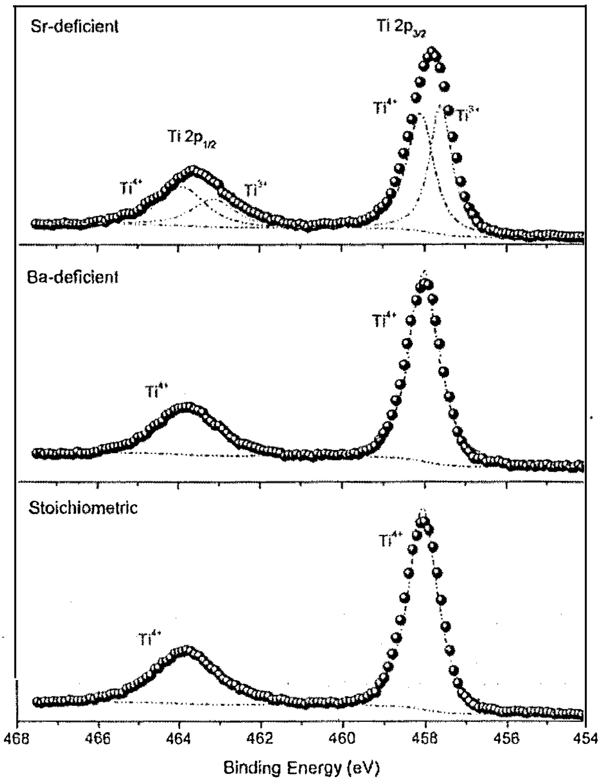

FIG. 6. XPS spectra of Ti 2p species for stoichiometric, 0.01 mol Ba-deficient, and 0.01 mol Sr-deficient compositions of $(Ba_{0.8}Sr_{0.2})TiO_3$ ceramics.

was found in the Sr-deficient composition, which suggests that the defect compensation mechanisms between Ba- and Sr-deficient compositions are different. A possible defect model that could explain this observation is (Ti^{3+}-V_O-V_A). The Ti^{3+} defect species could be induced by the ionized oxygen vacancy and the acceptor-type defect (A-cation vacancy). The co-existence of two acceptor species for Ti^{3+} and Na(K) acceptor-type defects was previously reported by Scharfschwerdt *et al.*[23] The defect model of [Ti^{3+}-V_O-Na(K)] was observed in Na/K acceptor-doped $BaTiO_3$. Therefore, it might be possible that the distortion of TiO_6 octahedra near the A-cation vacancy site of Ba- and Sr-deficient compositions exhibited different characteristics. In other words, it preferred to form only stable (V_A-V_O) defect species in the Ba-deficient composition, while it formed (V_A-V_O) and (Ti^{3+}-V_O-V_A) defect species in the Sr-deficient composition.

The presence of both Ti^{4+} and Ti^{3+} ions in the 0.01 mol Sr-deficient compositions could also be indicative of polaron hopping conduction mechanisms. In general, the activation energy of conduction found in a hopping mechanism is smaller than in an intrinsic mechanism. Thus, it could describe the observation of broad and nonsymmetrical relaxation peaks for Z″ shown in Fig. 4. Electrons could easily hop between Ti^{4+} and Ti^{3+} lattice sites. As temperature increases, polaron hopping could be easily activated. Therefore, the change in the conduction mechanism was observed as shown previously.

CONCLUSION

The perovskite phase can be formed with or without 0.01 mol A-cation deficiency. Ba-deficiency and Sr-deficiency do not affect the crystal structure. Dielectric permittivity increases when Ba-deficiency is introduced, while the dielectric loss increases at high temperature when Sr-deficiency is introduced. High temperature impedance spectra analysis reveals a different conduction process, in which homogeneous electrical characteristics exist in the stoichiometric and Ba-deficient compositions and heterogeneous electrical characteristics persist in the Sr-deficient composition. In addition, the Ti^{3+} ion accompanying Ti^{4+} ion in the Sr-deficient composition gives rise to the broad and asymmetric relaxation peak, indicating that the conduction process governs using polaron hopping mechanisms.

ACKNOWLEDGMENTS

This work was fully supported by a grant from the Thailand Research Fund (TRF—Grant No. TRG5880225). The author would like to thank the Electroceramics Research Laboratory, College of Nanotechnology and Advanced Materials Research Unit, Faculty of Science, King Mongkut's Institute of Technology Ladkrabang, Bangkok, Thailand, as well as the Electroceramics Research Laboratory, Department of Physics and Materials Science, Faculty of Science, Chiang Mai University, Chiang Mai, Thailand, and the School of Science, Mae Fah Luang University, Chiang Rai, Thailand for supporting electrical properties measurement.

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2018 ISAF-FMA-AMF-AMEC-PFM Joint Conference (IFAAP 2018)

May 27 - June 1, 2018 , Hiroshima

February 6th, 2018

Dear Dr. Natthaphon Raengthon

We are pleased to invite you to the ISAF-FMA-AMF-AMEC-PFM Joint Conference (IFAAP) to be held during May 27 - June 1, 2018 at the International Convention Center Hiroshima, Japan.

The IFAAP is the first joint conference between IEEE-International Symposium on Applications of Ferroelectrics (ISAF), Meeting on Ferroelectric Materials and Their Applications (FMA), Asian Meetings on Ferroelectrics (AMF), Asian Meetings on Electroceramcs (AMEC) and Piezoresponse Force Microscopy Workshop (PFM). This international conference aims to bring together leaders from academia, national laboratories and industrial research and development sectors, to discuss the most recent advancements in the science and technology of ferroelectric and dielectric materials, spanning a broad range of topics from the theory and modeling of the materials, to processing and characterization thereof, as well as development of new applications and devices.

On behalf of the Technical Program Committee of IFAAP, I hereby officially inform that your presentation entitled 'Influence of Cation Non-Stoichiometry on Electrical Properties of Titanate-based Ceramics' is accepted as an oral presentation.

It will be a matter of immense pleasure for us to have your presence at IFAAP Hiroshima 2018. We are looking forwards to seeing you at Hiroshima.

Best regards,

T. Tsurumi

Prof. Takaaki Tsurumi,
General Chair of IFAAP,
Professor of Tokyo Institute of Technology

Influence of Cation Non-Stoichiometry on Electrical Properties of Titanate-based Ceramics

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Metal oxide is commonly known to exhibit a wide range of significant electrical properties, which led to utilization in various advanced electronic technologies. Chemical modification by homo-valent and/or hetero-valent cations substitution affects electrical properties of the materials including change in magnitude of permittivity, transport behavior and shift in phase transition temperature. In this work, it is of interest to investigate influence of A-site cation deficiency on electrical properties of barium strontium titanate perovskite. A $(Ba_{0.80}Sr_{0.20})TiO_3$ was selected as a reference composition. Ba and Sr cations were intentionally deducted by 0.01 mol from the reference composition forming Ba-deficient, $(Ba_{0.79}Sr_{0.20})TiO_{3-x}$, and Sr-deficient ,$(Ba_{0.80}Sr_{0.19})TiO_{3-x}$, compositions. All compositions were prepared by solid-state reaction method. Single phase perovskite was observed in all compositions. No significant shift in phase transition temperature was found while permittivity maximum increased in Ba-/Sr-deficient compositions. Insulation resistance behavior at high temperature was investigated, which was found to be significantly different in all compositions. In addition, A-site deficiency affected valency of Ti as evident via XPS analysis which could provide support for the observed insulation resistance behavior.