Articles

Dielectric Properties and an EPR Study of Cu- or Zr-Doped BaTiO$_3$ Ceramics[#]

Mi-Nyeong Lee and Yoon-Chang Park

Department of Chemistry, Sung kyun Kwan University, Suwon 440-746, Korea
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The EPR spectra of Cu- or Zr-doped BaTiO$_3$ ceramics exhibited absorption signals with $g_\parallel = 2.380$ and $g_\perp = 2.063$ which are assigned, to Ba^{1+}(Ba^{2+} + e' → Ba^{1+}) ion reduced by an electron that was produced from the oxygen vacancy (V$_O$). The intensity of these signals decreased as the temperature increased indicating that Ba^{1+} was changed to Ba^{2+} as the temperature increased. These ceramics also showed the EPR signal with $g = 1.997$ around T$_C$ which arises from ionized Ba-vacancies, V$_{Ba}$'(V$_{Ba}$ + e' → V$_{Ba}$'). In the orthorhombic and tetragonal phase region $g = 1.997$ signal was not seen. The electrons generating from the oxidation of Ba^{1+} and ionized Ba-vacancies may contribute to a space charge which is responsible for a dielectric relaxation of these samples.

Introduction

It has been known that Mn-doped BaTiO$_3$ ceramics can trap the electrons produced during a sintering under a very low oxygen pressure[1] and show the different vibrational and electronic properties from those of the pure compound. When the sintering of pure BaTiO$_3$ is carried out under low oxygen pressure, oxygen vacancies are created according to Kröger and Vink notation (Eq. (1)).[2]

$$O_O = 1/2\ O_2 + V_O^{..} + 2\ e' \qquad (1)$$
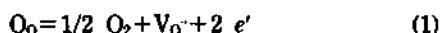
The produced electrons can be trapped by the titanium ions according to Eq. (2),

$$Ti_{Ti} + e' → Ti_{Ti}' \qquad (2)$$

however the electrons are almost fully delocalized on the titanium ions by means of the following equilibrium[1] (Eq. (3)).

$$Ti_{Ti}' + Ti_{Ti} \rightleftharpoons Ti_{Ti} + Ti_{Ti}' \qquad (3)$$

If some titanium sites are occupied by the acceptor dopants such as manganese ions which are more reducible than the titanium ions the electrons can be preferentially trapped on these sites. Then the ferroelectricity of BaTiO$_3$ is strongly affected by the presence of the acceptor dopants. On the other hand, the donor doped polycrystalline barium titanate exhibits the large positive temperature coefficient of electrical resistivity (PTCR) around Curie point (T$_C$).[3~6] However the acceptor doped BaTiO$_3$ are insulating.[7] This phenomenon may suggest that the acceptor dopants do not dissolve in the bulk but segregate preferentially at the grain boundaries.[8~10] We tried to correlate the temperature variation in dielectric constant with the changes in the EPR spectrum when copper or zirconium is introduced as an acceptor dopant into BaTiO$_3$ ceramics in order to explain the role of

those dopants.

Experimental

The starting materials (BaCO$_3$, TiO$_2$) and the additives (CuO, ZrO$_2$) were well mixed by zirconia ball milling in ethanol, and calcined in air at 1050-1100 ℃ for 2 hours. After calcining the powders were milled again and pressed into pellets (1000-2000 kg/cm^2) using 1 wt.% polyvinyl alcohol binder. The pellets were sintered at 1320-1370 ℃ for 2 hours in air (heating rate : 300 ℃/hr, cooling rate : 100 ℃/hr), giving rise to ceramics of 5-10 μm grain size and 93-95% sinter density.

The samples were identified as single phases by X-ray diffraction patterns and the dielectric constants were obtained by HP4194A Impedance Analyzer in the temperature range from 253 K to 423 K and the frequency range from 100 Hz to 15 MHz.

The EPR spectra for the crushed powders were taken with Bruker ER 031 X-band spectrometer in the temperature range of 93 K and 423 K. The EPR intensity is calculated from the following empirical relation.[11]

$$I = \frac{(\text{signal height})(\text{signal width})^2}{(\text{gain})(\text{sample weight})(\text{modulation amplitude})(\text{power})^{1/2}} \qquad (3)$$

The quantity of impurities of samples were determined by ICP-AES (Inductively Coupled Plasma-Atomic Emission Spectroscopy) analysis.

Results and Discussion

Dielectric measurements. Figure 1 shows the dielectric constant versus temperature of BaTiO$_3$ ceramics with different concentrations of Zr^{4+}. This figure shows that the ferroelectricity of Zr-doped BaTiO$_3$ ceramics are not greatly affected by the amount of Zr^{4+} ions although the dielectric constant of Zr-doped BaTiO$_3$ ceramics are somewhat less

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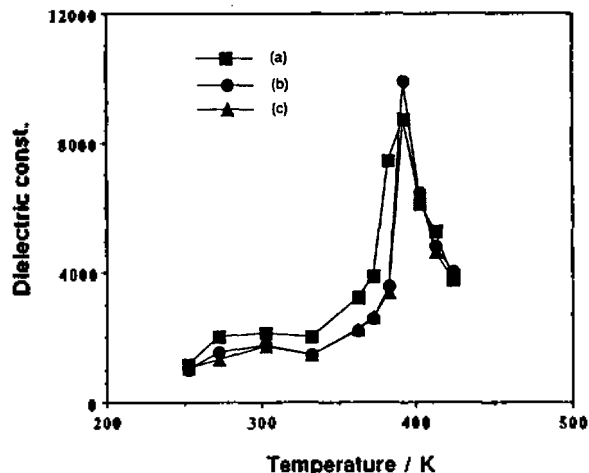*Bull. Korean Chem. Soc.* **1995,** Vol. 16, No. 10   909

Figure 1. The dielectric constants versus temperature of Zr-doped BaTiO₃ ceramics (a) with 0.8 at.% (b) with 2 at.% and (c) with 5 at.% (freq.=1 kHz).
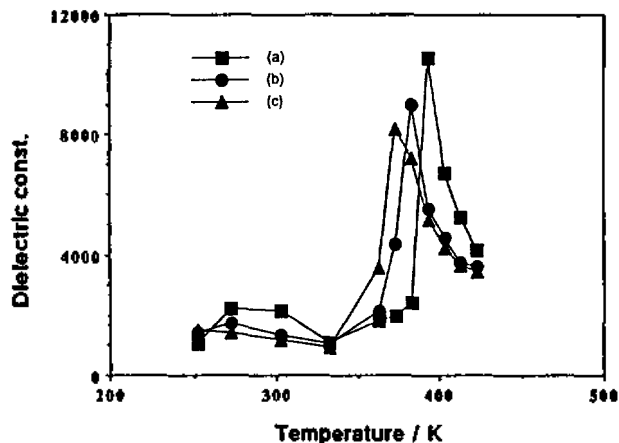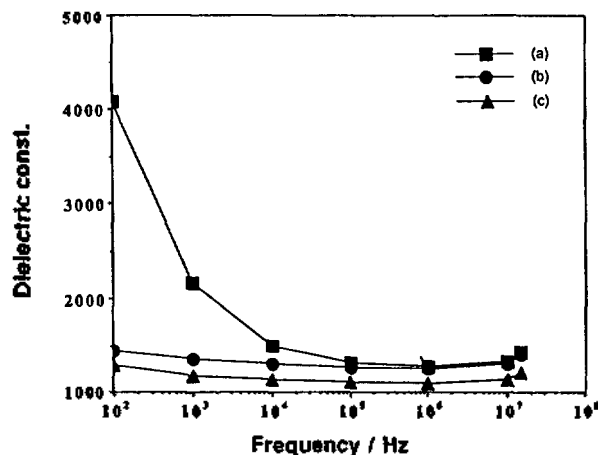

Figure 3. Dispersion of the dielectric constants of Cu-doped BaTiO₃ ceramics (a) with 0.3 at.% (b) with 0.8 at.% and (c) with 2 at.% at room temperature.
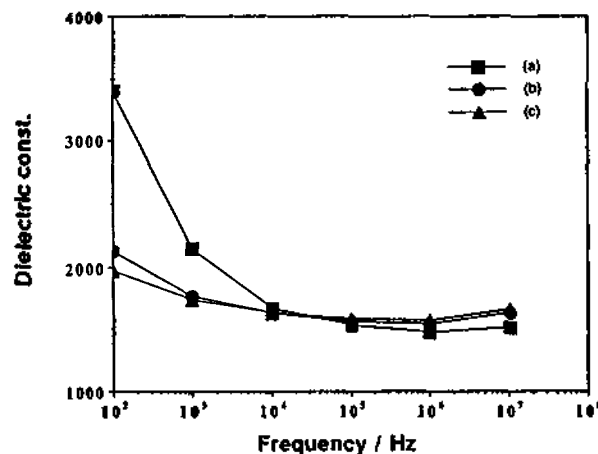

Figure 2. The dielectric constants versus temperature of Cu-doped BaTiO₃ ceramics (a) with 0.3 at.% (b) with 0.8 at.% and (c) with 2 at.% (freq.=1 kHz).

Figure 4. Dispersion of the dielectric constants of Zr-doped Ba-TiO₃ ceramics (a) with 0.8 at.% (b) with 2 at.% and (c) with 5 at.% at room temperature.

than that of pure BaTiO₃. The Curie point (T_C) of Zr-doped BaTiO₃ ceramics were almost same regardless of its composition.

On the other hand, the dielectric constant of Cu-doped BaTiO₃ ceramics are dependent on the amount of Cu^{2+} ions as shown in Figure 2. As the concentration of Cu^{2+} increases the dielectric constant decreases as well as T_C.

In case of Mn-doped BaTiO₃ ceramics,[1] the Curie peak disappears after sintering under Po₂ lower than 10^{-2} Pa when the manganese concentration is greater than 0.025 at.% indicating that the ferroelectricity of BaTiO₃ ceramics are strongly affected by the presence of a small amount of Mn^{2+} ions. The reason for this phenomenon was explained on the basis of the difference of the ionic radii between Ti^{4+} (0.68 Å) and Mn^{2+} (0.80 Å). However, the dielectric behavior of Zr-doped BaTiO₃ ceramics were different from that of Mn-doped BaTiO₃ ceramics, although Zr^{4+} has almost same ionic radius (0.79 Å) as Mn^{2+}. On the other hand, Cu-doped BaTiO₃ ceramics showed similar dielectric behavior with Mn-doped BaTiO₃ even if the ionic radius of Cu^{2+} (0.72 Å) is smaller.

Therefore, these features may be explainable on the basis of the oxidation states of the ions and charges rather than the ionic radii.

Low frequency dispersion measurements. The dielectric constant measurements at low frequency for Cu-doped BaTiO₃ ceramics are shown in Figure 3. This figure shows the existence of a dielectric relaxation at low frequency for BaTiO₃ ceramic with 0.3 at.% Cu^{2+}. However, it is seen that the dielectric relaxation was softened when the concentration of Cu^{2+} ions increased. Such phenomena observed also in pure and Mn-doped BaTiO₃ ceramics have been attributed to the existence of space charges due to the reduction of these ceramics.[1] Same phenomena were observed in the Zr-doped BaTiO₃ ceramics (Figure 4). However, in this case, the existence of a dielectric relaxation at low frequency is seen for BaTiO₃ ceramic with 0.8 at.% Zr^{4+}. Rather than Ti^{4+} ions, Zr^{4+} ions prefer cubic structure[12] and therefore the ferroelectricity of Zr-doped BaTiO₃ ceramics decreases with restraining TiO₆ octahedra distortion in BaTiO₃ lattice.

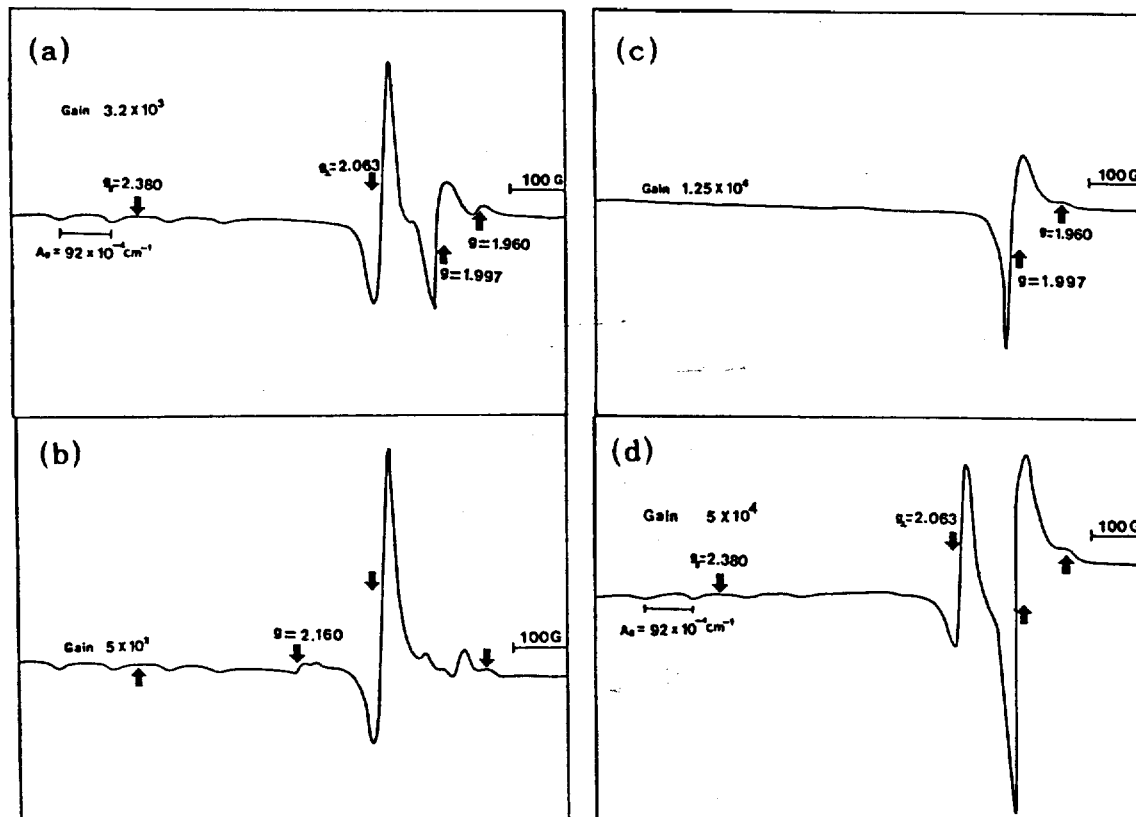**EPR studies.** The EPR spectra of Cu- or Zr-doped Ba-

Figure 5. EPR spectra of $BaTiO_3$ ceramics (a) with 0.3 at.% Cu (b) with 2 at.% Cu (c) with 0.8 at.% Zr and (d) with 5 at.% Zr at 93 K (freq.=9.426 GHz).
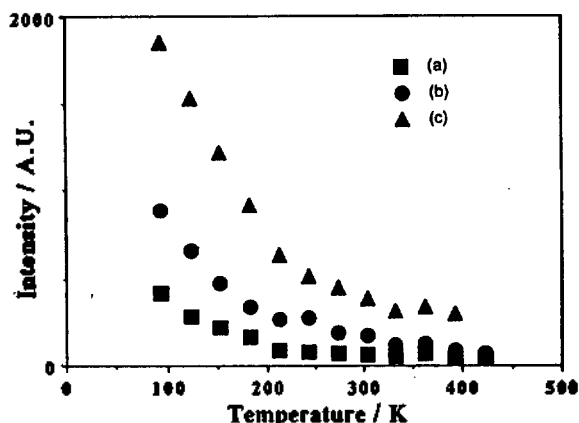

Figure 6. The intensity of $g=2.063$ signal versus temperature for Cu-doped $BaTiO_3$ ceramics (a) with 0.3 at.% (b) with 0.8 at.% and (c) with 2 at.%.

TiO_3 ceramics at 93 K are shown in Figure 5. At 93 K $BaTiO_3$ ceramics are known to have the rhombohedral phases. The EPR signals with $g_{\parallel}=2.380$ and $g_{\perp}=2.063$ are apparently due to Ba^{1+} ($Ba^{2+}+e'\rightarrow Ba^{1+}$) ions reduced by electrons producing from the oxygen vacancies ($V_O^{\cdot}$). Barium has two isotopes which have the same nuclear spins ($I=3/2$), Ba^{135} and Ba^{137} with the natural abundance of 6.59% and 11.32%, respectively. Therefore, the EPR spectra are expected to show a hyperfine splitting structure with 4 lines which is not distinguished because they have almost same nuclear magnetic

moments. These absorption signals are not found in case of PTCR $BaTiO_3$ ceramics.[13,14] Figure 6 shows the intensity variation of $g_{\perp}=2.063$ signal versus temperature for Cu-doped $BaTiO_3$ ceramics. The intensity of the signal decreases as the temperature increases and the concentration of Cu^{2+} ions decreases. Same phenomena were observed for Zr-doped $BaTiO_3$ ceramics. This result indicates that the concentration of Ba^{1+} ions increases as the concentration of the dopant increases and Ba^{1+} ions become Ba^{2+} ions releasing electrons as the temperature increases. These released electrons may contribute to a space charge which is responsible for a dielectric relaxation. In case of 0.3 at.% Zr-doped $BaTiO_3$ ceramic, the signal due to Ba^{1+} is not seen at 93 K. However, 0.3 at.% Cu-doped $BaTiO_3$ ceramic shows a strong signal due to Ba^{1+} at 93 K. This means that Cu-doped $BaTiO_3$ ceramics release more electrons than Zr-doped $BaTiO_3$ ceramics as the temperature increases. It is noticed that pure and H_2-reduced $BaTiO_3$ ceramics do not exhibit the signal due to Ba^{1+} and thus do not show a dielectric relaxation.

For H_2-reduced samples, the intensity of $g=1.997$ signal at 398 K, around the Curie point of $BaTiO_3$ ceramics, decreases with Ba/Ti ratio.[15] This means that the signal is related to Ba-vacancies (V_{Ba}).[13] Donor-doped $BaTiO_3$ ceramics show $g=1.997$ signal which acquires high intensity above T_C. This may be indicative of activation of the corresponding defect centers, possibly V_{Ba}'.[14] It is reported that the concentration of V_{Ba} is higher around the grain boundaries than that in the bulk of grains from the fact that the signal intensity decreases with increasing grain size.[13] As shown in Fig-

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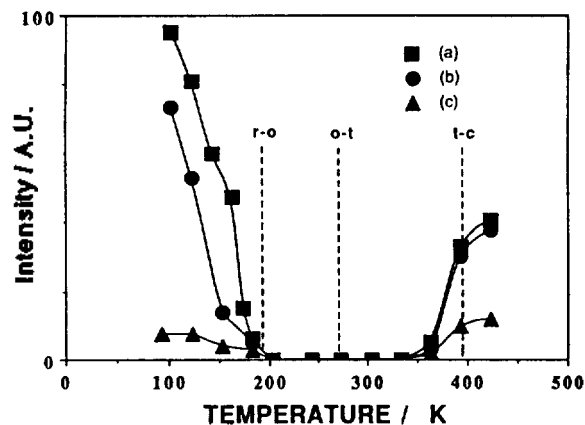*Bull. Korean Chem. Soc.* **1995**, Vol. 16, No. 10   911

Figure 7. The intensity of $g=1.997$ signal versus temperature for Cu-doped BaTiO₃ ceramics (a) with 0.3 at.% (b) with 0.8 at.% and (c) with 2 at.%.

ure 7 the intensity of $g=1.997$ signal for Cu-doped BaTiO₃ ceramics rapidly increases around T_C. In the tetragonal and orthorhombic phases, Ba-vacancies are neutral (V_{Ba}) and in the rhombohedral and cubic phases, they are singly ionized (V_{Ba}').[13] Same phenomena were observed in Zr-doped BaTiO₃ ceramics even if the intensity of the signal due to V_{Ba}' is very weak. Kutty *et al.*[13] have found same results in donor-doped BaTiO₃ ceramics which exhibit PTCR. It was explained that the trapping of conduction electrons by Mn^{3+} ions which are added as an acceptor augments the effect of $V_{Ba}+e'\rightarrow V_{Ba}'$ around the phase transition. Although EPR measurements of Mn-doped BaTiO₃ ceramics display the typical feature of Mn^{4+} ions in the starting powder and that of Mn^{2+} ions in the reduced ceramics,[14,16~18] it is expected that Zr-doped BaTiO₃ ceramics may not show a reduced form of Zr^{4+} ions because it is not easy for Zr^{4+} ions to be reduced. However, in case of Cu-doped BaTiO₃ ceramics, Cu^{2+} ions can trap some of conduction electrons augmenting the effect of $V_{Ba}+e'\rightarrow V_{Ba}'$ around the phase transition because Cu^{2+} can be reduced to Cu^{1+} although the standard reduction potential ($E^0=0.15$ V) of Cu^{2+} to Cu^{1+} is low comparing with that ($E^0=1.54$ V) of Mn^{3+} to Mn^{2+}.

$g=2.160$ signal comes from Cu^{2+} and its intensity gradually decreases as the temperature increases up to 250 K and remains almost constant afterwards up to 400 K. This phenomenon may suggest that some of the Cu^{2+} ions are reduced to the Cu^{1+} ions as the temperature increases.

$g=1.960$ signal exists below 100 K for Cu- or Zr-doped BaTiO₃ ceramics. This signal arises from a paramagnetic center of shallow donor character and the center may correspond to a trapped electron resonating between two Ti^{4+} located in adjoining oxygen octahedra and an oxygen vacancy shared by both the octahedra.

Conclusion

Cu- or Zr-doped BaTiO₃ ceramics showed the EPR signal

with $g=1.997$ which arises from ionized Ba-vacancies, V_{Ba}', above T_C. As the phase changes from the tetragonal to the cubic phase $V_{Ba}+e'\rightarrow V_{Ba}'$ occurs. This results in the decrease of the charge carrier concentration and hence, the concentration of the space charge decreases. T_C of Cu-doped BaTiO₃ ceramics decreased as the concentration of the dopant increased whereas T_C of Zr-doped BaTiO₃ ceramics remains almost constant. In case of Cu-doped BaTiO₃ ceramics, a space charge arising from the oxidation Ba^{1+} to Ba^{2+} increased as the concentration of Cu^{2+} increased. Although the effect of the difference of the ionic radii between Ti^{4+} and Cu^{2+} or Zr^{4+} could be a freezing of the vibration of the Ti-O chain which is responsible of the ferroelectricity,[19~21] space charges due to electrons coming out from the oxidation of Ba^{1+} and ionized Ba-vacancies ($V_{Ba}'\rightarrow V_{Ba}+e'$) seem to be more responsible for the dielectric relaxation at low frequency.

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