Lattice Parameters of BaTiO$_3$ Solid Solutions Containing Dy and Ho at High Temperature

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Abstracts

BaTiO$_3$ solid solutions containing Dy or Ho for capacitors with a multi-layer structure are examined in order to reveal the solubility mode of rare-earth in perovskite. As the ionic radii of Dy and Ho are located intermediate between ionic radii of Ba and Ti, both A and B-site replacements are considered in this case. As the crystal structure of the solid solutions changes from a tetragonal system to a cubic system at room temperature according to the amount of rare-earth, the change of the lattice parameters by means of the substitution with Dy and Ho is obscured. So in this work the lattice parameter was determined based on the cubic system at a higher temperature than the Curie point in order to avoid the crystal structure change. Three zones of substitution of rare earth Dy and Ho clearly depend on the lattice parameters. In the 1st zone, Ti ions located on the B-site are mainly replaced with R ions and in the 2nd zone Ba ions on the A-site are also mainly replaced with R ions. The last zone is over the limit of substitution and appears as a secondary phase. The determination of lattice parameter at high temperature was performed by WPPD using Pt-heating filament for an internal standard from which the lattice parameter was calibrated in this work.

Introduction

BaTiO$_3$ containing Dy or Ho are used for capacitors with multi-layer structure. The role of the rare-earth is in the temperature coefficient of the dielectric constant. They make a core-shell structure in which there are two zones, that is, a core and a shell with different crystal structure according to the amount of solubility of the rare-earth. Capacitors with multi-layer structure are expected to allow reduction in capacitor size and to have high dielectric properties. As the thickness of the layer become thinner, grain size are expected to be smaller.
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At the room temperature, the crystal structure changes from a tetragonal system to a cubic system depending on the amount of the substitution, which is similar to a phase transition. The change of the lattice parameters by means of the substitution with rare-earth ($R^{3+}$) would be obscured by that accompanied with the crystal structure change.

In this work, replacement modes of rare-earth are studied in order to clarify the solubility versus the grain size for the rare-earth elements in perovskite. In order to avoid the effects of the structure change, we determined the lattice parameters based on the cubic system at temperatures higher than the Curie point. And we also discuss the measurement of the lattice parameters at high temperature.

**Experimental**

We used regent grade BaCO$_3$ and TiO$_2$, 99.9% $R_2$O$_3$ for starting materials. These reagents are mixed into the compositions with a A and B-site replacement formula $(Ba_{1-x}R_x)(Ti_{1-x}R_x)O_3$($x<0.1$) and sintered at 1250°C for 2 hours.

Identification of precipitated phases was performed using a powder X-ray diffractometer (RAD-B system) made by Rigaku.

The lattice parameters of BaTiO$_3$ solid solutions containing Dy or Ho at high temperature are determined by the Whole-Powder-Decomposition Method (WPPD) of Toraya at 1986. Data collection was performed at 300°C using HTK high temperature equipment (Anton PAAR KG) attached on the Phillips diffractometer X’Pert-MPD under normal atmosphere. The heating filament used is a 100% platinum plate with 132x9x1mm dimensions. The change in the filament length occurring during heating is compensated for by setting an appropriate prestress. The heating filament must be straight before the measurement. The powder sample is applied thinly and uniformly with ethanol taking care not to add the force on the filament. To minimize the difference in temperature between the sample surface and the heating filament, care was taken to make sure the sample thickness was a maximum of 0.1 mm.

Conditions used for WPPD data collection were: Step scanning is used during 20 to 125 degree of 20 angle with 0.02 degree step. Soller slit is 0.04 radian, automatic divergence slit with irradiated length 10.0mm by which diffraction lines at high angle become stronger than obtained with a fixed divergence slit. Receiving slit is 0.30mm and Beam mask is 15mm. Counting time is 5 sec. The internal standard for calibration of the diffraction angle is the Pt-heating filament which is in the high temperature attachment of X’pert, and will be described in more detail later.

The procedure of WPPD is described in detail by Toraya (1986). The computer program of WPPD used in the present study adopts an angle-dependent profile shape model, and can refine the X-ray powder pattern of a multi-component material without reference to a structure model. It corrects automatically the peaks shift due to the instrument and the specimen. The method has a much higher resolving power for complex powder patterns and a high accuracy in refining lattice parameters. The profile function used was a Pearson VII function and the root of the profile was terminated when the intensity was smaller than 1 cps. The lattice parameters were refined simultaneously with the peak-shift correction parameter, while the lattice parameters of the standard material Pt at 300°C were fixed to the value of 3.934747Å described as follow during the refinement.
A calibration line

The Pt-heating filament in the high temperature attachment is used for the internal standard of the WPPD method. In order to obtain an accurate lattice parameter of Pt-filament at 300°C, X-ray diffraction powder patterns of Pt-filament were collected at several temperatures: 25, 100, 200, 250, 300, 400°C. Conditions for data collection are almost same with the lattice parameter determination except 2θ angle: 36 to 125. And the lattice parameters at several temperatures were refined without internal standard by the WPPD method and plotted on a curve as function of temperature. Subsequently, the observed curve of Pt-filament was adjusted with the lattice parameter refined at room temperature using 99.9% Si powder with the lattice parameter 5.430825Å reported by Hubard (1983) for an internal standard. The lattice parameter of Pt-filament at room temperature was 3.924329Å. A calibration line of the lattice parameter of the Pt-filament for an internal standard is shown as function of temperature on the dotted line with solid circles in Fig.1 up to 400°C. The solid line in Fig.1 is a calibration line derived by Hahn et al. (1972), which is good agree with the obtained calibration curve. The calculation equation by Hahn et al. is as follow.

\[
\frac{(L_T - L_{293})}{L_{293}} \times 10^6 = -2279 + 6.117T + 8.251 \times 10^{-3}T^2 - 1.1187 \times 10^{-5}T^3 - 9.1523 \times 10^{-8}T^4 - 3.6754 \times 10^{-12}T^5 + 5.893 \times 10^{-16}T^6
\]

\[L_T\text{: Lattice parameter at } TK\]
\[L_{293}\text{: Lattice parameter at 293K. The value was used}
the lattice parameter of Pt-filament refined.

Figure 1. Calibration line of lattice parameter of Pt-heater for internal standard at high temperature

From these results, the unit cell parameters of the Pt-filament for standard material at 300°C were fixed to the value of 3.934747Å during the refinement by the WPPD method.
Results and Discussion

Three modes for the solubility of rare-earth (Dy or Ho) in BaTiO₃ are considered, that is A-site replacement, B-site replacement and both A and B-site replacement. The ionic radii with 6 coordinate of Dy and Ho are 0.912 and 0.901Å, respectively. And ones with 12 coordinate is 1.253 and 1.234Å, respectively, which was derived from the relationship between coordination number and effective ionic radii after the Shannon’s table(1976). On the other hand, the radius of a tetravalent Ti located in octahedron with 6 coordinate is 0.605Å and that of Ba ion in 12 coordinate is 1.61Å. As the sizes of the ionic radii of Dy and Ho are intermediate between the sizes of Ba and Ti, the replacement of Dy or Ho would occur to make solid solutions where they occupy both the A and B-site. Then, we selected a A and B-site replacement formula for starting sample compositions: (Ba₁₋ₓRx)(Ti₁₋ₓRx)O₃.

X-ray diffraction patterns of sintered samples with x=0.0 to 1.0 composition in the (Ba₁₋ₓRx)(Ti₁₋ₓRx)O₃ (R=Dy) formura performed at 300°C are shown in Fig.2 including diffraction lines of Pt-heating filament. The X-ray diffraction lines from BaTiO₃ solid solutions, which were observed in all compositions, have a cubic perovskite pattern because they are observed at 300°C which is higher than Curie temperature. Full width half maximum (FWHM) of the diffraction lines from BaTiO₃ becomes larger with increasing the composition x. The reliability factors in the results of WPPD method are shown in Table1.
Table 1. Reliability factors in the results of WPPD.

\[ R_p = \frac{\Sigma (I_0 - I_C)}{\Sigma I_0}, \quad R_{wp} = \left( \frac{\Sigma w(I_0 - I_C)^2}{\Sigma w I_0^2} \right)^{\frac{1}{2}} \]

where \( I_0 \) and \( I_C \) are observed and calculated profile intensities, respectively, and \( w \) is a weight assigned to the observation on the form, \( w = I_0^{-1} \).

<table>
<thead>
<tr>
<th>Composition</th>
<th>( R = \text{Dy} )</th>
<th>( R = \text{Ho} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>x</td>
<td>( R_p ) (%)</td>
<td>( R_{wp} ) (%)</td>
</tr>
<tr>
<td>0.000</td>
<td>6.544</td>
<td>9.315</td>
</tr>
<tr>
<td>0.005</td>
<td>6.294</td>
<td>8.380</td>
</tr>
<tr>
<td>0.020</td>
<td>5.782</td>
<td>8.022</td>
</tr>
<tr>
<td>0.040</td>
<td>5.770</td>
<td>8.141</td>
</tr>
<tr>
<td>0.050</td>
<td>5.780</td>
<td>8.042</td>
</tr>
<tr>
<td>0.080</td>
<td>7.639</td>
<td>10.433</td>
</tr>
<tr>
<td>0.100</td>
<td>10.130</td>
<td>13.370</td>
</tr>
</tbody>
</table>

As the composition \( x \) increases, the reliability factors increase to near 10%, which is concerned with increasing the FWHM mentioned above. The precipitated phases in all composition are identified. Up to \( x=0.01 \) composition, a single phase of BaTiO3 solid solution is obtained. As secondary phase, pyrochlore (Dy\(_2\)Ti\(_2\)O\(_7\)) appears at \( x=0.03 \) composition, and another rare-earth oxide (Dy\(_2\)O\(_3\)) appeared at \( x=0.05 \) composition.

Fig.3 shows the resulting pattern of WPPD which is composed of two patterns: an observed pattern and a pattern showing the difference between the observed and the calculated pattern. The diffraction pattern with an \( x=0.0 \) composition is well fit over the whole range of 20 as shown in Fig.3a with less difference on the difference pattern. On the contrary, some peaks which are residual lines of the eliminated diffraction lines of BaTiO3 and Pt appear on the difference line for the pattern with \( x=0.1 \) composition as shown in Fig.3b. They are secondary phases: pyrochlore and rare-earth oxide. In the case of Ho, the diffraction patterns are similar.

The lattice parameters of the \( a \)-axis of the BaTiO3 solid solutions at 300°C obtained by WPPD are shown in Fig.4 as a function of compositions \( x \). The lattice parameter change became clear when compared with that measured below the Curie point, and the change is divided into three zones as follows: In the first zone up to about \( x=0.028 \) composition, the lattice parameter increases linearly. In the second zone up to about \( x=0.044 \), it decreases linearly and in the third zone becomes constant value. This phenomena shows different modes of substitution of rare-earth for cation sites. In the first zone, the increase of the lattice parameter means that Ti ions located in octahedron are substituted for \( R \) ions, because the ionic radii of \( R \) with 6 coordinate is greater than that of Ti with 6 coordinate as mentioned before. Then, the first step of the substitution in the BaTiO3 solid solutions is mainly dependent on the B-site replacement. In the second zone, the decrease of the lattice parameter means that Ba with 12 coordinate are substituted for \( R \) ions because the ionic radii of \( R \) is smaller than that of Ba ions as mentioned before. Then, the second step of the substitution mainly depends on the A-site replacement. In the
Figure 3. X-ray diffraction patterns with a difference line of BaTiO$_3$ s.s. with composition $x=0.0$ (a) and $x=0.1$ (b) fitted by WPPD using Pt for an internal standard. On the difference line of (b) Residual Peaks show secondary phases; Dy$_2$Ti$_2$O$_7$ and Dy$_2$O$_3$. Super imposed BaTiO$_3$ peaks with the secondary phases showed by arrows affected the lattice parameter. They shift the lattice parameter to large value as shown in Fig. 4.

In the last zone, no change of the lattice parameter shows that the limit of the solid solutions is reached because the composition of the phase is same over the immiscibility zone according to the phase rule and is about $x=0.044$ located on the boundary between the solid solutions area and the second phase area. But the observed values of the lattice parameter in this zone are not unique because it is affected by the secondary phases such as pyrochlore and rear-earth oxides ($R_2$O$_3$). The main peaks of BaTiO$_3$ overlapped with peaks of secondary phases as shown by arrows in Fig. 3b. Thus, the lattice parameters are

Figure 4. Lattice parameters of BaTiO$_3$-$R_2$O$_3$ solid solutions at 300°C as function of composition $x$. 

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shifted to a larger value. Moreover, reliabilities of refinement of the lattice parameters are dependent on the amount of the replacement by rare-earth.

Measurement of the lattice parameters at higher temperature than the Curie point has succeeded in revealing the replacement mode of rare-earth in the perovskite structure avoiding the lattice parameter change due to the phase transition. But when collecting data with the WPPD method, care must be taken to maintain a flat heating element. Also, the amount of power put on the heating element has to be adjusted to keep the peak height of internal standard similar to the peak height of the sample and to keep the temperature of sample uniform.

Conclusion

We clarified the mode of substitution of rare-earth Dy and Ho within the intermediate size between A-site and B-site. In the 1st step, Ti ions on the B-site are replaced with $R$ ions and in the 2nd step, Ba ions on the A-site are also replaced with $R$ ions. And we found the limit compositions of the solid solutions. These phenomena has been studied using the cubic system above the Curie point to avoid the change of the lattice parameter due to the structural change form a tetragonal to a cubic system. Up to about $x=0.028$ composition, rare-earth elements solved in the B-site increase the lattice parameter and up to about $x=0.044$ composition, rare-earth elements found in A-site decrease the lattice parameter. Above about $x=0.044$ composition, the limit of solid solutions is reached and secondary phases appear.

References