Grain boundary segregation and secondary-phase transition of (La,Nb)-codoped TiO₂ ceramic

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ABSTRACT

The formation and transition of secondary phases in (La, Nb)-codoped TiO₂ ceramics were investigated using samples prepared by traditional solid-state sintering from anatase TiO₂, Nb₂O₅, and La₂O₃ oxide powders. From the microstructure, crystal structure and chemical composition of these samples, as measured by SEM, XRD and EDS, the formation mechanism of the secondary phase is determined through point defect thermodynamical analysis. The results show that LaNbO₄ and LaNbTiO₆ secondary phases originate from segregation of the point defects Nb⁵⁺ and La³⁺ at grain boundaries, with elastic strain energy providing the main driving force for this segregation. An increase in sintering temperature causes more of the LaNbO₄ secondary phase to transition to LaNbTiO₆. A ternary phase diagram of La₂O₃–Nb₂O₅–TiO₂ was plotted based on binary phase diagrams of La₂O₃–Nb₂O₅, Nb₂O₅–TiO₂ and La₂O₃–TiO₂, which can be used to estimate the relative content of secondary phases in samples sintered at different temperatures.

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1. Introduction

Titanium dioxide (TiO₂) ceramic is an important functional material in varistors, capacitors and sensors [1]; however, its crystalline phase composition, microstructure, Schottky barrier structure and electrical properties can be effectively improved by doping with metal oxides such as CaO, SrO, Y₂O₃, BaO, Ta₂O₅, MnO₂, CeO₂, Co₂O₃, Nb₂O₅, V₂O₅ and La₂O₃. The influence of these different dopants on the physical properties of polycrystalline TiO₂ is highly distinguishable [2]; i.e., Nb has an effect on the electrical properties, Ba and Zr on grain growth, and Al, Ca, and Y on grain boundary segregation behavior. In the case of the latter, Y³⁺ ions are an aliovalent dopant that provides both an elastic strain-energy driving force to the grain boundaries for segregation, as well as an electrostatic driving force for segregation. With regards to electrical properties, Nb-doping lowers the varistor voltage (V₁ma) and provides a nonlinear coefficient (α) [3], whereas La-doped TiO₂ ceramics possesses a higher V₁ma and α [4]. Thus, in order to develop TiO₂ ceramics with a low V₁ma and high α, both La and Nb can be co-doped into TiO₂.

In addition to the main rutile TiO₂ crystalline phase, secondary phases are often observed in doped-TiO₂ ceramics. The chemical composition, microstructure, crystalline phase and crystal lattice of these secondary phases can be characterized using techniques such as SEM, XRD, TEM, EDS and Raman spectroscopy [5–9]. This has revealed that the dopant ion Nb⁵⁺ is close in radius to Ti⁴⁺, and so has a high solid solubility in the TiO₂ lattice. However, the solid solubility limit of Y³⁺ and La³⁺ dopant ions is very low, as these have radii far greater than that of Ti⁴⁺. As secondary phases form when the doping ion concentration is greater than its solid solubility limit [10,11], their existence is dependent on the size and concentration of the dopant ion, as well as the sintering temperature.

Recent studies have principally focused on formation mechanisms, measuring methods and secondary phase characteristics, as well as the influence of secondary phases on the structure and properties of the ceramic matrix. This has revealed that secondary phases generally originate from the segregation of dopants or impurities. That is, the pentavalent cation Nb⁵⁺, which is close in size to Ti⁴⁺, will tend to segregate at Ti sites in the grain boundaries of TiO₂ ceramics using electrostatic potential as the driving force [12,13]. The trivalent cation Y³⁺, on the other hand, is much larger than Ti⁴⁺, and so tends to segregate at interstitial sites in the grain boundary using elastic strain energy as the driving force [11].

Our previous works have demonstrated that the majority of Nb⁵⁺ ions dissolve into the TiO₂ lattice, with only any remaining cations segregating at the grain boundaries. In contrast, La³⁺ is almost completely segregated at the grain boundaries. When the concentrations of Nb⁵⁺ and La³⁺ at the grain boundaries reach a critical value, there is a chemical reaction between Nb₂O₅ and La₂O₃ that produces a LaNbO₄ secondary phase.
doped TiO2 ceramics, however, has not been explored. As the formation and transition of these secondary phases are relevant to the type and distribution of point defects segregated at the grain boundaries, further investigation of the grain boundaries and grain boundary segregation is warranted. Mandal developed a novel, simple and nondestructive 3D electron backscatter diffraction method that can not only simultaneously measure all five degrees of freedom in grain boundary structures, but also perform segregation analysis [16]. Thanks to this, we now know that both the grain structure and grain boundary structure have an obvious effect on segregation in grain boundaries [17,18]. In addition to experimental methods, density functional theory and ab initio calculations can also be used to study grain boundary segregation [19,20]. For example, of the several point defects that exist in polycrystalline TiO2, oxygen vacancies play a key role in defining the microstructure and segregation behavior [21–23]. The segregation of space charge at grain boundaries can therefore be calculated by point defect thermodynamical analysis using defect chemical reaction equations at different oxygen partial pressures [11,12,24]. The driving force for the segregation of (La, Nb)-co-doped TiO2 ceramics, however, has not been explored.

In this study, SEM, EDS, XRD, XPS and phase diagram measurements were carried out to investigate the crystal structure, chemical composition, and transition/formation mechanisms of secondary phases in (La, Nb)-co-doped TiO2 ceramic sintered at different temperatures. The driving force and mechanism of segregation was also investigated to determine the correlation between grain boundary segregation and secondary phases.

2. Experiments

Samples of Nb-doped, La-doped, and (La, Nb)-co-doped TiO2 ceramics with molar percentage compositions of 98% TiO2 + 0.8% Nb2O5, 98% TiO2 + 0.7% La2O3, and 98% TiO2 + 0.8% Nb2O5 + 0.7% La2O3, respectively, were prepared using a traditional electronic ceramic procedure and single sintering technique. The raw oxide materials were analytical-grade TiO2 (99.5%), Nb2O5 (99.5%), SiO2 (99.5%), and La2O3 (99.5%), which were mixed and wet-milled in an agate jar with agate balls for 12 h in deionized water. The milled powders were dried and granulated with a PVA binder, and then pressed into discs of 13 mm diameter and 1.0 mm thickness under a pressure of 140 MPa. After burning out the PVA at 650 °C the discs were placed in Al2O3 crucibles, sintered in air at 1300–1400 °C for 1 h, and then cooled to room temperature automatically. Analysis of the phase composition of the samples was performed using a Bruker D8 XRD. Microstructure characterization and chemical composition analysis were performed using a Philips XL30-ESEM with an EDS attachment.

3. Results and discussion

3.1. Grain boundary segregation

Samples of Nb-doped, La-doped, and (La, Nb)-co-doped TiO2 ceramics with molar percentage compositions of 98% TiO2 + 0.8% Nb2O5, 98% TiO2 + 0.7% La2O3, and 98% TiO2 + 0.8% Nb2O5 + 0.7% La2O3, respectively, were prepared using a traditional electronic ceramic procedure and single sintering technique. The raw oxide materials were analytical-grade TiO2 (99.5%), Nb2O5 (99.5%), SiO2 (99.5%), and La2O3 (99.5%), which were mixed and wet-milled in an agate jar with agate balls for 12 h in deionized water. The milled powders were dried and granulated with a PVA binder, and then pressed into discs of 13 mm diameter and 1.0 mm thickness under a pressure of 140 MPa. After burning out the PVA at 650 °C the discs were placed in Al2O3 crucibles, sintered in air at 1300–1400 °C for 1 h, and then cooled to room temperature automatically. Analysis of the phase composition of the samples was performed using a Bruker D8 XRD. Microstructure characterization and chemical composition analysis were performed using a Philips XL30-ESEM with an EDS attachment.

3.1.1. Microstructure and composition

The microstructure and XRD patterns of Nb-doped TiO2 ceramics in Fig. 1(a) show no obvious composition segregation on the surface, but both segregation and a La4Ti9O24 secondary phase are present on the surface of the La-doped TiO2 ceramic shown in Fig. 1(b) and (c). The absence of a secondary phase in the 1.6 mol% Nb-doped ceramics can be explained by the high solid solubility of Nb in TiO2 (5 mol%) that is created by the similarity in ionic radius between Nb5+ and Ti4+. In contrast, La could not completely dissolve in the TiO2 lattice because the ionic radius of La5+ is far larger than that of Ti4+, which leads to segregation and the formation of a La4Ti9O24 secondary phase.

The microstructure and chemical composition of 0.7 mol% La2O3 + 0.8 mol% Nb2O5-codoped TiO2 ceramic sintered at 1350 °C (Fig. 2 and Table 1) indicate substantial segregation and secondary phase formation occurs in (La, Nb)-codoped TiO2 ceramics. The EDS results show that the grains numbered 1–3 have similar compositions, with their main elements being Ti (37.08 at%), O (62.55 at%) and Nb (0.37 at%). The absence of La and Si within the grains suggests that these elements segregate at grain boundaries or form secondary phases, and indeed, O, Ti, Si, Nb and Ca were observed at the grain boundaries marked 5–9. Generally speaking, once the grain boundary segregation exceeds saturation, a secondary phase should emerge and there should be no dispersion of La in the grains or grain boundaries. The secondary phase marked as 4 in Fig. 2, however, consisted mainly of O (68.85 at%), Nb (6.09 at%), Ti (17.32 at%) and La (7.27 at%). The presence of La in the secondary phase can be explained by its large ionic radius, which prevents the stable existence of La in rutile TiO2 grains and grain boundaries. Thus, secondary phases of LaNbO4 and LaNbTiO6 can exist in (La, Nb)-co-doped TiO2 ceramics in addition to the main TiO2 rutile phase.

3.1.2. Segregation of point defects at grain boundaries

3.1.2.1. Point defect thermodynamic model of grain boundary segregation. There are many different types of point defects in (La, Nb)-co-doped TiO2 ceramics, which as shown in the defect chemical reaction equations (1–5), include intrinsic thermal defects, electronic defects, non-stoichiometric ratio point defects and impurity defects. Grain boundary segregation is simply the sum of all these point defects at the grain boundaries, with the distribution of point defects at grain boundaries obtainable using the chemical defect equations for TiO2 grains and point defect thermodynamics [25,26]. The concentration of point defects can be calculated according to the chemical defect and point defect thermodynamics presented in Eqs. (6)–(10). The concentrations of interstitial titanium, titanium vacancies and oxygen vacancies are determined by the defect formation energy, grain boundary electrostatic potential and temperature, as shown in Eqs. (6)–(8). The actual defect formation energy should decrease with increasing temperature if it is assumed that defect formation energy is independent of temperature [27,28]. The concentration of donor-doping and acceptor-doping defects with respect to the doping concentration, static potential and temperature is shown in Eqs. (9) and (10). Specifically, the concentration of acceptor-doping defects might be related to the elastic strain energy Us(x).

Intrinsic thermal defects: null→2V0 + V0

Electronic defects: null→e + h

Non-stoichiometric ratio point defects: O0→2½O2 + V0 + 2e

Donor-doping defects: 2Nb2O5→4NbTi + V0

Acceptor doping defects: 2La2O3→4LaTi + Ti4– + 8O2

(Ti4–)(x) = exp(-Eg0 + 4eΦ(x))/kT

(V0)(x) = exp(-Eg0–4eΦ(x))/kT

where x is the doping concentration, Φ is the static potential at the grain boundary, k is the Boltzmann constant, and T is the temperature.
\[ [V_0(x)] = 2 \exp \left( -\frac{g_{\text{VO}} + 2e\phi(x)}{kT} \right) \]  
\[ [\text{Nb}_2\text{i}](x) = C \exp \left( -\frac{e\phi(x) - e\phi_\infty}{kT} \right) \]  
\[ [\text{La}_\text{i}](x) = C \exp \left[ -\frac{e\phi_\infty - e\phi(x) - U_\text{s}(x)}{kT} \right] \]  

In Eqs. (6)–(10), \( g_{\text{Ti}}, g_{\text{SN}}, \) and \( g_{\text{VO}} \) are the formation energies of interstitial Ti, Ti vacancies, and O vacancies, respectively. In addition, \( e \) is the charge of an electron \((1.602 \times 10^{-19} \text{ C})\), \( \phi(x) \) is the electrostatic potential at a distance of \( x \) from the grain boundary interface center, \( k \) is the Boltzmann constant \((1.381 \times 10^{-23} \text{ J K}^{-1})\), \( T \) is the absolute temperature, \( \phi_\infty \) is the electrostatic potential in a grain when the electrostatic potential of the grain boundary interface center is zero, \( U_\text{s}(x) \) is the elastic strain energy at distance of \( x \) from the grain boundary interface center, and \( C \) is the dopant concentration.

For dopant ions with a radius close to that of \( \text{Ti}^{4+} \) (0.68 Å) the driving force for segregation is the electrostatic potential. Since the radius of a \( \text{La}^{3+} \) ion (1.18 Å) is much larger than this, the elastic strain energy generated by the lattice mismatch cannot be ignored [11]. The elastic strain energy \( U_\text{s} \) at the center of the grain boundary interface can be calculated using Eq. (11) and the distribution of \( U_\text{s}(x) \) can be calculated using:
where $\varepsilon_0$ is vacuum dielectric constant of a vacuum $(8.854 \times 10^{-12} \text{ F m}^{-1})$. The static TiO$_2$ dielectric constant, $\varepsilon$, is 120. The terms $N_i$ and $Z_i$ represent respectively the concentration and charge of each point defect, $i$, in the bulk phase per cm$^3$. Using Eq. (13), the grain boundary electrostatic potential $\Phi(x)$ is determined by the Debye length $\delta$ and bulk phase electrostatic potential $\Phi_\infty$.

The latter is directly related to the defect formation energy, oxygen partial pressure, dopant concentration and temperature. The Debye length $\delta$, on the other hand, is determined by the concentration and charge of dopant ions, as well as the temperature. The concentration and charge of dopant ions are themselves dependent on defect chemistry, oxygen partial pressure, doping and other factors. In this study, point defect concentration distributions at grain boundaries in doped TiO$_2$ were calculated for 1 atm pressure with different sintering temperatures and doping concentrations.

### 3.1.2.2. Donor Nb doping

There are several defect chemistry equations for donor Nb doping in TiO$_2$ ceramics (see Eqs. (1)–(4)), of which the most significant is Eq. (4). The approximate electroneutrality condition in bulk-phase TiO$_2$ is given by

$$\left[\text{Nb}_{\text{Ti}}\right]_\infty = 4 \left[V_{\text{Ti}}\right]$$

(15)

According to Eqs. (7) and (15), the bulk-phase electrostatic potential $\Phi_\infty$ can be calculated as

$$e\Phi_\infty = \frac{g_{\text{V}_{\text{Ti}}}}{4} + \frac{kT}{4} \ln \left[\frac{\left[\text{Nb}_{\text{Ti}}\right]_\infty}{4}\right]$$

(16)

With low doping concentrations, it can be assumed that all Nb ions completely dissolve in the TiO$_2$ lattice. In other words, Nb$^{5+}$ ions substitute for Ti$^{4+}$ in the TiO$_2$ lattice and become point defects, Nb$_{\text{Ti}}$. Thus, when 1.6 mol% Nb-doped TiO$_2$ ceramic samples are sintered at 1350 °C, the $[\text{Nb}_{\text{Ti}}]_\infty$ concentration is 1.6 mol%. The bulk phase electrostatic potential $\Phi_\infty = 0.4319$ V can be calculated by substituting $g_{\text{V}_{\text{Ti}}} = 2.5$ eV, $[\text{Nb}_{\text{Ti}}]_\infty$, $T$, and $k$ into Eq. (16) [12], and then used in Eqs. (13) and (14) to calculate the electrostatic potential $\Phi(x)$ distribution at grain boundaries, as shown in Fig. 3(a).

### Table 1

Composition of (La, Nb)-codoped TiO$_2$ samples obtained using EDS.

<table>
<thead>
<tr>
<th>Sites in Fig. 2(a)</th>
<th>Element (at%)</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>63.65</td>
<td>Grain composition</td>
</tr>
<tr>
<td>Ti</td>
<td>36.02</td>
<td>Grain composition</td>
</tr>
<tr>
<td>Nb</td>
<td>0.33</td>
<td>Grain composition</td>
</tr>
<tr>
<td>La</td>
<td>0.44</td>
<td>Grain composition</td>
</tr>
<tr>
<td>Si</td>
<td>0.34</td>
<td>Grain composition</td>
</tr>
<tr>
<td>Ca</td>
<td>0.27</td>
<td>Grain boundary composition</td>
</tr>
<tr>
<td>1</td>
<td>47.19</td>
<td>Grain boundary composition</td>
</tr>
<tr>
<td>2</td>
<td>41.19</td>
<td>Grain boundary composition</td>
</tr>
<tr>
<td>3</td>
<td>36.02</td>
<td>Grain boundary composition</td>
</tr>
<tr>
<td>4</td>
<td>31.81</td>
<td>Grain boundary composition</td>
</tr>
<tr>
<td>5</td>
<td>27.32</td>
<td>Grain boundary composition</td>
</tr>
<tr>
<td>6</td>
<td>23.32</td>
<td>Grain boundary composition</td>
</tr>
<tr>
<td>7</td>
<td>20.04</td>
<td>Grain boundary composition</td>
</tr>
<tr>
<td>8</td>
<td>16.34</td>
<td>Grain boundary composition</td>
</tr>
<tr>
<td>9</td>
<td>12.34</td>
<td>Grain boundary composition</td>
</tr>
</tbody>
</table>

$$U_0 = \left(\frac{\Delta r}{r}\right)^2 \left(3.45 - \frac{T}{1700}\right) \text{eV}$$

(11)

$$U_x(x) = \begin{cases} U_0 \left[1 - \left(\frac{x}{2a}\right)^2\right], & x \leq 2a \\ 0, & x > 2a \end{cases}$$

(12)

where $U_0$ is the elastic strain energy at the grain boundary interface center, $r$ is the radius of Ti$^{4+}$ in rutile TiO$_2$, $\Delta r$ is the difference in radius between the dopant ion and Ti$^{4+}$, $a$ is the lattice parameter (taken as the average value of $a$ and $c$ for rutile TiO$_2$), and $x$ is the distance from the grain boundary interface center. Note that when $x=0$ it represents the center of the grain boundary, and when $x=\infty$ it represents the grain interior where the bulk phase electrostatic potential $\Phi_\infty$ is constant. The distribution of grain boundary electrostatic potential $\Phi(x)$ can therefore be obtained using

$$\Phi(x) = \Phi_\infty [1 - \exp(-x/\delta)]$$

(13)

In Eq. (13), the Debye length $\delta$ is the shielding ability and radius of the electrostatic potential. It can be calculated using

$$\delta = \left[\frac{e\varepsilon_kT}{\varepsilon_0^2 \sum N_iZ_i^2}\right]^{1/2}$$

(14)

Fig. 3. (a) Electrostatic potential and (b) concentration of point defects at grain boundaries in Nb-doped TiO$_2$. 

$\text{(a)}$ 

$\text{(b)}$
3.1.2.3. Acceptor La doping. Of the defect chemistry equations for acceptor La-doping in TiO2 (Eqs. (1)-(3) and (5)), the most significant is Eq. (5). The approximate electro-neutrality condition in bulk-phase TiO2 is

$$\Phi_\infty = 4 \left[ \text{La}^- \right]_\infty$$  \hspace{1cm} (17)

According to Eqs. (6) and (17), the bulk phase electrostatic potential $\Phi_\infty$ can be calculated as

$$e\Phi_\infty = -\frac{g_{\text{fi}}}{4} kT \ln \left[ \frac{\text{La}^-}{\text{Ti}^+} \right]_\infty$$  \hspace{1cm} (18)

When 1.4 mol% La-doped TiO2 ceramic samples are sintered at 1350 °C, the $\left[ \text{La}^- \right]_\infty$ concentration is 1.4 mol%. The bulk phase electrostatic potential $\Phi_\infty = -0.30195$ V can be calculated by substituting $g_{\text{fi}} = 2$ eV, $\left[ \text{La}^- \right]_\infty$, $T$, and $k$ into Eq. (18), and then used with Eqs. (13) and (14) to calculate the electrostatic potential $\Phi(x)$ distribution at the grain boundaries. The point defect concentration $\left[ \text{Ti}^+_i \right](x)$ and $\left[ \text{La}^- \right](x)$ can be calculated by substituting the interstitial Ti formation energy $g_{\text{fi}} = 2$ eV, sintering temperature $T = (1350 + 273.15)$ K, and doping concentration $C = 1.4$ mol% into Eqs. (6) and (10), as shown in Fig. 4(a). This reveals that the concentration of La point defects at the grain boundaries is very high, which demonstrates that La can segregate strongly at the grain boundaries. This is consistent with the microstructure, EDS chemical composition analysis and XRD patterns presented in Section 3.1.1. The $\left[ \text{La}^- \right](x)$ point defect concentration can be calculated using Eq. (19) if the elastic strain energy is neglected, which as shown in Fig. 4(b), suggests that there is no La segregation at the grain boundaries. This, however, is not consistent with the experimental results. As mentioned earlier, with doping ions close in radius to Ti$^{4+}$, the driving force to segregate at grain boundaries is the electrostatic potential. However, as the ionic radius of La$^{3+}$ (1.18 Å) is much larger than that of Ti$^{4+}$ (0.68 Å), the elastic strain energy originating from lattice mismatch cannot be ignored [11].

$$\left[ \text{La}^- \right](x) = C \exp \left[ \frac{e\Phi_{\infty} - e\Phi(x)}{kT} \right]$$  \hspace{1cm} (19)

3.1.2.4. (La, Nb)-codoping. According to Eqs. (16) and (18), the electrostatic potential $e\Phi_{\infty}$ in (La, Nb)-codoped TiO2 ceramics can be obtained by subtracting $\Phi_{\infty}^\text{Nb}$ from $\Phi_{\infty}^\text{La}$.

$$e\Phi_{\infty} = e\Phi_{\infty}^\text{La} - e\Phi_{\infty}^\text{Nb}$$

$$= \left( \frac{g_{\text{fi}}}{4} + kT \ln \left[ \frac{\text{Nb}^+_i}{4} \right]_\infty \right) - \left( \frac{g_{\text{fi}}}{4} - kT \ln \left[ \frac{\text{La}^-}{4} \right]_\infty \right)$$

$$= \frac{g_{\text{fi}}}{4} + kT \ln \left[ \frac{\text{Nb}^+_i}{\text{La}^-} \right]_\infty$$

$$e\Phi_{\infty} = 1.125 + \frac{kT}{4} \ln \left[ \frac{\text{Nb}^+_i}{\text{La}^-} \right]_\infty$$  \hspace{1cm} (20)
The electrostatic potential of the bulk phase $\Phi_1 = 1.1297$ V can be calculated by substituting $g_T = 2$ eV, $[La]_L = 1.4$ mol%, $[Nb]_L$ = 1.6 mol%, $T$, and $k$ into Eq. (20), from which the point defect concentration can be calculated using the method described above. Figs. 4(a) and 5 indicate that there should be a reduction in the concentration of $La^+_L$ point defects due to the effect of $Nb^+_L$ point defects; however, as the $La^+_L$ concentration is far higher than the $Nb^+_L$ concentration, La will instead heavily segregate at grain boundaries and form a second phase.

The microstructure, chemical composition, XRD pattern and segregation of point defects at the grain boundary all indicate that the driving force for segregation in single-La-doped and (La, Nb)-codoped TiO$_2$ ceramic is elastic strain energy, while that of single-Nb-doped TiO$_2$ ceramic is electrostatic potential. This means that the secondary phase in co-doped TiO$_2$ ceramics is initiated by the segregation of doped $La^+_L$ and $Nb^+_L$ ions at the grain boundaries, and that the elastic strain energy is mainly dominated by the radius of the doping ion used.

Eq. (11) can be used to calculate the elastic strain energy at the grain boundary interface center $U_0$, as shown in Table 2. This reveals that La-doped TiO$_2$ possesses a higher $U_0$ than Nb-doped TiO$_2$ samples. For a constant sintering temperature, the point defect concentration in La-doped and (La, Nb)-codoped TiO$_2$ is determined by the elastic strain energy, but by the electrostatic potential in Nb-doped TiO$_2$ ceramics. Segregation is controlled by the size of acceptor ions, with a large acceptor ion such as La$^{3+}$ promoting the segregation of Nb$^{5+}$ at grain boundaries. These results show that there is no secondary phase formed in Nb-doped TiO$_2$ ceramics, but secondary phase LaNbO$_4$ can be observed in (La, Nb)-codoped TiO$_2$ ceramics.

3.2. Secondary-phase transitions

3.2.1. Microstructure

The SEM image and EDS profiles in Fig. 6 were obtained from samples sintered at temperatures of 1300, 1350 and 1400 °C. These demonstrate that higher sintering temperatures facilitate the growth of TiO$_2$ grains and increase the density of the samples. The EDS analyses of individual points show that the overall composition of the TiO$_2$ grains remains essentially the same regardless of...
sintering temperature; however, the composition of brighter areas in which segregation of La and Nb has occurred is very different. That is, sintering at 1300 °C produces bright regions with 6.8 and 6.24 mol% La and Nb, respectively, but this increases to 9.5 and 9.8 at 1350 °C and 7.36 and 7.95 at 1400 °C. It should be noted though that the molar ratio of La to Nb in these brighter areas remains at almost one regardless of the sintering temperature.

### 3.2.2 Crystal structure

To confirm whether a secondary phase is formed in TiO₂ ceramics because of La and Nb segregation, XRD was used to observe the crystal structure. As shown in Fig. 7, peaks corresponding to rutile TiO₂ were detected, with other crystalline phases such as LaNbO₄ and LaNbTiO₆ also being observed. This indicates that a secondary phase was present, though only LaNbO₄ was detected in the sample sintered at 1300 °C, and only LaNbTiO₆ was present in samples sintered at 1400 °C. Since, the molar ratio of La:Nb in the chemical composition of both LaNbO₄ and LaNbTiO₆ secondary phases is one, this agrees with the EDS analysis in Section 3.2.1. Thus, the XRD, SEM, and EDS results demonstrate that LaNbO₄ and LaNbTiO₆ secondary phases corresponding to brighter areas in SEM images are formed through the segregation of La and Nb, and that LaNbO₄ changes to LaNbTiO₆ at higher temperatures.

The TiO₂ raw material used in this study was anatase TiO₂, which transforms into rutile TiO₂ at about 900 °C. Rutile TiO₂ is a tetragonal system with lattice parameters of a=b=4.594 Å, c=2.959 Å, and α=β=γ=90°. In contrast, secondary phase LaNbO₄ is a monoclinic system in which a=5.5735 Å, b=11.5418 Å, c=5.2159 Å, α=90°, β=94.070°, and γ=90°. The LaNbTiO₆ secondary phase is an orthorhombic system, where a=10.934 Å, b=7.572 Å, c=5.446 Å, and α=β=γ=90°. Fig. 8 shows the crystal structures of rutile TiO₂, LaNbO₄, and LaNbTiO₆. At higher temperatures, a chemical reaction similar to Eq. (21) may take place, whereby rutile TiO₂ and LaNbO₄ produce LaNbTiO₆. Fig. 9 presents a binary phase diagram of LaNbO₄–TiO₂, which also indicates the formation mechanism of a LaNbTiO₆ secondary phase according to Eq. (21).

\[\text{TiO}_2 + \text{LaNbO}_4 \rightarrow \text{LaNbTiO}_6\]  

### 3.2.3 Phase composition and varistor properties

In order to investigate the mechanism of change and relative
content of the LaNbO4 and LaNbTiO6 secondary phases, a La2O3–TiO2–Nb2O5 ternary phase diagram was based on the binary phase diagrams of LaxOy–TiO2, LaxOy–Nb2O5, and Nb2O5–TiO2 [30–32]. As shown in Fig. 10, the 0.25LaO1.6–0.72TiO2–0.03Nb2O5 ternary oxide [33] includes LaNbTiO6 (Point C) and La0.64Ti0.92Nb0.08O3 (Point F), with the latter being produced by doping the binary oxide La2/3TiO3 (Point E) with Nb. This gives a La:Nb molar ratio of eight, which is significantly different to the EDS analysis results in Fig. 7. It can therefore be concluded that the current experimental samples do not contain any La0.64Ti0.92Nb0.08O3, only LaNbO4 or LaNbTiO6. The XRD analysis in Fig. 8 further confirms this.

The molar composition of the sample at Point B in Fig. 10 is 0.98TiO2–0.007La2O3–0.008Nb2O5. The main crystal phase in TiO2 ceramic is rutile TiO2, shown as Point A in Fig. 5. The secondary phases of LaNbO4 and LaNbTiO6 correspond to Points D and C, respectively, in Fig. 10. Thus, the content of different solid phases in (La, Nb)-codoped TiO2 varistor ceramics can be evaluated using the straight line ABCD. According to Fig. 8, only TiO2 and LaNbO4 exist in samples sintered at 1300 °C. Using the ABD line, and basic principles of ternary phase diagrams, we get a molar composition of 97.22% TiO2 as a primary phase and 2.78% LaNbO4 as a secondary phase. At 1400 °C, only TiO2 and LaNbTiO6 exist in quantities determined from the line ABC of 94.48% and 5.52%, respectively. At 1350 °C, TiO2, LaNbO4, and LaNbTiO6 phases all co-exist, making their relative contents difficult to evaluate.

The varistor properties presented in Fig. 11 are the result of interactions between the secondary phases, point defects and microstructure. Increasing the sintering temperature causes TiO2 grains to become larger, reducing both $\alpha$ and $V_{\text{m}}$, but also increasing the amount of secondary phase. Given that LaNbO4 is a domain-structured, insulating ferroelastic material with a large band gap of 4.8 eV [34,35], whereas LaNbTiO6 has a low dielectric constant and high electrical resistivity [36,37], an increase in insulating secondary phases causes $\alpha$ and $V_{\text{m}}$ to rise.

4. Conclusions

Polycrystalline Nb doped, La doped and (La, Nb)-codoped TiO2 samples were prepared by solid-state sintering and found through SEM and EDS analysis to exhibit composition segregation that does not occur in comparable Nb-doped samples. Specifically, while only primary-phase rutile TiO2 is observed in Nb-doped samples, La-doping produces a La4Ti5O24 secondary phase. Co-doping with La and Nb, however, produces both LaNbO4 and LaNbTiO6 secondary phases. Simulation by point defect thermodynamics has indicated that the electrostatic potential $\Phi(x)$ and point defect concentration in Nb-doped TiO2 is determined by the concentration of Nb, Ti vacancy defect formation energy $E_{\text{Gr}}$, and sintering temperature. The electrostatic potential $\Phi(x)$ and point defect concentration, on the other hand, are mainly influenced by the La doping concentration. The formation of secondary phases is initiated by La segregation, which in the case of La-doped and (La, Nb)-codoped TiO2 ceramics is driven by elastic strain energy. In Nb-doped TiO2 ceramics, however, the driving force is the electrostatic potential. Although La and Nb segregation was observed by SEM in La-doped TiO2 and (La, Nb)-codoped TiO2 samples, EDS analysis revealed that the overall chemical composition of the TiO2 grains remains much the same. In the La and Nb segregation areas, however, the La and Nb content is very different to the TiO2 grains, with a molar ratio of La:Nb of almost one. XRD analysis has shown that LaNbO4 and LaNbTiO6 secondary phases are formed in (La, Nb)-codoped TiO2 ceramics at different sintering temperatures, with monoclinic LaNbO4 changing to orthorhombic LaNbTiO6 as the temperature is increased.

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