Second Phases of (La,Nb)-Codoped TiO2 Varistor Ceramic

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Abstract. Crystal structure, chemical composition and phase transition of second phases in (La,Nb)-Codoped TiO2 varistor ceramics was investigated. SEM, XRD, XPS and EDS were carried out the analytic studies on the microstructure, chemical composition and crystal structure of TiO2 ceramics. The results showed that the second phases existed in (La,Nb) doped TiO2 varistors ceramics. With sintering temperature increasing, second phases will transit from LaNbO4 to LaNbTiO6. Ternary phase diagram of La2O3-Nb2O5-TiO2 was plotted based on binary phase diagram of La2O3-Nb2O5, Nb2O5-TiO2 and La2O3-TiO2. According to the ternary phase diagram, the relative content of second phases in TiO2 ceramics sintered at different temperature was estimated. It is suggested that increasing of both second phases and titanium vacancies will result in a higher varistor voltage V1mA and nonlinear coefficient α.

1. Introduction
Titanium Dioxides (TiO2) ceramic is a double functional material with varistor and capacity properties [1]. For more wide applications, TiO2 ceramics with better properties were developed by doping to improve microstructure, barrier structure and electrical properties. Some dopants, including Ca, Sr, Y, Ba, Ta, Mn, Ce, Co, Nb, V, La and etc, were added into TiO2 ceramics. For instance, the Nb doped TiO2 ceramic exhibits lower varistor voltage and nonlinear coefficient [2]. On the contrary, La doped TiO2 ceramic possesses higher varistor voltage and nonlinear coefficient [3]. In order to get a kind of ceramic with low varistor voltage and high nonlinear coefficient, a feasible method is to codope La and Nb into TiO2.

Usually, there exist second phases besides main crystal phase rutile titanium dioxide in doped-TiO2 ceramics. The variety of secondary phases may be dependent on ionic diameter and content of dopants, sintering temperature. The doped ion with ionic diameter close to diameter of Ti4+, such as Nb5+, has a higher solid solubility in TiO2 lattice. For the doped ion with ionic diameter far greater than Ti4+, such as Y3+ and La3+, its solid solubility limit is very low. When doping ion concentration is greater than its solid solubility limit, secondary phases is formed[4-5]. Secondary phases will grow up with increasing of sintering temperature.

Studies about secondary phases were principally focused on formation mechanism, detection method, characteristics of secondary phases and their influences on structure and properties of matrix ceramics. The formation of secondary phases generally originated from segregation of dopants or impurities. Pentavalent cation Nb5+ close in ionic size to Ti4+ will segregate at Ti site in grain boundary of TiO2 ceramics using electrostatic potential as driving force [6-7]. Trivalent cation Y3+ far larger in ionic size than Ti4+ will segregate at interstitial site in grain boundary using elastic strain energy as driving force[5]. In the current works, most of Nb5+ ions were dissolved into TiO2 lattices.
and the remaining Nb$^{5+}$ cation segregated at the grain boundary of TiO$_2$ ceramics. However, almost complete cation La$^{3+}$ segregated at grain boundaries. When concentrations of Nb$^{5+}$ and La$^{3+}$ in grain boundary reached a certain values chemical reaction Nb$_2$O$_5$+La$_2$O$_3$=2LaNbO$_4$ occurred and then second phase LaNbO$_4$ was formed. With sintering temperature increasing, reaction products was observed between LaNbO$_4$ and rutile TiO$_2$ resulting in another second phase LaNbTiO$_6$.[8]. Chih-Chung T Yang studied formation mechanism of secondary phases at the interface between Sr-doped LaMnO$_3$ and Y-stabilized ZrO$_2$.[9]. The result showed that second phases SrZrO$_3$ and La$_2$Zr$_2$O$_7$ indeed occurred at the interface between LSM and YSM co-fired at 1400$^\circ$C while no interfacial reaction were found at the interface between LSM and YSZ by the modified process. Moreover, the long-term stability results showed that no reaction products can be detected either made by co-fired or modified process when annealed at 1000$^\circ$C for 120h. The segregation and diffusion of La, Sr, Mn into YSZ had a significant effect on microstructure leading to the formation of a denser region.

Characterization techniques of secondary phases mainly included SEM, XRD, EDAX, TEM, EDS, Raman and etc. E. Brzozowskia researched the secondary phase of BaTiO$_3$ ceramic doped with Nb$_2$O$_5$ by means of EDAX and SEM.[10]. Jianying Li utilized SEM, XRD and EDAX to study the secondary phase of (Nb, Ce, Si, Ca)-doped TiO$_2$ ceramic.[11]. R. Parra made use of SEM, TEM, EDS and ED to investigate the secondary phase existed in SnO$_2$ varistor ceramic.[12]. Hong Peng He inspected the secondary phase of Sr doped LaInO$_3$ through XRD and Raman.[13]. Zhi-Cheng Li used series SAED to get 3-D spatial points of secondary phase, and determine its spatial group and crystal lattice.[14].

Secondary phase influences ceramic on microstructure, chemical composition, and mechanics and electrical performance. The second phase segregates at the grain surface during sintering process and makes an insulating layer which result in a higher $V_{1mA}$[11]. N.S.Hari studied PTRC ceramic BaTiO$_3$ whose secondary phase BaAl$_6$TiO$_{12}$ formed segregation layer and changed the charge distribution around BaTiO$_3$ crystal grains. In this case, $V''_{Ba}$ become main electron traps and induced an acceptor energy level which influences n-type BaTiO$_3$ ceramic PTRC on positive temperature coefficient[15].

For current study, SEM, EDS, XRD, XPS and phase diagram are carried out to investigate crystal structure, chemical composition and the transition of the secondary phase and its effects on varistor properties of (La, Nb) codoped TiO$_2$ ceramic sintered at different temperature.

2. Experiments

TiO$_2$ varistor samples with a molar composition 0.98TiO$_2$ + 0.008Nb$_2$O$_5$ + 0.007La$_2$O$_3$ were prepared by the classical electronic ceramic procedure and single sintering technique. The oxides raw materials used in this study were analytical-grade TiO$_2$ (99.5%), Nb$_2$O$_5$ (99.5%), SiO$_2$ (99.5%) and La$_2$O$_3$ (99.5%). The chemicals were mixed in proportion and wet-milled in agate jar with agate balls for 12h in deionized water. The milled powders were dried and granulated with a PVA binder. The granulated powder was pressed into discs 13 mm in diameter and 1.0 mm thickness under the pressure of 140MPa. After burning out PVA at 650$^\circ$C, the discs were placed in Al$_2$O$_3$ crucibles and sintered in air at 1300$^\circ$C ~1400$^\circ$C for 1h, and then cooled to room temperature automatically. Silver paste was coated on both sides of TiO$_2$ samples to form electrodes by firing at 600$^\circ$C for 30 min. XRD analysis of the sample phase was observed by Bruker D8 XRD. The microstructure characterization and chemical compositions were measured by Philips XL30-ESEM with EDS attachment. XPS spectra were measured by Phi5500 XPS meter. The varistor properties of TiO$_2$ ceramics were measured by CJ1001 varistor test meter.

2. Results and discussions

2.1. Microstructure and composition

Figure 1 gives the SEM image and EDS profile of the sample mentioned above, which corresponds to sintering temperature 1300$^\circ$C, 1350$^\circ$C and 1400$^\circ$C. In Figure 1 (a), (b) and (c), the middle picture is
backscattered electron image, and the left picture is the chemical composition of secondary phase obtained via energy spectrum instrument corresponding to high light area in SEM image, and then the right picture is the chemical composition of TiO₂ grain. From Figure 1, with the rising of sintering temperature, TiO₂ grains grow up and the TiO₂ sample becomes denser. There exist some highlight areas in microstructure photos of TiO₂ ceramic. The highlight areas may be caused by the segregation of La and Nb which have larger atomic number.

![Figure 1](image)

**Figure 1.** SEM images and EDS of TiO₂ varistor ceramic samples at different sintering temperature (a) 1300°C, (b) 1350°C and (c) 1400°C.

To determine the element and content of highlight area, point analysis method of EDS is used to measure chemical composition of highlight area and TiO₂ grain, measured results shown in Figure. 1. According to EDS, the compositions of TiO₂ grain are the same basically at different sintering temperature. However, the compositions are very different in corresponding highlight area. Obviously, there exist serious segregation of La and Nb. La and Nb mole percent are, respectively, 6.8 and 6.24 at the temperature 1300°C, 9.5 and 9.8 at 1350°C, 7.36 and 7.95 at 1400°C. It can be noted that the molar ratio of La and Nb in highlight area is almost one.
2.2. Crystal structure

To confirm whether secondary phase is formed in TiO₂ ceramic because of La and Nb segregation, X-ray diffraction is carried out to observe crystal structure of TiO₂ ceramic, shown as Figure 2. From the Figure 2, peaks corresponding to TiO₂ were detected; other crystalline phase besides rutile (TiO₂) was also observed, such as LaNbO₄ and LaNbTiO₆. X-ray diffraction analysis indicated that there exist secondary phase in TiO₂ varistor ceramic besides main crystal phase rutile TiO₂. LaNbO₄ is only secondary phase of TiO₂ ceramics sintered at 1300℃ while for the sample sintered at 1350℃, secondary phases contains LaNbO₄ and LaNbTiO₆. LaNbTiO₆ is only secondary phase of TiO₂ ceramics sintered at 1400℃. The molar ratio of La/Nb in the chemical composition of secondary phase LaNbO₄ and LaNbTiO₆ is one. These accords with the EDS analysis in section 3.1. XRD, SEM and EDS synthetically demonstrate that the secondary phase LaNbO₄ and LaNbTiO₆ corresponding to highlight area in SEM images is formed through the segregation of La and Nb. With the rising of sintering temperature, the secondary phase will change from LaNbO₄ to LaNbTiO₆.

![Figure 2. X-ray diffraction spectrum of samples at different sintering temperature](image)

In current works, TiO₂ raw materials is anatase TiO₂, which will transform into rutile TiO₂ at about 900℃. Rutile TiO₂ is tetragonal system with lattice parameter a=b=4.594 Å, c=2.959 Å, α=β=γ=90. Secondary phase LaNbO₄ is monoclinic system, a=5.5735 Å, b=11.5418 Å, c=5.2159 Å, α=90, β=94.070, γ=90. Secondary phase LaNbTiO₆ is Orthorhombic system, a=10.934 Å, b=7.572 Å, c=5.446 Å, α=β=γ=90. Figure 3 shows crystal structures of rutile TiO₂, LaNbO₄ and LaNbTiO₆. At high temperature, there maybe exists a chemical reaction as equation (1). So rutile TiO₂ and LaNbO₄ maybe produce LaNbTiO₆. Figure 4 presents the binary phase diagram of LaNbO₄-TiO₂, which also indicates formation mechanism of secondary phases LaNbTiO₆ according to equation (1).

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

(1)

![Figure 3. Crystal structures of (a) Rutile TiO₂; (b) LaNbO₄ and (c) LaNbTiO₆](image)
2.3. Varistor properties

In order to investigate the change mechanism and the relative content of secondary phase LaNbO$_4$ and LaNbTiO$_6$, the ternary phase diagram of La$_2$O$_3$-TiO$_2$-Nb$_2$O$_5$ is drawn based on the binary phase diagram of La$_2$O$_3$-TiO$_2$, La$_2$O$_3$-Nb$_2$O$_5$ and Nb$_2$O$_5$-TiO$_2$ [16-18], seeing Figure 5. It is reported that the ternary oxide of La$_2$O$_3$-TiO$_2$-Nb$_2$O$_5$ includes LaNbTiO$_6$ (C point in Figure 5) and La$_{0.64}$ (Ti$_{0.92}$Nb$_{0.08}$) O$_3$ (F point in Figure 5). The latter is produced by the binary oxide La$_{2/3}$TiO$_3$ (E point in Figure 5) doped with Nb. Its molar composition is 0.25La$_2$O$_3$-0.72TiO$_2$-0.03Nb$_2$O$_5$ [19]. The molar ratio of La/Nb in La$_{0.64}$ (Ti$_{0.92}$Nb$_{0.08}$) O$_3$ is eight, which have a big difference from EDS analysis in Figure 1, so that the current experiment samples don’t contain ternary oxide La$_{0.64}$ (Ti$_{0.92}$Nb$_{0.08}$) O$_3$ but LaNbO$_4$ or LaNbTiO$_6$. XRD analysis in Figure 2 also confirms this.

The composition of sample is presented at B point in Figure 5, which is 0.98molTiO$_2$ + 0.007molLa$_2$O$_3$ + 0.008molNb$_2$O$_5$. The main crystal phase in TiO$_2$ ceramic is rutile TiO$_2$, shown as A point in Figure 5. The secondary phase is LaNbO$_4$ and LaNbTiO$_6$, corresponding to D and C points, respectively, in Figure 5. Thus, the contents evaluation of different solid phases in (La, Nb) doped TiO$_2$ varistor ceramic can be worked out via straight line ABCD.

According to Figure 2, there only exist TiO$_2$ and LaNbO$_4$ at 1300°C. Via ABD line and the basic principle of ternary phase diagram, the molar content of TiO$_2$ is evaluated as 97.22%, and secondary phase LaNbO$_4$ is 2.78%. At 1400°C, there only exist TiO$_2$ and LaNbTiO$_6$. From line ABC, the content of TiO$_2$ is calculated as 94.48% and LaNbTiO$_6$ is 5.52%. At 1350°C, there coexist ternary phase TiO$_2$, LaNbO$_4$ and LaNbTiO$_6$. Their relative contents are difficult to evaluate. LaNbO$_4$ is a ferroelastic material with domain structure and also is a insulator with larger band energy of 4.8ev[20-21]. LaNbTiO$_6$ may be one of ReTiNbO$_6$ microwave dielectric ceramics with low dielectric constant and high electrical resistivity[22]. As the rising of sintering temperature, the TiO$_2$ grains become larger and the content of secondary phase increase. Larger grains make $\alpha$ and $V_{1mA}$ reduce while insulating second phases make $\alpha$ and $V_{1mA}$ rise.

XPS profile of O1s in TiO$_2$ varistor ceramics consist of two peaks as showed in Figure 6. The peak at 529.7ev is assigned to lattice oxygen in TiO$_2$. The peak at 531.8ev is corresponding to adsorption oxygen. Quantity of adsorption oxygen increases with concentration of vacancy oxygen increasing. Yang Seng-lu[23] reported that mass transport during sintering process mainly depend on oxygen vacancies and that chief point defect of rutile TiO$_2$ is vacancy oxygen under atmosphere and high temperature. With sintering temperature increasing, XPS spectra peak of absorbed oxygen was enhanced. This indicated that concentration of oxygen vacancies increased. Titanium vacancies and oxygen vacancies were intrinsic defect of rutile TiO$_2$[24]. So increment of oxygen vacancies implied
that increase of Titanium vacancies. On the other hand, \( V_{Ti}^{‴″″} \) is main electron potential trap and it will form acceptor energy level, which will leads to the increase of varistor voltage and nonlinear coefficient [11, 15]. The varistor properties presented in Figure .7 is the result of combined action of secondary phase, point defect and microstructure.

Figure 6. XPS profile of O1s in TiO2 varistor ceramics

Figure 7. Influence of sintering temperature on \( V_{1mA} \) and \( \alpha \)

3. Conclusions
(1) SEM analysis denoted that La and Nb will segregation in (La, Nb) codoped TiO2 sample. EDS analysis showed that the chemical composition and content ratio in TiO2 grain were kept the same. In the segregation area of La and Nb, the contents of La and Nb are very different from TiO2 grain. Their molar ration La/Nb of the segregation area is almost one.
(2) XRD research indicated that secondary phase LaNbO4 and LaNbTiO6 will be formed in (La, Nb) codoped TiO2 ceramic at different sintering temperature. With the rising of temperature, the secondary phase can change from LaNbO4 to LaNbTiO6, the secondary phase can make \( V_{1mA} \) and \( \alpha \) to be increased.
(3) XPS spectra showed that with sintering temperature increasing, the concentration of Ti vacancy increased. As a main electron potential well, \( V_{Ti}^{‴″″} \) can form acceptor energy level and lead to the increase of varistor voltage and nonlinear coefficient.

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