Varistor properties of TiO$_2$–Ta$_2$O$_5$–CaCO$_3$ ceramics doped with GeO$_2$

Kunyong KANG$^{1,2,3}$, Kaimeng XU$^{1,2,3}$, Gang ZHU$^{1,2,3}$, Can LIU$^{1,2,3}$, Yuanbo HUANG$^{1,2,3}$, Xiaoqing YANG$^{2,3}$, Zhenguan TANG$^4$ and Zhifeng ZHENG$^{2,3,†}$

$^1$Faculty of Materials Science and Engineering, Southwest Forestry University, Kunming 650024, P R China
$^2$Yunnan Provincial Engineering Laboratory for Highly-Efficient Utilization of Biomass, Kunming 650024, Yunnan Province, P. R. China
$^3$Yunnan Provincial University Key Laboratory for Biomass Chemical Refinery & Synthesis, Kunming 650224, Yunnan Province, P. R. China
$^4$School of Chemical and Biomolecular Engineering, Georgia Institute of Technology, Atlanta, GA 30332, United States

This study investigates the influence of GeO$_2$ on the nonlinear coefficient ($\alpha$) and breakdown voltage ($E_B$) of TiO$_2$–Ta$_2$O$_5$–CaCO$_3$ varistor ceramics doped with GeO$_2$ and prepared according to a conventional ball milling–molding–sintering process. The electrical performance parameters, including the nonlinear coefficient ($\alpha$), breakdown electric field ($E_B$), and leakage current ($J_l$), were assessed using a varistor direct-current instrument. The average barrier height $\Phi_B$ of each sample was calculated using the relevant formula. Analyses conducted by X-ray diffraction, scanning electron microscopy, and scanning transmission electron microscopy demonstrated that GeO$_2$ doping changed the microstructures of TiO$_2$–Ta$_2$O$_5$–CaCO$_3$ ceramics, resulting in increased $\alpha$ and decreased $E_B$ values. Ceramics doped with 0.2 mol % Ta$_2$O$_5$, 0.2 mol % CaCO$_3$ and 0.9 mol % GeO$_2$ exhibited the maximum $\alpha$ value ($\alpha = 9.8$) and the highest grain boundary barrier ($\Phi_B = 0.92$ eV) but a low $E_B$ value ($E_B = 17.2$ V·mm$^{-1}$).

©2018 The Ceramic Society of Japan. All rights reserved.

Key-words: Varistor, TiO$_2$, Nonlinear coefficient, Breakdown voltage, GeO$_2$

[Received July 21, 2017; Accepted December 28, 2017]

1. Introduction

Varistors made of varistor ceramics are widely used as devices for protection against transient overvoltages and surge arresters in electronic and industrial equipment. The typical characteristic of these materials is nonlinear current–voltage ($J$–$V$) feature characterized by the empirical equation

$$ J = (kE)^\alpha $$

(1)

where $k$ is a dimensionless constant that depends on the microstructure of the ceramic and $\alpha$ is a nonlinear coefficient obtained by the formula

$$ \alpha = \log(I_2/I_1)/\log(V_2/V_1) = 1/\log(V_{\text{ImA}}/V_{0.1mA}) $$

(2)

where $V_1$ and $V_2$ are the voltage at current $I_1$ and $I_2$, respectively. Thus, the higher the $\alpha$ value, the better the nonlinear properties of the material. The nonlinear properties of any given varistor depend on the potential barriers of the grain boundaries of polycrystalline ceramic. The earliest varistors were made from SiC-based ceramics. These SiC-based ceramic varistors were later gradually replaced by ZnO-based varistors due to their high nonlinear coefficients. Compared with ZnO-based varistors, TiO$_2$ ceramics have a relatively high dielectric constant, which could satisfy capacitor–varistor double functional demands. In recent years, electrical appliance designs require varistors to contain more functions facilitated by high-density integrated circuits. There has therefore been growing interest in the study of TiO$_2$-based varistors.

In 1982, (Nb, Ba)-doped TiO$_2$ varistor ceramics first reported by Yan and Rhodes showed that this system also had varistor properties, with a nonlinear coefficient in the range between 3 and 4. Since that time a large number of studies on the influences of sintering conditions and dopants on the microstructures and electrical properties of TiO$_2$-based varistors have been carried out. Sousa et al. prepared a varistor by doping TiO$_2$ with the oxides Ta$_2$O$_5$, Cr$_2$O$_3$, and MnO$_2$ with a nonlinear coefficient of $\alpha = 8.23$ and a varistor voltage (i.e. the voltage applied to a thickness of 1 mm corresponding to the current density of ImA·cm$^{-2}$) of $E_B = 34$ V·cm$^{-1}$. Yang et al. studied the influence of sintering time on (Ba, Bi, Nb)-doped TiO$_2$ varistor ceramics and found that a sample with a sintering time of 2 h had the highest activation energy and exhibited optimum varistor properties with $\alpha = 8$. Luo et al. studied a (Ca, Si, Ta)–TiO$_2$ system and found that 0.8 mol % Ta$_2$O$_5$ doping could significantly reduce the varistor voltage to 14.7 V·mm$^{-1}$. The high valence state Ta$^{5+}$ replaced Ti$^{4+}$ and occupied the Ti$^{4+}$ lattice sites, thus
releasing free electrons to promote grain conductivity and reducing the varistor voltage of TiO₂. Hsiang and Wang¹³ investigated the cooling rate effects on the electrical properties of TiO₂-based varistors and found that the acceptor concentration of Bi⁺³ in the rutile grain in quenched samples was higher than that in furnace-cooled samples. As a result, the quenched samples formed higher grain boundary barriers during cooling and exhibited a higher α parameter. Penneweiss and Hoffmann¹⁴ doped TiO₂ with Al and used freezing to retain high-temperature defects, thus preparing TiO₂ low-voltage varistors. Li et al.¹⁵ studied the effect of sintering temperature on the electrical properties of TiO₂-based varistors and pointed out that the 99.3% TiO₂ + 0.6% Y₂O₃ + 0.1% Nb₂O₅ composition sintered at 1400°C had optimum non-linear properties, a result attributed to the formation of the highest and narrowest grain-boundary defect barriers. Zhang et al.¹⁶ reported that a change in the oxygen concentration at the grain boundaries can directly impact the acceptor defect density and the width and height of the grain boundary potential barrier, thus affecting the electrical properties of TiO₂ varistors. Gong et al.¹⁷ studied the electrical properties of Ta₂O₅-doped TiO₂ varistor ceramics sintered at 1300°C and obtained good electrical properties with Eᵣ = 14.9 V·mm⁻¹, α = 4.48, ε₁ = 9.68 × 10⁴, and tan δ = 0.36. Zhao et al.¹⁸ studied the effect of thermal treatment on TiO₂ varistors doped with Nb₂O₅ and Bi₂O₃ in different atmospheres. The results indicated that after oxygen atmosphere thermal treatment, the acceptor state density and the height and width of the potential barriers increase, the conductivity decreases, and the varistor voltage improves significantly as a result of oxygen accumulation at the grain boundaries.

A low α value restricts practical application of TiO₂ varistors, however. In order to improve the α value and decrease the Eᵣ value of TiO₂-based varistors, the semiconductor GeO₂ with a low melting point was adopted in this work, and a investigation was carried out on the influence of doping with GeO₂ on the α and Eᵣ values of TiO₂-Ta₂O₅-CaCO₃ varistor ceramics.

### 2. Experimental details

Table 1 shows the initial doping content of each sample. Powdered samples were obtained through conventional oxide mixing using the following compounds (in mol %): (99.6 - x) TiO₂ (purity 99.9%), 0.2 Ta₂O₅ (purity 99.99%), 0.2 CaCO₃ (purity 99.99%), and x (x = 0, 0.1, 0.3, 0.6, 0.9, 1.2, and 1.5) GeO₂ (purity 99.99%). All reagents were obtained from Shanghai Chemical Reagent Co., Ltd., China. The materials were mixed for 8 h in a ball mill according to the mass ratio of 1:2:3 of powder to water blended with alcohol (water:alcohol = 4:1) to balls. After homogenization, each blend was oven dried at 80°C for 12 h and de-agglomerated in a 420 mesh sieve. The obtained powder was isostatically pressed at 150 MPa into tablets (10 mm in diameter and 1 mm thick). The tablets were degummed at 600°C for 0.5 h in a box-type resistance furnace and sintered at 1240, 1260, 1280, 1300, 1320, 1340, 1360, 1380, and 1400°C for 3 h in a tube furnace. The tablets were cooled to room temperature by furnace cooling. The shrink rates were calculated using Δd/d (where d is the diameter of the samples). The densities of the samples were obtained using the Archimedes principle, and the relative densities were calculated. The tablets were electronically characterized after slight polishing. Silver electrodes were deposited on the two surfaces of the sintered pellets and treated at 600°C for 15 min to ensure electrode fixation. Parameters such as α, Eᵣ, and leakage current (Iₘ) were measured using a varistor direct-current instrument. The grain boundary barrier height (Φ₉) of the samples was calculated using the following formula:¹⁹⁻²³

\[
J = A^*T^2 \exp(\beta E_1/2 - \phi_B)/kT
\]

where A* is the Richardson constant, K is the Boltzmann constant, and T is the absolute temperature. Φ₉ and β can be calculated using the following equations, which were established by measuring the current density in the ohmic region and maintaining the temperature of the tested varistor constant for the two different application fields:

\[
J_1 = A^*T^2 \exp(\beta E_1/2 - \phi_0)/kT
\]

\[
J_2 = A^*T^2 \exp(\beta E_2/2 - \phi_0)/kT
\]

X-ray diffraction (XRD, Rigaku D/Max-2200) analysis was performed using CuKα radiation to identify the sample phases. The fracture surfaces of the samples were observed using scanning electron microscopy (SEM, XL30ESEM-TMP) to determine the influence of doping with GeO₂ on the α and Eᵣ values of TiO₂-Ta₂O₅-CaCO₃ varistor ceramics.

### 2. Experimental details

Table 1: Doping content of samples

| Sample | Ta₂O₅ (mol %) | CaCO₃ (mol %) | GeO₂ (mol %) |
|--------|--------------|--------------|--------------|
| #1     | 0.2          | 0.2          | 0.0          |
| #2     | 0.2          | 0.2          | 0.1          |
| #3     | 0.2          | 0.2          | 0.3          |
| #4     | 0.2          | 0.2          | 0.6          |
| #5     | 0.2          | 0.2          | 0.9          |
| #6     | 0.2          | 0.2          | 1.2          |
| #7     | 0.2          | 0.2          | 1.5          |

### 3. Experimental results and analysis

Table 2 shows the influence of sintering temperature (T) on the nonlinear coefficients (α) and breakdown voltages (Eᵣ) of samples #1, #2, and #3. Samples #2 and #3 exhibited optimal electrical properties at a sintering temperature of 1320°C. However, the optimal sintering temperature for sample #1 was found to be 1360°C. The electrical properties of all samples sintered at 1320°C were therefore extensively investigated.

Table 3 shows the electrical properties of TiO₂-Ta₂O₅-CaCO₃ ceramics doped with different amounts of GeO₂. The shrink rate and density increased with increases in...
GeO₂ content. Sample #2 doped with 0.1 mo\% GeO₂ presented higher \( \alpha \) and lower \( E_B \) values (\( \alpha = 3.8 \), \( E_B = 27.5 \text{ V mm}^{-1} \)) compared with those of sample #1 without GeO₂ doping (\( \alpha = 3.1 \), \( E_B = 29.3 \text{ V mm}^{-1} \)). The \( \alpha \) value increased, whereas the \( E_B \) value decreased with increases in GeO₂ content. When the GeO₂ content was increased to 0.9 mo\%, the \( \alpha \) value (\( \alpha = 9.8 \)) increased significantly while the \( E_B \) value (\( E_B = 17.2 \text{ V mm}^{-1} \)) decreased in sample #5. The obtained values are higher than those reported in the literature.\(^{24-26}\) \( \Phi_B \) was calculated as 0.92 eV in sample #5, moreover, which exhibited the highest \( \alpha \) value of 9.8. As shown in Table 3, the \( \alpha \) and \( \Phi_B \) values increased, whereas the \( E_B \) and \( J_L \) values decreased, with increases in GeO₂ content. When the GeO₂ content was increased to 0.9 mo\%, the nonlinear coefficient (\( \alpha \)) and grain boundary barrier-height (\( \Phi_B \)) exhibited the maximum values. However, subsequent addition of 1.2 mo\% GeO₂ resulted in a decreased \( \alpha \) value (\( \alpha = 9.1 \)). This finding may be attributed to the segregation of GeO₂ at the grain boundary when the GeO₂ content is higher than its solid solubility in the TiO₂ lattice, thereby diluting the acceptor interface state density \( N_S \). This phenomenon results in a decreased \( \Phi_B \) value based on the following formula and a consequent decrease in the \( \alpha \) value:

\[
\Phi_B = \frac{e^2 N_S^2}{2\varepsilon_0 \varepsilon R N_D} \tag{6}
\]

where \( \varepsilon_0 \) is the dielectric constant of a vacuum, \( \varepsilon_r \) is the relative dielectric constant of the semiconducting ceramic, \( N_D \) is the donor concentration in the semiconductor depletion layer, \( N_S \) is the acceptor interface state density, and \( e \) is the electron charge. Figure 1 shows the influence of the GeO₂ doping content on the current–voltage (\( J-E \)) characteristics of TiO₂–Ta₂O₅–CaCO₃ ceramics.

As is clear from the XRD patterns shown in Fig. 2(a), all samples possess only one phase, which corresponds to the rutile crystalline phase. Figure 2(b) shows enlarged partial spectra of Fig. 2(a) near \( 2\theta = 27.5^\circ \). Compared

### Table 2. Influence of sinter temperature on the electrical properties of samples (\( E_B / \text{V mm}^{-1} \))

| Sample | 1240°C | 1260°C | 1280°C | 1300°C | 1320°C |
|--------|--------|--------|--------|--------|--------|
| \( \alpha \) | \( E_B \) | \( \alpha \) | \( E_B \) | \( \alpha \) | \( E_B \) |
| #1     | 2.5    | 30.4   | 2.7    | 29.8   | 3.1    | 29.3   |
| #2     | 3.7    | 27.2   | 4.1    | 26.3   | 4.2    | 25.1   |
| #3     | 3.4    | 28.4   | 3.6    | 28.1   | 3.7    | 26.3   |

### Table 3. Electrical properties of TiO₂–Ta₂O₅–CaCO₃ ceramics with different GeO₂ doping content sintered at 1320°C

| Sample | \( \rho_s \) | \( \Delta d/d \) | \( \alpha \) | \( J_L / \text{µA cm}^{-2} \) | \( E_B / \text{V mm}^{-1} \) | \( \Phi_B / \text{eV} \) |
|--------|---------------|-----------------|--------------|-----------------|-----------------|-----------------|
| #1     | 92.5          | 13.5            | 3.1          | 29.3            | 12.8            | 0.27            |
| #2     | 94.8          | 14.8            | 3.8          | 27.5            | 11.6            | 0.43            |
| #3     | 95.6          | 15.2            | 4.9          | 24.3            | 10.7            | 0.49            |
| #4     | 96.7          | 15.8            | 7.2          | 20.4            | 9.3             | 0.68            |
| #5     | 97.2          | 16.6            | 9.8          | 17.2            | 8.4             | 0.92            |
| #6     | 97.4          | 16.9            | 9.1          | 15.7            | 7.9             | 0.81            |
| #7     | 97.8          | 17.3            | 7.6          | 14.1            | 7.1             | 0.74            |

Fig. 1. The \( J-V \) characteristics of TiO₂–Ta₂O₅–CaCO₃ ceramics with different GeO₂ doping contents.

Fig. 2. X-ray diffraction patterns of samples with different GeO₂ doping contents.
with that of sample #1 without GeO₂ doping, the peaks of samples #2, #3, #4, #5, #6, and #7 shifted to different levels in the low-angle direction. These results indicate that doping with GeO₂ changed the microstructures of TiO₂-Ta₂O₅-CaCO₃ ceramics. The radius of the Ge⁴⁺ cation (53 pm) was smaller than that of Ti⁴⁺ (60.5 pm); thus, the interplanar spacing value (d) increased slightly because Ti⁴⁺ was replaced with Ge⁴⁺ in the TiO₂ lattice. The Bragg formula is presented as follows:

$$\lambda = 2d \sin \theta$$  \hspace{1cm} (7)

where \(\lambda\) is the X-ray wavelength, \(d\) is the atomic plane spacing, and \(\theta\) is the angle between the incident X-ray and the crystal plane, at which the diffraction peak moved slightly in the low-angle direction. The trend for the peak to move in the low-angle direction became increasingly apparent with increases in the GeO₂ doping concentration. GeO₂ increases the semiconducting capability of TiO₂ grains when dissolved in the TiO₂ lattice, thereby decreasing the \(E_B\) values.

Figure 3 illustrates the surface microstructures of samples #1, #4, #5, and #6. The average grain sizes of samples #1, #4, #5, and #6 estimated by the SEM scale were approximately 3.8, 7.2, 8.5, and 9.8 µm, respectively. The grain sizes of samples #4, #5, and #6 were found to be larger than that of sample #1. The grain size increased because GeO₂ accelerated grain enlargement. Similarly, previous studies showed that doping with GeO₂ promoted CaCu₃Ti₄O₁₂ grain growth. The addition of GeO₂ accelerated grain growth, decreased the number of grain boundaries per unit thickness, and subsequently decreased the \(E_B\) value based on the following formula:

$$E_B = \bar{n} \cdot v_b$$  \hspace{1cm} (8)

where \(\bar{n}\) is the number of grain boundaries along the thickness direction of the sample, and \(v_b\) is the voltage applied to a single grain boundary.

Figures 4(a) and 4(b) show the point scan spectra of STEM-EDX for samples #1 and #5, respectively. In the figures, points 1 and 2 are located at the grain boundaries, and points 3 and 4 are located in the grains. The elemental contents of the samples in Figs. 4(a) and 4(b) are shown in Tables 4 and 5, respectively. The initial doping contents of Ca in samples #1 and #5 were the same. The average Ca content at the grain boundary in sample #5 was higher, however, in the two analyzed samples with 0.97 At% of point 1 and 1.23 At% of point 2; sample #1 exhibited lower values, moreover, with 0.65 At% of point 1 and 0.73 At% of point 2. By contrast, the average Ca content in the grains in sample #5 was lower than that in sample #1. These results show that the addition of GeO₂ changed the Ca distribution in sample #5. After the addition of GeO₂, which has a low melting point of about 1100°C, the liquid phase was formed in sample #5 during sintering at 1320°C; this phase formation reduced the energy required by Ca²⁺ to move to the grain boundary and facilitate full segregation of Ca²⁺ there. GeO₂ accelerated grain growth, thereby reducing the grain boundary width, which is to say, the barrier width (\(X_D\)); the acceptor interface state density (\(N_A\)) and \(\Phi_B\) consequently increased in accordance with Formula (6). Thus, the \(\alpha\) value also increased.

4. Discussion

The nonlinear coefficient (\(\alpha\)) and the breakdown voltage (\(E_B\)) are important parameters of varistor ceramics. TiO₂-based low-voltage varistors generally require high \(\alpha\) and low \(E_B\) values. The \(\alpha\) parameter is based on the grain boundary barrier (\(\Phi_B\)) and barrier width (\(X_D\)). Increasing \(\Phi_B\) reduces the background current, whereas decreasing \(X_D\) enhances the electron tunneling effect. The \(\alpha\) value can therefore be increased by increasing \(\Phi_B\) and decreasing \(X_D\) can be used to increase. According to Formula (6), decreasing \(N_A\) increases \(\Phi_B\) and subsequently increases \(\alpha\). The following formula shows, however, that decreasing \(N_D\) increases \(X_D\), which is not conducive to improvement of the \(\alpha\) value.

$$X_D = \sqrt{2E_Be\Phi_B/eN_D}$$  \hspace{1cm} (9)

Decreasing \(N_D\) reduces the semiconducting capability of the grains, moreover, which is not conducive to the low breakdown voltage required by low-voltage varistors. Thus, a varistor with excellent varistor properties has an optimal donor content. Similarly, increasing \(N_A\) results in increased \(\Phi_B\) and consequently increases the \(\alpha\) and \(X_D\) values. There is also an optimal acceptor content for a varistor. Once the optimal doping contents of donor and acceptor are determined, the \(\alpha\) and \(E_B\) values can no longer be optimized by adjusting the doping contents of the donor and the acceptor. GeO₂ doping can be used, however, to optimize the \(\alpha\) and \(E_B\) values of the TiO₂-Ta₂O₅-CaCO₃ varistor ceramics. This finding can be explained as follows:
Fig. 4. Continued on next page.
The influencing factors for the nonlinear coefficient $\alpha$ are greater: barrier height, barrier width, donor density, accepter density, grain orientation and growth. Among these, the barrier-height is one of the main factors affecting the nonlinear coefficient $\alpha$. GeO$_2$ acts as a sintering agent because of its low melting point. The liquid phase formed during sintering facilitates segregation of the acceptor ion Ca$^{2+}$ at the grain boundary to the greatest extent possible. This phenomenon increases the acceptor.

Fig. 4. EDX spectrums of TiO$_2$–Ta$_2$O$_5$–CaCO$_3$ ceramics: (a) without GeO$_2$, and (b) doped with 0.9 mol % GeO$_2$. 

(1)
Table 4. Element contents of sample #1 detected by EDX

| Position | Element (At%) |
|----------|---------------|
|          | OK TiK TaK CaK |
| 1        | 75.52 23.56 0.27 0.65 |
| 2        | 78.66 20.43 0.18 0.73 |
| 3        | 78.14 21.39 0.35 0.12 |
| 4        | 74.30 25.09 0.46 0.15 |

Table 5. Element contents of sample #5 detected by EDX

| Position | Element (At%) |
|----------|---------------|
|          | OK TiK TaK CaK GeK |
| 1        | 73.32 25.12 0.21 0.97 0.38 |
| 2        | 74.65 23.78 0.14 1.23 0.20 |
| 3        | 74.50 24.29 0.45 0.00 0.76 |
| 4        | 77.17 21.57 0.38 0.07 0.81 |

interface state density $N_S$ and the barrier height $\Phi_B$ values of a single junction on barrier formation, which is beneficial to increasing the $\alpha$ value.

(2) GeO$_2$ doping accelerates grain growth, thereby reducing the grain boundary width, which is to say, barrier width ($X_B$). This phenomenon increases the interface state density ($N_S$) of the acceptor and decreases the number of grain boundaries along the thickness direction of the sample. Thus, the $\alpha$ value increases and the $E_B$ value decreases.

(3) GeO$_2$ increases the semiconducting capability of grains when dissolved in TiO$_2$ lattices, thereby decreasing the $E_B$ value.

5. Conclusions

GeO$_2$ doping changes the microscopic structures and improves the nonlinear properties of TiO$_2$–Ta$_2$O$_5$–CaCO$_3$ varistor ceramics. When doped with 0.2 mol % Ta$_2$O$_5$, 0.2 mol % CaCO$_3$ and 0.9 mol % GeO$_2$, varistor ceramic exhibit the maximum nonlinear coefficient ($\alpha = 9.8$) and the highest grain boundary barrier ($\Phi_B = 0.92$ eV), as well as low breakdown voltage ($E_B = 17.2$ V·mm$^{-1}$) and low leakage current ($J_L = 8.4$ μA·cm$^{-2}$). Further improvement of the process will render TiO$_2$–Ta$_2$O$_5$–CaCO$_3$–GeO$_2$ ceramics potential novel varistors.

Acknowledgments This work was supported by the Natural Science Foundation of China (Grant No. 31670599) and the Key Project of Yunnan Provincial Science Foundation (Grant No. 2014FA 034).

References

1) S. L. Yang and J. M. Wu, J. Am. Ceram. Soc., 76, 145–152 (1993).
2) W. Y. Wang, D. F. Zhang, T. Xu, X. F. Li, T. Zhou and X. L. Chen, J. Alloys Compd., 335, 210–215 (2002).
3) M. Matsuoka, Jpn. J. Appl. Phys., 10, 736–746 (1971).
4) S. H. Luo, Z. L. Tang, H. Y. Li, J. P. Yan, Z. T. Zhang and X. Z. Xiong, Rare Metal Mater. Eng., 33, 748–751 (2004).
5) H. I. Hsiang and S. S. Wang, Jpn. J. Appl. Phys., 47, 4626–4629 (2008).
6) T. G. Wang, Q. Qin and W. J. Zhang, Adv. Mater. Res., 214, 168–172 (2011).
7) Z. B. Sun, X. Wang, Y. S. Yin, W. H. Yao, B. Y. Liu, Y. H. Fan and W. G. Li, Mater. Mech. Eng., 37, 86–89 (2013).
8) J. Z. Zhao, B. X. Wang and K. Lu, Ceram. Int., 40, 14229–14234 (2014).
9) M. F. Yan and W. W. Rhodes, Appl. Phys. Lett., 40, 536–537 (1982).
10) V. C. Sousa, E. R. Leite and J. A. Varela, J. Eur. Ceram. Soc., 22, 1277–1283 (2002).
11) S. L. Yang and J. M. Wu, J. Mater. Sci. Lett., 14, 748–751 (1995).
12) S. H. Luo, Z. L. Tang, J. Y. Li and Z. T. Zhang, Ceram. Int., 34, 1345–1347 (2008).
13) H. I. Hsiang and S. S. Wang, Mater. Sci. Eng. B, 128, 25–29 (2006).
14) J. Pennewiss and B. Hoffmann, Mater. Lett., 9, 219–226 (1990).
15) C. P. Li, J. F. Wang, W. B. Su, H. C. Chen, Y. J. Wang and D. X. Zhuang, Mater. Lett., 57, 1400–1405 (2003).
16) J. Zhang, Z. X. Yue, Y. Y. Zhou and B. Peng, J. Eur. Ceram. Soc., 36, 1923–1930 (2016).
17) Y. Y. Gong, R. Q. Chu, Z. J. Xu, J. Sun, F. X. Chao, S. Ma, J. G. Hao, H. Y. Li and G. R. Li, Ceram. Int., 41, 9183–9187 (2015).
18) J. Z. Zhao, C. G. Zhang, C. Y. Hu and K. Lu, J. Eur. Ceram. Soc., 37, 3353–3359 (2017).
19) K. Y. Kang, J. K. Yan, J. H. Yi, Z. D. Li, Q. C. Ge, F. C. Yan, J. Yang, C. X. Zhao and G. Y. Gan, J. Am. Ceram. Soc., 99, 158–166 (2016).
20) K. Y. Kang, J. K. Yan, G. Y. Gan, J. H. Du, J. M. Zhang and Y. C. Liu, Ceram. Int., 42, 4739–4747 (2016).
21) K. Y. Kang, J. K. Yan, J. M. Zhang, J. H. Du, J. H. Yi, Y. C. Liu, R. Bao, S. L. Tan and G. Y. Gan, J. Alloy. Compd., 649, 1280–1290 (2015).
22) C. P. Li, J. F. Wang, X. S. Wang, H. C. Chen and W. B. Su, Mater. Chem. Phys., 74, 187–191 (2002).
23) S. C. Navale, A. Vadivel Murugan and V. Ravi, Ceram. Int., 33, 301–303 (2007).
24) D. J. Lan and S. Q. Wan, Adv. Mater. Res., 852, 12–16 (2014).
25) C. P. Li, J. F. Wang and X. S. Wang, Mater. Sci. Eng. B, 85, 6–10 (2001).
26) F. M. Meng, F. Lu and L. Xiao, J. Cent. South Univ. Technol., 16, 897–901 (2009).
27) F. Amaral, L. C. Costa and M. A. Valente, J. Non-Cryst. Solids, 355, 2160–2164 (2009).
28) F. Amaral, M. A. Valente and L. C. Costa, J. Non-Cryst. Solids, 356, 822–827 (2010).
29) J. T. Animura, O. W. Ada, H. K. Urokawa, N. F. Uruse and M. K. Obayashi, Jpn. J. Appl. Phys., 39, 4493–4496 (2000).
30) J. M. Carlsson, H. S. Domingos, B. Hellsing and P. D. Bristowe, Interface Science, 9, 143–148 (2001).
31) N. Wakiya, S. Y. Chun and C. H. Lee, J. Electroceram., 4, 15–23 (1999).
32) A. A. Dakhel, J. Cryst. Growth, 311, 4183–4187 (2009).
33) G. Li, M. H. Wang and B. Wu, Electronic Components & Materials, 30, 15–17 (2011).
34) M. H. Wang, Z. Y. Zhao and T. T. Liu, J. Alloy. Compd., 621, 220–224 (2015).