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Sintering and properties of low-firing non-ohmic $SrTiO_3$ ceramics

LIQIN ZHOU, CHANGKUI YU
Department of Materials Science and Engineering, University of Electronic Science and Technology of China, Chengdu 610054, People's Republic of China

The sintering and properties of non-ohmic $SrTiO_3$ ceramics in the presence of Nb^{5+} as a donor dopant and Li^+ as an acceptor dopant and sintering agent have been studied. Different sintering parameters, such as sintering temperature, sintering time, cooling rate, and the ambient atmosphere at the cooling stage, were investigated. The changes induced by each parameter on the electrical properties have been discussed. The segregation of lithium at the grain boundaries is mainly fulfilled at the cooling stage. The correct slow cooling rate and oxygen atmosphere are both favourable to the segregation of lithium at the grain boundaries, and thus result in an improvement of non-linear $I-V$ characteristics. The lithium content and different lithium salts (Li_2CO_3, $LiNO_3$, LiF) were also investigated.

1. Introduction

$SrTiO_3$ ceramic varistor is one of the most successful electronic components in which the grain boundary plays an active role in determining the electrical properties. Such varistors have both varistor and capacitor function. They are widely used in the electronic circuits.

$SrTiO_3$ ceramic varistors are generally made with the so-called "painting oxidizing method" [1, 2], that is by sintering a mixture of $SrTiO_3$ doped with a small amount of Nb_2O_5 and SiO_2, etc., at about 1300–1500 °C in a reducing atmosphere, then painting the insulating reagent which contained Na_2O or K_2O, etc., on the sample surface and annealing the sample at 1000–1250 °C for grain-boundary diffusion. This treatment results in a semiconducting grain–insulating grain boundary–semiconducting grain (SIS) microstructure which leads to a high apparent permittivity and excellent varistor characteristics.

One approach to fabricate the varistors with high capacitance and low varistor voltage is to fabricate the multilayer varistors. However, it is difficult to fabricate multilayer varistors with multilayer ceramic technology using the $SrTiO_3$ ceramics mentioned above as dielectric. The high sintering temperature leads to a potential reaction between the electrodes and the dielectric, and the presence of internal electrodes prevents the diffusion of the insulating reagent.

In this paper, we propose a "segregating oxidizing method" with which a low-firing non-ohmic $SrTiO_3$ ceramic was fabricated successfully. This ceramic need not be painted with the insulating reagent on the sample surface. It can be used in multilayer technology. This ceramic is obtained by sintering a mixture of $SrTiO_3$ doped with donor dopant and acceptor dopant in a reducing atmosphere and cooling slowly in an oxidizing atmosphere. The donor dopant is used for the semiconducting of grains, while the acceptor dopant is used for the segregating at the grain boundaries and enhancing their insulation. The electrical properties of the ceramics are controlled by the semiconduction of grains and insulation of grain boundaries. Compared with the "painting oxidizing method", the insulation of grain boundaries is more difficult for the "segregating oxidizing method". Not only is the choice of the dopants (especially the acceptor dopant) important, but also the sintering technology plays a great role in determining the electrical properties of the ceramics. This present work studied the influence of sintering conditions on the electrical properties of the ceramics in detail. The effects of lithium content and different lithium salts were also investigated.

2. Experimental procedure

Nb_2O_5 is usually used as a dopant for the semiconducting of $SrTiO_3$ ceramics by introducing niobium as a donor on the titanium sites of the perovskite [3]. The lithium ion is an important liquid-phase sintering additive for $SrTiO_3$ ceramics [4]. Furthermore, lithium cations can occupy the octahedral sites of the perovskite and behave as an acceptor dopant, according to the equation [5]

$$Li^+ \rightarrow Li'''_{Ti} + 3h \quad (1)$$

In the present work, the Nb^{5+} was chosen as a donor dopant and Li^+ as an acceptor dopant and sintering agent. In order to improve the overall electrical properties of the ceramics, a very small amount of additives, such as $Mn(NO_3)_2$ and Bi_2O_3 were added to the ceramics.

$SrTiO(C_2O_4)\cdot 4H_2O$, Nb_2O_5, Li_2CO_3 ($LiNO_3$ or LiF), $Mn(NO_3)_2$ and Bi_2O_3 in a desired molar ratio

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were mixed, wet-milled for 15 h, dried, calcined at 850 °C for 1 h in air, remilled, then dried. The powder was pressed into chips of 10 mm diameter and 1 mm thickness at a pressure of 6×10^7 Pa. The chips were sintered at different temperatures for different times in a reducing atmosphere (70 % N_2 + 30 % H_2 cylinder gas with a flow rate of 20 ml min^{-1}), and cooled with different cooling rates in different atmospheres.

Contacts of an In–Ga alloy were applied for electrical measurements. The capacitance, C, and loss factor, tan δ, were measured with an automatic LCR meter in a temperature region of − 40–120 °C. The resistance is measured with an ohmmeter. The varistor voltage, V_{1mA} and $V_{10\ mA}$, was measured with an automatic varistor meter. The non-linear coefficient, α, was determined from

$$\alpha = 1/\log(V_{10\ mA}/V_{1\ mA}) \quad (2)$$

3. Results and discussion

3.1. Influence of sintering temperature and sintering time

After being properly sintered in a reducing atmosphere and rapidly quenched to room temperature in oil, the samples were found to be semiconducting and to have weak non-linear current–voltage characteristics. The influence of the sintering temperature and sintering time on the electrical properties of the ceramics is shown in Table I.

The resistivity of the Nb_2O_5-doped $SrTiO_3$ ceramics is quite small, about $10^{-1} - 10^2$ Ω cm, [3]. However, by adding Li^+ to the Nb_2O_5-doped $SrTiO_3$ ceramics, the resistivity of the samples increases to about 10^2–10^5 Ω cm, as shown in Table I. This is because lithium can occupy the titanium sites of the perovskite as an acceptor, and leads to the increase in the resistivity.

TABLE I The electrical properties for $SrTiO_3$ + 0.5 mol % Nb_2O_5 + 6 mol % Li_2CO_3, etc., sintered at different temperatures for different times under N_2–30 % H_2 (flow rate 20 ml min^{-1}) and then rapidly quenched to room temperature in oil

Sintering temperature (°C)	Sintering time (h)	Resistivity (Ω cm)	V_{1mA} (V)	α
1100	1	1.2×10^5	15	2.8
1150	1	1.0×10^5	12	3.0
1200	1	7.6×10^4	9	2.6
1250	1	3.4×10^4	4	2.3
1300	1	9.0×10^2	–	–
1150	2	8.8×10^4	10	3.5
1150	3	7.0×10^4	8	3.2

As can be seen in Table I, after being sintered in a reducing atmosphere, the samples have weak non-linear I–V characteristics. It is possible that a very small amount of lithium segregated to the grain boundaries at the sintering stage and formed the low grain-boundary barriers. When the sintering temperature is too high (⩾ 1300 °C), the non-linear I–V characteristics disappear, because lithium is a volatile element.

3.2. Influence of the cooling rate

Fig. 1 shows the electrical properties of the ceramics as a function of cooling rate. The apparent permittivity, ε, increases to 4.1×10^4 with decreasing cooling rate above 150 °C h^{-1} while the loss factor, tan δ, decreases abruptly. ε decreases with decrease in cooling rate below 150 °C h^{-1}, while tan δ remains at about 6%. The varistor voltage, $V_{1\ mA}$, and non-linear coefficient, α, increase with decreasing in cooling rate. From Fig. 1 we can see that when the cooling rate is 150 °C h^{-1}, the samples have overall electrical properties of $\varepsilon = 4.1 \times 10^4$, $\tan\delta = 6\%$, $V_{1\ mA} = 17$ V, $\alpha = 8$.

It is well known that a slow cooling rate is favourable to ion segregation at the grain boundaries. For this reason, the amount of lithium segregated at the grain boundaries increases with decrease in cooling rate. This leads to an increase of the grain-boundary barrier height. So the V_{1mA} and α increase. The improvement of the insulation of the grain boundaries results in a decrease of tan δ and an increase of ε. Conversely, when the cooling rate is too slow (< 150 °C h^{-1}), the increase in grain-boundary thickness results in a decrease of ε.

Comparing Fig. 1 with Table I it can be seen that the cooling stage is the main stage at which lithium segregates to the grain boundaries.

3.3 Influence of ambient atmosphere at the cooling stage

Table II shows the influence of ambient atmosphere at the cooling stage on the electrical properties of the

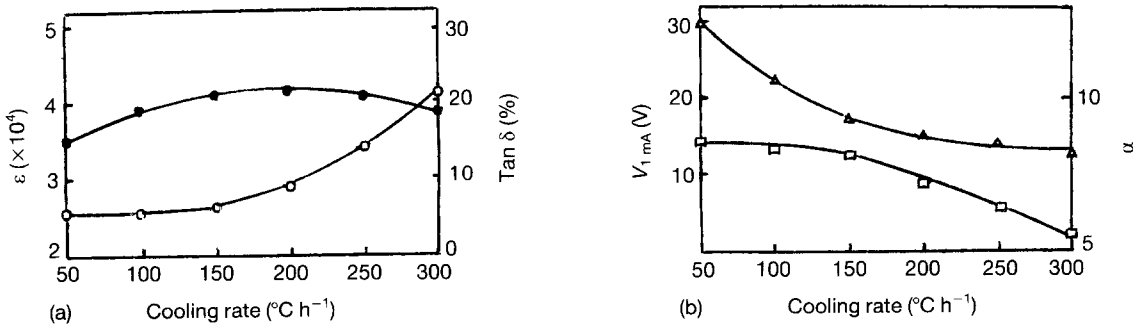

Figure 1 The cooling rate dependence of (a) (●) apparent permittivity, ε, and (○) loss factor, tan δ, (b) (△) varistor voltage, V_{1mA}, and (□) non-linear coefficient, α, for $SrTiO_3$ + 0.5 mol % Nb_2O_5 + 6 mol % Li_2CO_3, etc., sintered at 1150 °C for 2 h under N_2–30% H_2 (flow rate 20 ml min^{-1}) and then cooled at a different rate under nitrogen (flow rate 20 ml min^{-1}).

TABLE II The electrical properties for $SrTiO_3$ + 0.5 mol % Nb_2O_5 + 6 mol % Li_2CO_3, etc., sintered at 1150 °C for 2 h under N_2–30 % H_2 (flow rate 20 ml min^{-1}) and then cooled at a rate of 150 °C h^{-1} under different ambient atmosphere (gas flow rate 20 ml min^{-1})

Ambient atmosphere	ε (×10^4)	Tan δ (%)	V_{1mA} (V)	α
70%N_2 + 30%H_2	4.8	16.0	13	4.0
N_2	4.1	6.0	17	8.0
Air	5.0	5.5	20	11.2
O_2	5.5	4.8	22	12.0

ceramics. ε, V_{1mA} and α increase on changing the ambient atmosphere from a reducing atmosphere to an oxidizing atmosphere at the cooling stage, while tan δ decreases.

Fig. 2 shows the dependence of the flow rate of the oxygen gas at the cooling stage on the electrical properties of the samples. On increasing the flow rate of the oxygen, ε, V_{1mA} and α increase, while tan δ decreases. When the flow rate increases to above 60 ml min^{-1}, ε, tan δ, V_{1mA} and α remain almost at 6.0×10^4, 4%, 24 V and 14, respectively.

When cooling in an oxidizing atmosphere, the anionic vacancies present at the grain boundaries will be partially occupied by oxygen from the atmosphere. This leads to an increase of the grain-boundary barrier height. So ε, V_{1mA} and α increase and tan δ decreases.

3.4. Influence of the lithium content and lithium salts

In the present work, the Li^+ was added as an acceptor dopant and liquid-phase sintering agent. Therefore, the influence of lithium content on the electrical properties of the ceramics could be studied; the result is shown in Fig. 3. Finally, the effects of the different lithium salts (Li_2CO_3, $LiNO_3$, LiF) were also investigated. The electrical properties and microstructures of these ceramics are shown in Table III and Fig. 4, respectively.

As can be seen in Fig. 3, the sintering temperature and tan δ decrease with increase in the amount of Li^+ below 12 mol %, while ε, V_{1mA} and α increase. The sintering temperature is almost unchanged above 12 mol%, while ε, V_{1mA} and α decrease slowly and tan δ increases slowly.

For the sintering process in the presence of the liquid phase, the liquid phase has a great influence on the sintering of the ceramics. In the present work, lithium may introduce such a liquid phase, so the sintering temperature decreases obviously with increase in lithium content. On the other hand, lithium is added as an acceptor. So the lithium content has an

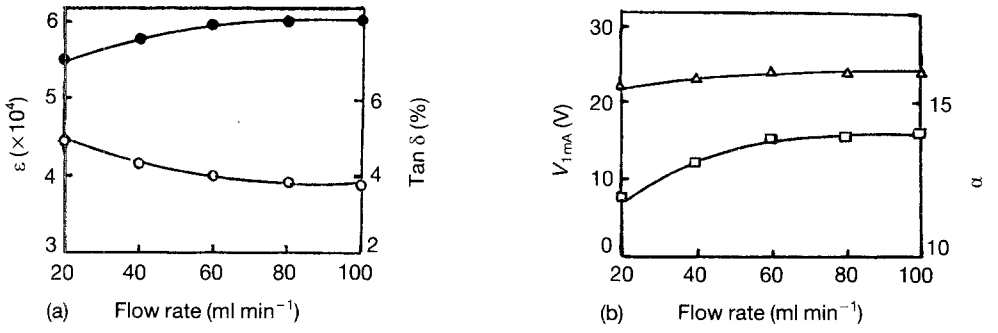

Figure 2 The effect of flow rate of oxygen gas on (a) (●) apparent permittivity, ε, and (○) loss factor, tan δ, (b) (△) varistor voltage, V_{1mA}, and (□) non-linear coefficient, α, for $SrTiO_3$ + 0.5 mol % Nb_2O_5 + 6 mol %Li_2CO_3, etc., sintered at 1150 °C for 2 h under N_2–30% H_2 (flow rate 20 ml min^{-1}) and then cooled at a rate of 150 °C h^{-1} under oxygen (different flow rate).

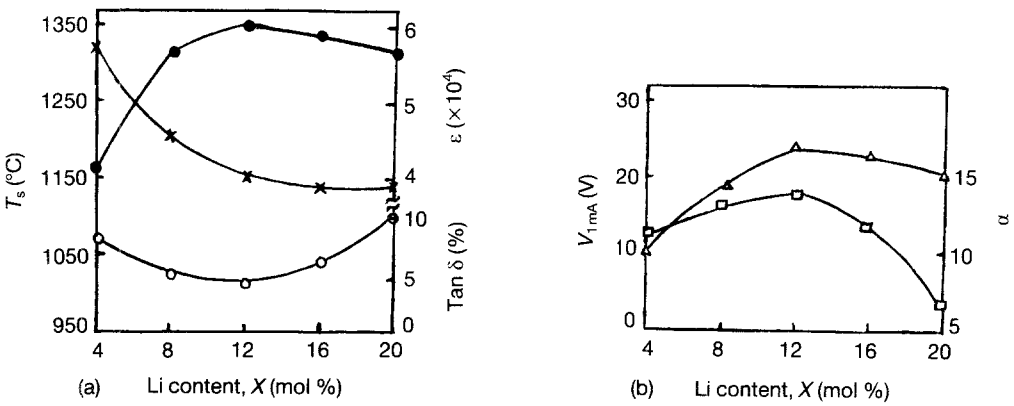

Figure 3 The effect of lithium content on (a) (×) sintering temperature T_s, (●) apparent permittivity, ε, and (○) loss factor, tan δ, (b) (△) varistor voltage, V_{1mA}, and (□) non-linear coefficient, α, for $SrTiO_3$ + 0.5 mol % Nb_2O_5 + $X/2$ mol % Li_2CO_3, etc., sintered at 1150 °C for 2 h under N_2–30% H_2 (flow rate 20 ml min^{-1}) and then cooled at a rate of 150 °C h^{-1} under oxygen (flow rate 60 ml min^{-1}).

TABLE III Effect of lithium salts on the electrical properties for $SrTiO_3$ + 0.5 mol % Nb_2O_5 + 6 mol % Li^+, etc., sintered at 1150 °C for 2 h under N_2–30% H_2 (flow rate 20 ml min^{-1}) and then cooled at a rate of 150 °C h^{-1} under oxygen (flow rate 60 ml min^{-1})

Li salts	ε ($\times 10^4$)	tan δ (%)	V_{1mA} (V)	α
Li_2CO_3	6.0	4.0	24	14
$LiNO_3$	5.9	4.1	25	14
LiF	4.7	4.1	32	14

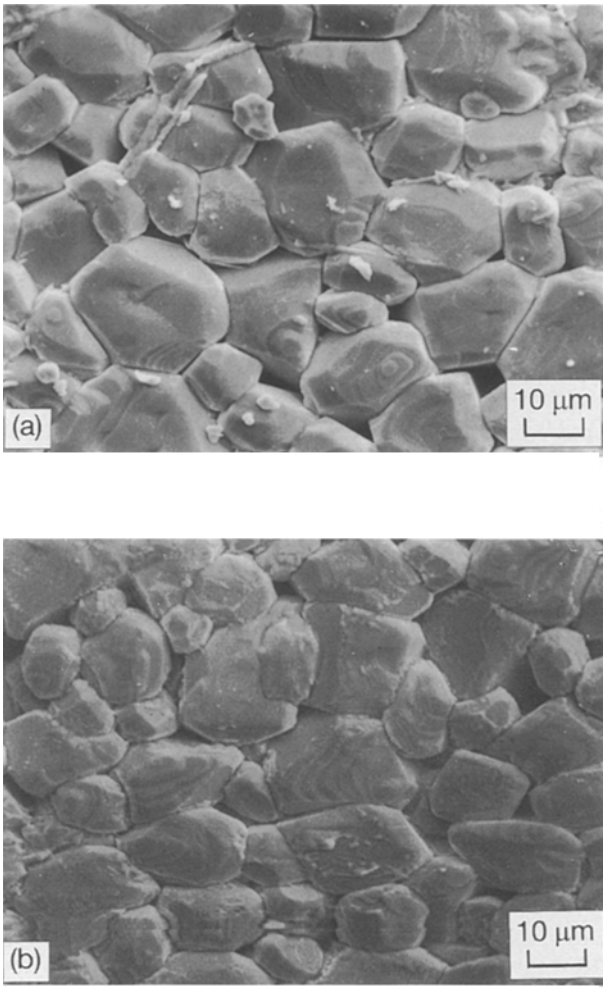

Figure 4 Microstructures corresponding to the materials characterized in Table III: (a) Li_2CO_3, (b) $LiNO_3$, (c) LiF.

influence on the acceptor density of the grain boundaries. When the lithium content is less than 12 mol %, the acceptor density of the grain boundaries increases with increase in lithium content and results in a decrease of tan δ and an increase of ε, V_{1mA} and α. When the lithium content is too high (> 12 mol %), lithium cannot fully segregate to the grain boundaries. Part of the lithium remains at the grains and leads to a weakening of their semiconduction. Therefore, ε, V_{1mA} and α decrease and tan δ increases.

As can be seen in Table III, for the LiF sample, ε is smaller and V_{1mA} is higher, while tan δ and α are very close to those of Li_2CO_3 and $LiNO_3$ samples. However, there are hardly any differences between the Li_2CO_3 and $LiNO_3$ samples. The grain size of the LiF sample is smaller than those of Li_2CO_3 and $LiNO_3$ samples, as shown in Fig. 4. On the other hand, doctor blading is more difficult for LiF and $LiNO_3$ ceramic materials than for Li_2CO_3 ceramic materials. Details about this will be reported separately. Thus, Li_2CO_3 is chosen when fabricating multilayer varistors.

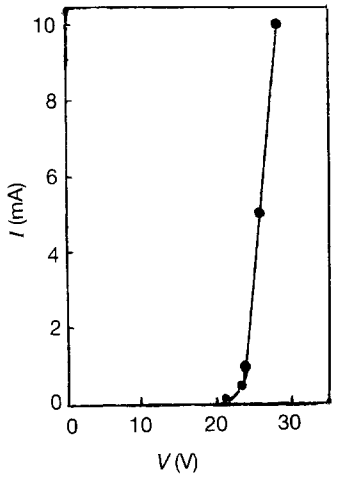

Figure 5 The I–V characteristics for $SrTiO_3$ + 0.5 mol % Nb_2O_5 + 6 mol % Li_2CO_3, etc., sintered at 1150 °C for 2 h under N_2–30% H_2 (flow rate 20 ml min^{-1}) and then cooled at a rate of 150 °C h^{-1} under oxygen (flow rate 60 ml min^{-1}).

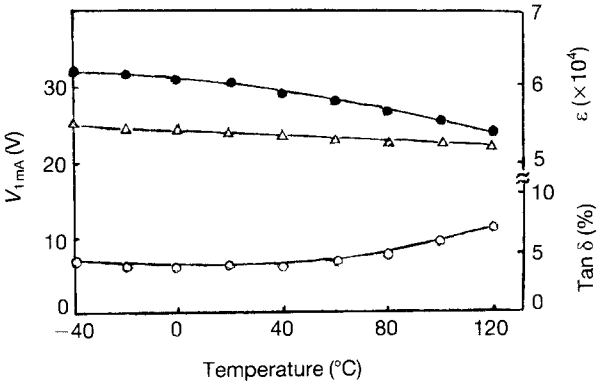

Figure 6 Temperature dependence of (△) V_{1mA}, (●) ε and (○) tan δ for $SrTiO_3$ + 0.5 mol % Nb_2O_5 + 6 mol% Li_2CO_3, etc., sintered at 1150 °C for 2 h under N_2–30% H_2 (flow rate 20 ml min^{-1}) and then cooled at a rate of 150 °C h^{-1} under oxygen (flow rate 60 ml min^{-1}).

The electrical properties of the resultant ceramics ($SrTiO_3$ + 0.5 mol % Nb_2O_5 + 6 mol % Li_2CO_3, etc., sintered at 1150 °C for 2 h under N_2–30% H_2, flow rate 20 ml min^{-1}, and then cooled at a rate of 150 °C h^{-1} under oxygen, flow rate 60 ml min^{-1}) are shown in Figs 5 and 6, from which we can see that these ceramics have excellent varistor and capacitor characteristics. The apparent permittivity, ε, and varistor voltage, $V_{1\ mA}$, change slowly in the temperature region of −40–120 °C. The change of ε against a standard value at 20 °C is 3% at −40 °C and −10% at 120 °C, respectively. The change of V_{1mA} is 4% at −40 °C and −8% at 120 °C, respectively. The value of tan δ remains at about 4% when the temperature changes from −40 °C to 20 °C and increases slowly to 7% when temperature changes from 20 °C to 120 °C.

4. Conclusion

Low-firing $SrTiO_3$ ceramics doped with Nb^{5+} and Li^+, etc., with excellent varistor and capacitor characteristics can be obtained using the "segregating oxidizing method". Nb^{5+} is added to the ceramics as a donor dopant to promote the semiconduction of grains, while Li^+ is added as an acceptor to promote segregation at the grain boundaries to enhance their insulation. The semiconduction of grains is fulfilled at the sintering stage, while the segregation of Li^+ at the grain boundaries is mainly fulfilled at the cooling stage. The correct slow cooling rate and oxygen atmosphere are both favourable to the segregation of lithium, and so result in a decrease of tan δ and improvement of non-linear I–V characteristics. Increasing the lithium content may decrease the sintering temperature and improve the varistor and capacitor characteristics. Conversely, when the lithium content is too high (> 12 mol %), ε decreases. Different lithium salts (Li_2CO_3, $LiNO_3$, LiF) have an influence on the electrical properties of the ceramics.

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