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Effects of SiO_2 and Cr_2O_3 on the formation process of ZnO varistors

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The effects of SiO_2 and Cr_2O_3 on the formation process of ZnO varistors were investigated. Prior to formation of the $Zn_{2.33}Sb_{0.67}O_4$ spinel phase (Sp-phase), a spinel-like phase forms. However, this phase does not control the varistor microstructure. The Sp-phase and the Bi_2O_3-phase which were formed by the decomposition of the $Bi_2(Zn_{4/3}Sb_{2/3})O_6$ pyrochlore phase played important parts in the control of the varistor microstructure. That is, the Bi_2O_3 phase produced in the reaction promotes the initial sintering of the varistor and the Sp-phase inhibits the ZnO grain growth. In this reaction, SiO_2 and Cr_2O_3 play a role in decreasing the decomposition temperature of the pyrochlore phase. Decreasing the decomposition temperature below 900° C (where ZnO grain growth begins) leads to the inhibition of ZnO grain growth.

1. Introduction

The varistor composed of the $ZnO–Bi_2O_3$ system is an electronic ceramic device with excellent voltage–current nonlinear characteristics. These nonlinear characteristics and other electrical properties depend on the varistor microstructure, which is related to the formation process of the varistors. Therefore, it is important in controlling the electrical characteristics of the varistor to clarify the formation process.

The formation process of the varistor was investigated in detail by Inada [1], who studied the formation phases as functions of composition and firing temperature in the $ZnO–Bi_2O_3–Sb_2O_3–Co_2O_3–MnO_2–Cr_2O_3$ system. Inada reported that a $Zn_7Sb_2O_{12}$ spinel is produced through a unknown phase above 1300° C. However, in compositions which do not contain chromium, the spinel phase is produced above 700° C without the formation of the unknown phase. Depending on composition, the spinel formation temperature changes. According to Sainkar *et al.* [2], the spinel was formed above 900° C in the $ZnO–Sb_2O_3$ system.

The effects of Cr_2O_3 and SiO_2 on phases formed in simple compositions (ZnO, Bi_2O_3, CoO, MnO_2, Sb_2O_3) have been investigated in detail. Cr_2O_3 reacts with Bi_2O_3 to form $12Bi_2O_3 \cdot Cr_2O_3$ above 900° C and to form $14Bi_2O_3 \cdot Cr_2O_3$ under 900° C [1]. SiO_2 is an essential element for the formation of the zinc orthosilicate phase [3].

However, in systems which contain more components (ZnO + Bi_2O_3 + CoO + Sb_2O_3 + other additives), the effects of Cr_2O_3 and SiO_2 on the spinel formation and ZnO grain growth have not been clarified sufficiently. It is the object of this paper, therefore, to clarify the effects of Cr_2O_3 and SiO_2 on the formation reactions of ZnO varistors in multi-component systems.

2. Experimental details

In this study, four compositions were used. Table I shows additives to the base composition which consists of ZnO, Bi_2O_3, CoO, Sb_2O_3, and other additives.

The varistor component powders were mixed in water for 24 h, dried, granulated and pressed into cube compacts with a length of 5 mm. The samples were obtained by heating compacts at the rate of 200° C h^{-1} and dropping them into water at the desired temperatures. The identification of the phases formed in the quenched samples was carried out by powder X-ray diffraction (XRD) method. In order to resolve the small peaks better, XRD was also done on samples etched with 4 N HCl solution to remove the ZnO phase.

Compacts were also used for differential thermal analysis (DTA) (TGD-3000, Shinkuriko). The thermal shrinkages of compact samples (5 mm × 5 mm × 30 mm) were measured at the rate of 10° C min^{-1}.

The grain sizes were investigated using samples which were obtained by heating compacts (25 mm × 2 mm) at the rate of 100° C h^{-1} and sintering them at 1250° C for 2 h.

3. Results and discussion

3.1. Formation reactions and phases formed

Fig. 1a shows the XRD patterns of the samples, composition H1, which were quenched at various

TABLE I Additives to the base composition

Sample	SiO_2	Cr_2O_3
H1	–	–
H2	x	–
H3	–	x
H4	x	x

Notes: 1. The base composition consists of ZnO, Bi_2O_3, CoO, Sb_2O_3, and other additives.
2. "x" indicates the addition of the element to the base composition.

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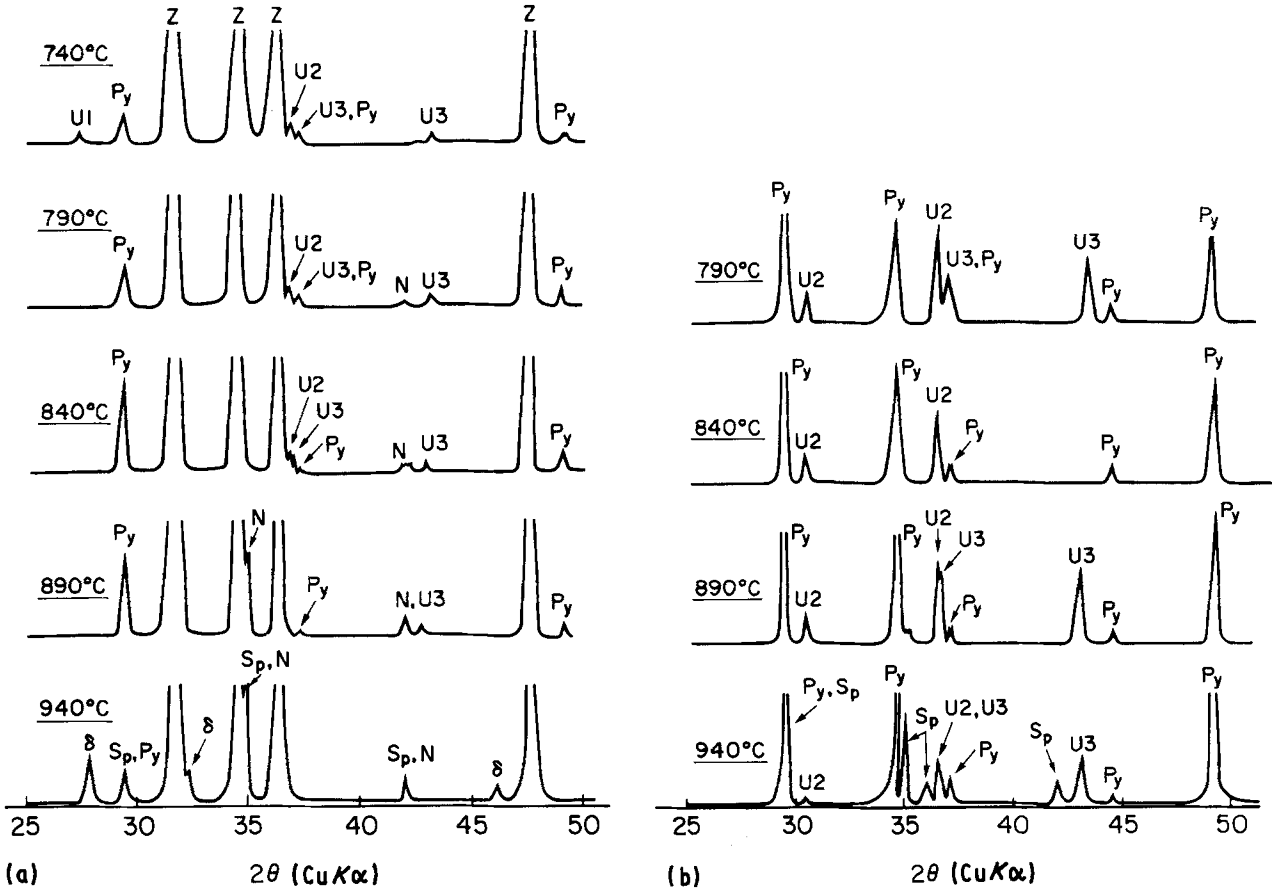

Figure 1 X-ray diffraction patterns of (a) samples (composition H1) quenched at various temperatures, (b) etched samples.

temperatures and Fig. 1b shows those of the etched samples.

At 740° C, a ZnO phase (Z-phase), $Bi_2(Zn_{4/3}Sb_{2/3})O_6$ pyrochlore phase (Py-phase) and unknown phases (U1, U2, and U3 phases) were present. The main peaks for the unknown phases appeared at $2\theta = 27.7°$ (X1 peak), 36.9° (X2 peak), and 43.3° (X3 peak), respectively. These phases are not the Py-phase or the Sp-phase because these peaks do not agree with the peaks of those phases. In addition, they have not been reported previously. Although the X1 peak might indicate a Bi_2O_3 phase because the main peaks of the Bi_2O_3 phases appear at $2\theta \approx 28°$, it is too small to identify.

At 790° C, the X1 peak has disappeared and a new phase (N-phase) has appeared at 42.1°, which is almost the same angle as that of the Sp-phase. Although the extraction of the new phase was tried, this phase dissolved together with the Z-phase in the HCl solution.

At 840° C, the peak height of the new phase has increased slightly, but the diffraction pattern showed a broad peak. This new phase dissolved in HCl solution. The X3 peak shifted down 0.3°, and the phase corresponding to this peak dissolved in the HCl solution.

At 890° C, although the peak of the new phase is sharp and its height has increased, the phase dissolved in HCl solution. On the other hand, the X2 and X3 peak heights have decreased. The X2 peak shifted down 0.3°, but the X3 peak did not shift. However, the phase corresponding to the X3 peak did not dissolve in the HCl solution.

At 940° C, it can be seen from Fig. 1a that the Py-phase and the unknown phases corresponding to the X2 and X3 peaks have disappeared and the Sp-phase and the δ-Bi_2O_3 phase have appeared. A large amount of the Py-phase is observed in Fig. 1b. A possible reason might be that phases other than the Py-phase partially dissolved in the HCl solution. As a result, the remainder became rich in the Py-phase.

Table II shows the results for all the samples. As mentioned above, the new phase appeared at almost the same angle as that of the Sp-phase, even though it dissolved in HCl solution. In addition, although the peak height of the new phase increased with an increase in temperature, it disappeared with the appearance of the Sp-phase. Therefore, these facts lead to the inference that the structure of the new phase has a strong resemblance to that of the Sp-phase: that is, the new phase is a kind of precursor to the Sp-phase. However, no attempts have been made to characterize the unknown phases corresponding to the X1, X2 and X3 peaks.

Fig. 2 shows the DTA curves of samples H1 to H4. The starting temperatures of the endothermal reaction are 910° C in H1, 820° C in H2, 820° C in H3 and 820° C in H4. These temperatures almost coincide with the starting temperatures of the Sp-phase formation in Table II. It is well known that the Sp-phase is formed by the decomposition of the Py-phase according to the following formula [4]

$$Bi_2(Zn_{4/3}Sb_{2/3})O_6 \overset{ZnO}{\rightleftharpoons} Zn(Zn_{4/3}Sb_{2/3})O_4 + Bi_2O_3$$

Therefore, the decomposition reaction of the pyrochlore is an endothermal reaction. The sample H1

TABLE II Phases formed in samples fired at several temperatures

Sample	Quenching temperature (° C)					
	740	790	840	890	940	(1250)
H1	Py, U1, U2, U3	Py, N, U2, U3	Py, N, U2, U3	Py, N, U2, U3	N, Sp, δ, U2, U3, Py	Sp, β
H2	Py, U1, U2, U3	Py, N, U2, U3, ZS	Py, N, Sp, δ, U2, U3, ZS	Py, Sp, δ, N, U2, U3, ZS	Sp, δ, ZS	Sp, β, ZS
H3	Py, A, U2, U3	Py, N, A, U2, U3	Py, N, Sp, δ, U2, U3	Py, Sp, δ, U2, U3	Sp, δ	Sp, β, δ
H4	Py, N, A, U2, U3	Py, N, δ, U2, U3, ZS	N, Sp, δ, U2, U3, ZS	Sp, δ, ZS	Sp, δ, ZS	Sp, β, δ, ZS

Notes: 1. "(1250)" indicates a firing temperature.
2. "A" indicates the Bi_2O_3 phase which corresponds to that reported by Inada [1].
3. "ZS" indicates Zn_2SiO_4 phase.

shows a sharp endothermal peak, while the samples H2, H3, H4 show broad endothermal patterns. In addition, the starting temperatures of the endothermal reactions in H2, H3 and H4 are lower than that of H1. A possible reason is that because the Py-phase has a defect structure [5], silicon and chromium could dissolve into the pyrochlore, and their dissolution would make the structure unstable. Consequently, silicon and/or chromium-doped Py-phase can transform into the Sp-phase at the lower temperatures.

3.2. Sintering of ZnO

Fig. 3 shows the shrinkage curves of H1 and H4. The shrinkage starts at 800° C and reaches 10% at 950° C in H4. On the other hand, in H1, the shrinkage begins at 900° C and reaches 10% at 950° C. it is characteristic of H1 that the starting temperature of shrinkage is 100° C higher than that of H4, the shrinkage is very sharp and the final shrinkage is smaller than that of H4 (it is 20% in H1 and 22% in H4.).

The green densities of the compact samples (5 mm × 5 mm × 30 mm) of H1 and H4 were 2.55 and 2.34 g cm^{-3}, while final sintering densities were 5.42 and 5.45 g cm^{-3}, respectively.

The sintering reaction of ZnO can be explained as follows. As mentioned above, because the decomposition of the Py-phase occurred over a wide range of temperatures between 800 and 900° C in H4, the yield rate of liquid Bi_2O_3 is slow in H4. Therefore, over a short period of time, sufficiently high capillary pressures of viscous Bi_2O_3, which are the driving force for densification, were not produced and the rearrangement of ZnO particles did not take place. Consequently, the rate of the initial sintering was very slow, and the shrinkage of H4 was not abrupt. In addition, because the Bi_2O_3 phase was formed earlier in H4 than H1, the initial sintering began earlier and the starting temperature of the shrinkage was lower in H4. Moreover, the reason why the final shrinkage of H4 was greater than that of H1 can be explained by the difference of the green densities.

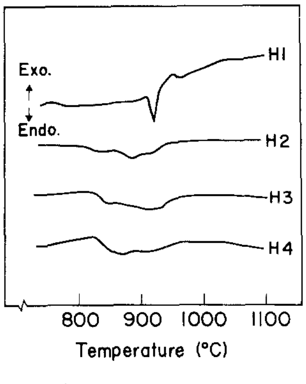

Figure 2 DTA curves of samples H1 to H4.

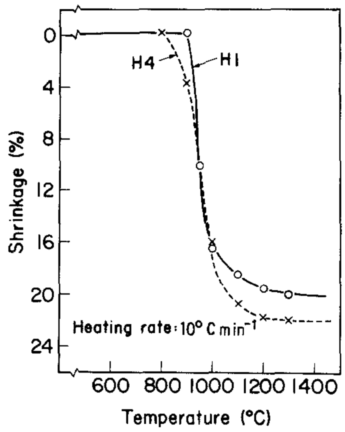

Figure 3 Thermal shrinkage curves of samples H1 to H4.

3.3. Grain growth of ZnO

Fig. 4 shows scanning electron micrographs. The samples were sintered at 1250° C for 2 h, mirror-polished and thermally etched at 900° C for 0.5 h. The grain sizes of ZnO are 21 μm for H1, 14 μm for H2, 14 μm for H3 and 14 μm for H4. Because the Sp-phase formed below 900° C in H2, H3 and H4, the spinel particles impeded the ZnO grain growth which begins at temperatures over 900° C [6]. In H1, however, the grain growth occurred coincidently with the spinel formation. Therefore, the grain growth took place more easily in H1 than in the others.

TABLE III Lattice constants of β-Bi_2O_3

Sample	Lattice constant (nm)	
	a	*c*
H1	1.108	0.548
H2	1.096	0.548
H3	1.080	0.570
H4	1.078	0.570

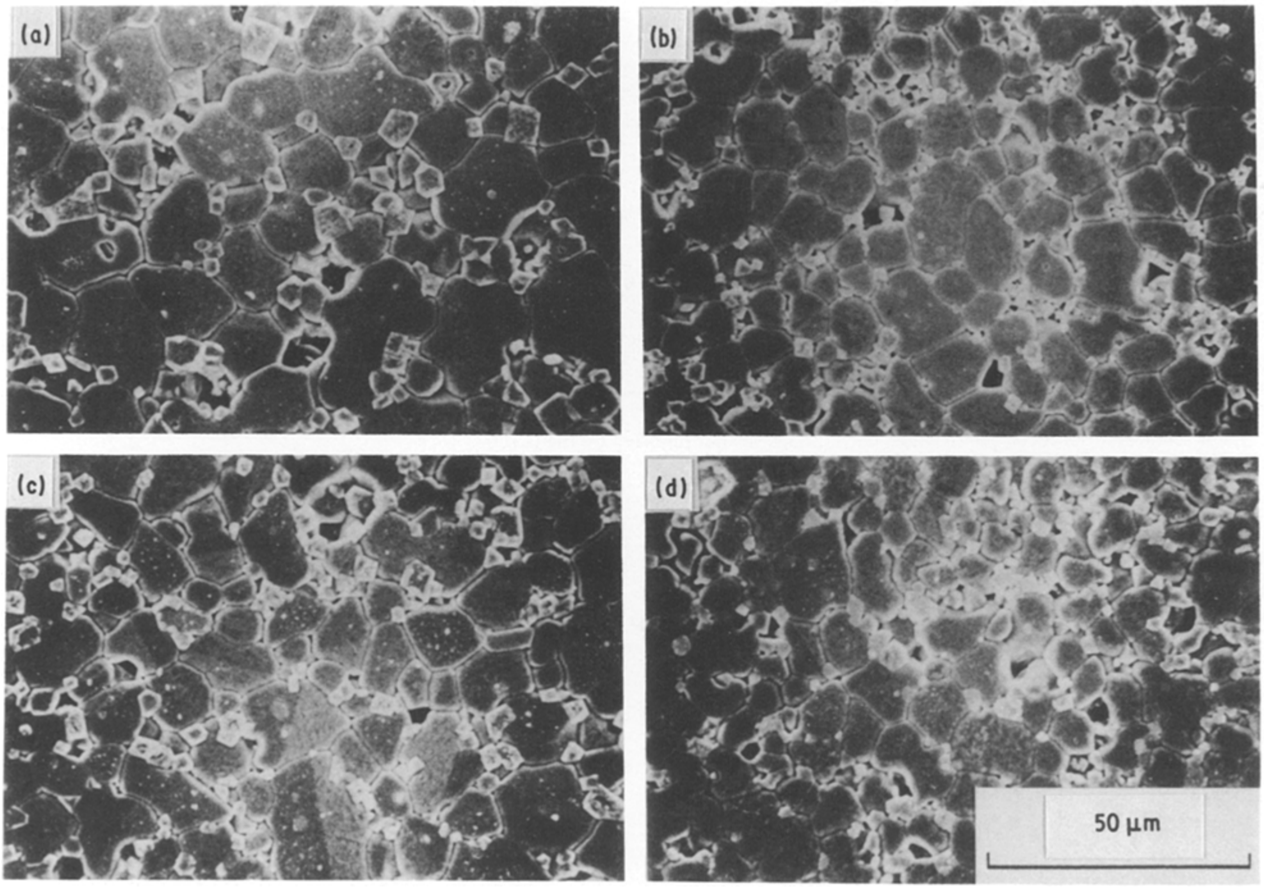

Figure 4 Scanning electron micrographs of samples H1 to H4 fired at 1250° C for 2 h. (a) H1, (b) H2, (c) H3, (d) H4.

3.4. Bi_2O_3 phase

The phase identification of all samples sintered at 1250° C was carried out. Although the ZnO phase, Bi_2O_3 phase and the spinel phase existed in all the samples, remarkable differences were observed in the Bi_2O_3 phase. In the case of H1 and H2 (H1 + SiO_2), it was β-phase, while in the case of the compositions with Cr_2O_3 added, it was a combination of β-phase and δ-phase. The δ-phase is a stable phase at high temperatures. Therefore, it can be concluded that Cr_2O_3 renders the δ-phase stable at room temperature without a phase transformation to the β-Bi_2O_3 in the cooling process.

Table III shows the lattice constants of the β-Bi_2O_3. Although the Bi_2O_3 phase did not change due to the addition of SiO_2, the *a*-axis shrunk by 1.1%. On the other hand, the addition of Cr_2O_3 caused the *a*-axis to shrink by 2.5% and the *c*-axis to expand by 4.0%. Therefore, the SiO_2 dissolved into Bi_2O_3 and transformed the lattice without a phase transformation, while the Cr_2O_3 transformed the lattice and the phase of Bi_2O_3.

4. Conclusions

1. SiO_2 and Cr_2O_3 played a role in decreasing the formation temperature of the Sp-phase. Because the addition of SiO_2 or Cr_2O_3 caused the formation temperature to decrease below 900° C, which nearly equals the starting temperature of the grain growth of ZnO, the Sp-phase produced by the decomposition reaction of the pyrochlore phase impeded the grain growth of ZnO.

2. Although a spinel-like phase formed prior to the $Zn_{2.33}Sb_{0.67}O_4$ spinel, the phase did not control the varistor microstructure.

3. SiO_2 played a part in transforming the Bi_2O_3 lattice without a phase transformation. On the other hand, Cr_2O_3 played a part in stabilizing the δ-Bi_2O_3 phase.

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