

# On the phases formation in the calcination process of ZnO varistor

J. P. MAH, J. S. CHOI, S. H. PAEK

*Department of Materials Engineering, Engineering College, Hanyang University, Seoul, 133-791, Korea*

The degree of phase formation was investigated by  $\text{Sb}_2\text{O}_3$  behaviour in the calcination process, and the change of microstructure and breakdown properties due to the phases formation in ZnO varistor. The samples were calcined at several temperatures for 2 h and were sintered at 1150 to 1300°C, respectively, for 1 h. After that,  $V-I$  characteristics were investigated. Phase analysis by X-ray diffraction and microstructures observation by SEM were done. As a result, spinel phase was not formed and low nonlinear resistance was shown in the samples without  $\text{Sb}_2\text{O}_3$ . In the samples containing  $\text{Sb}_2\text{O}_3$ , it was shown that the pyrochlore and spinel phase are formed at the conventional calcination temperature or even below that temperature. This primary spinel phase and the spinel phase transformed from pyrochlore phase in sintering process inhibit ZnO grain growth, and so nonlinear resistances should be changed. Hence ZnO grain growth in ZnO-based varistor system is strongly dependent on the  $\text{Sb}_2\text{O}_3$  behaviour in the calcination process.

## 1. Introduction

Varistors as a transient overvoltage protection device have been investigated with the ZnO-based metal oxide system since 1957. In the early 1970s Matsuoaka [1] reported that slight additions of  $\text{Bi}_2\text{O}_3$ ,  $\text{MnO}$ ,  $\text{CoO}$ ,  $\text{Cr}_2\text{O}_3$  and  $\text{Sb}_2\text{O}_3$  to ZnO raise the nonlinear exponent ( $\alpha$ ) up to 50.

ZnO varistors are composed of ZnO grains, dissolved cobalt and manganese, Bi-rich phase (pyrochlore phase, etc.) and spinel phase [2-8]. Of these additive oxides, Bi, Co, Mn-oxides increase the nonlinear exponent value,  $\text{Sb}_2\text{O}_3$  forms spinel phase ( $\text{Zn}_7\text{Sb}_2\text{O}_{12}$ ) and  $\text{Cr}_2\text{O}_3$  stabilizes that spinel phase [9].

Besides, Wong [5] reported that the intergranular pyrochlore phase which develops the ZnO grain is related directly with the breakdown properties of the ZnO varistor, and spinel phases which are located at the grain boundaries has an indirect effect of inhibiting ZnO grain growth by their distributed shape of discrete faceted crystal. The pyrochlore phase contributes to the breakdown properties and the spinel phase raises the nonlinear resistance ( $C$ ) by its inhibiting effect for ZnO grain growth. Wong also found that pyrochlore phases are transformed to spinel phases in a high temperature sintering process [5].

But, in the initial stage of varistor fabrication using ceramic powders, the calcination process must be done and at a temperature of 700°C, or higher. Then, at the calcination temperature,  $\text{Sb}_2\text{O}_3$  of m.p. 656°C, should be melted and has strong mobility. So,  $\text{Sb}_2\text{O}_3$  combines easily with ZnO and  $\text{Bi}_2\text{O}_3$ . As a result, pyrochlore and spinel phase would be formed at that stage.

In this study, we expect the possibility of phase

formation by  $\text{Sb}_2\text{O}_3$  behaviour in the calcination process and consider the effects that those phases affect ZnO grain growth in the subsequent sintering process with non-ohmic properties and microstructural characteristics. We will show the role of the calcination process and  $\text{Sb}_2\text{O}_3$  behaviour in the varistor characteristics.

## 2. Experimental procedure

### 2.1. Sample preparations

2N purity of ZnO and an extra pure grade of additive oxides were used. As shown in Table I, type AS and type NS were prepared. Then, they were mixed in plastic container with methyl alcohol and plastic balls for 3 h, and were dried sufficiently. After that, samples were calcined at several temperatures for 2 h, as shown in Table II. They were then mixed for 10 h and pressed into discs of 11 mm in diameter and 2 mm in thickness at a pressure of 0.8 ton  $\text{cm}^{-2}$ . The compacts were sintered at temperatures ranging from 1150 to 1300°C in air, furnace-cooled to 600°C and air-cooled to room temperature.

### 2.2. Voltage-current characteristics

Both sides of samples were coated with silver paste and then were fired at 300°C for 3 h to make ohmic electrodes. The voltage-current characteristics of samples were measured by a d.c. power supply in a current range from  $10^{-6}$  to  $10^{-1}$  A. The  $V-I$  characteristics of ZnO varistors are expressed by the following empirical equation (1).

$$I = (V/C)^{\alpha} \quad (1)$$

Where, the nonlinear resistance,  $C$ , is defined by a

TABLE I Composition of the sample

	Type AS (md %)	Type NS (md %)
ZnO	97.0	98.0
Bi <sub>2</sub> O <sub>3</sub>	0.5	0.5
Co <sub>2</sub> O <sub>3</sub>	0.5	0.5
MnO <sub>2</sub>	0.5	0.5
Cr <sub>2</sub> O <sub>3</sub>	0.5	0.5
Sb <sub>2</sub> O <sub>3</sub>	1.0	0

voltage per unit length ( $V\text{mm}^{-1}$ ) when  $1\text{mA cm}^{-2}$  of current flows through the body and nonlinear exponent,  $\alpha$ , is calculated by the following equation.

$$\alpha = \frac{dI/I}{dV/V} = \frac{(\ln I)}{(\ln V)} = \frac{\ln I_2 - \ln I_1}{\ln V_2 - \ln V_1} \quad (2)$$

### 2.3. Microstructure and phase analysis

The samples sintered at 1200 and 1300°C, respectively, were fine-polished and etched by 1 : 1000 HClO<sub>4</sub> aqueous solution, and their microstructures were observed with SEM. Besides, model samples with the composition of 50 ZnO–25 Bi<sub>2</sub>O<sub>3</sub>–25 Sb<sub>2</sub>O<sub>3</sub> were fabricated and their X-ray diffraction peaks were analysed to find the formation possibility of pyrochlore and spinel phase in the calcination process. Also, the relative intensities of X-ray peaks which reveals the amount of spinel phase for each calcination condition.

## 3. Results and discussion

### 3.1. Sb<sub>2</sub>O<sub>3</sub>-added samples

In the AS-type samples, change of  $\alpha$  and  $C$  value with the calcination temperatures are shown in Fig. 1 for the various sintering temperatures. In Fig. 1, up to 700°C,  $\alpha$  and  $C$  values increased at all sintering temperatures, and above 700°C, those values decreased. Above 700°C calcination, Sb<sub>2</sub>O<sub>3</sub> should be liquidized and its mobility must be higher. Then high movable Sb<sub>2</sub>O<sub>3</sub> can easily form the spinel phase, etc. in calcination process. And so the calcination process seems to play an important role to the varistor properties.

To confirm it, the X-ray diffraction pattern shown in Fig. 2 for the model sample with composition of 50ZnO–25Bi<sub>2</sub>O<sub>3</sub>–25Sb<sub>2</sub>O<sub>3</sub> which was calcined at 700°C was analysed. In Fig. 2 it was confirmed that

TABLE II Sample number and calcination temperature

Type	Sample no.	Calcination temperature (°C)
AS	AS0	(not calcined)
	AS5	500
	AS7	700
	AS8	800
NS	NS0	(not calcined)
	NS5	500
	NS7	700
	NS8	800

spinel and pyrochlore phase, etc., are formed in the calcination process. And, in the case of the calcination temperature below the m.p. of Sb<sub>2</sub>O<sub>3</sub>,  $C$  and  $\alpha$  values were lower than those of AS7. Increase of  $C$  value means reduction of ZnO grain size and increase of  $\alpha$  value means sharper breakdown property. Reduction of  $C$  value is caused by formation of spinel phase which inhibits ZnO grain growth. Therefore, in the case of the calcination temperature below a m.p. of Sb<sub>2</sub>O<sub>3</sub>, those Sb<sub>2</sub>O<sub>3</sub> would form a spinel phase and pyrochlore phase or little is formed. In the subsequent sintering process very small amounts of spinel and pyrochlore phase forms and grows, and then, a part of the pyrochlore phase can be transformed to the spinel phase, however, the major part of Sb<sub>2</sub>O<sub>3</sub> should remain in its original state. During the sintering process, they would vaporize, and then the amount of spinel phase would be largely decreased, thus the effect of inhibiting ZnO grain growth is contracted, finally, largely grown, i.e., unstable ZnO varistors are formed. In fact, the model sample calcined at 500°C had relatively weaker X-ray peaks of spinel and pyrochlore phase which were not shown in Fig. 2.

In the calcination process for AS7, spinel and pyrochlore phases are formed and in the subsequent sintering those phases grow and inhibit effectively ZnO grain growth, and as a result, maximum  $C$  and  $\alpha$  values are revealed.

Also, SEM microstructures of AS0 and AS7 sintered at 1200 and 1300°C are shown in Fig. 3. In Fig. 3 the grain size of AS0 sintered at 1300°C is much larger than that of AS7, so we found that spinel phase, etc., formation in calcination process plays an important role in the final ZnO grain size.

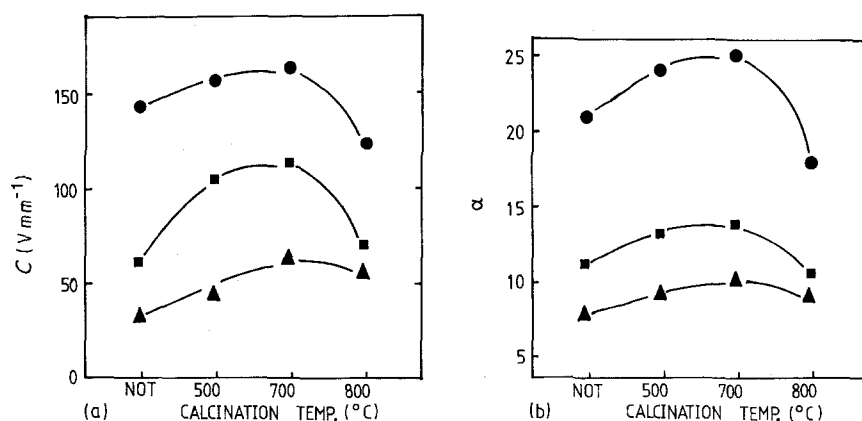


Figure 1 (a)  $C$  and (b)  $\alpha$  values of samples with added Sb<sub>2</sub>O<sub>3</sub>. (●) 1200°C sintered, (■) 1250°C, (▲) 1300°C.

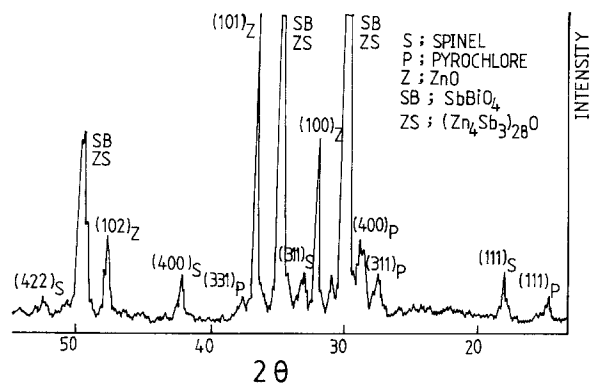


Figure 2 X-ray diffraction peaks of model-sample at 700°C for 2h. CuK $\alpha$  was used, 0.90 kV. S.S. (scanning speed) 40 min<sup>-1</sup>, C.S. (counting speed) 4 cm min<sup>-1</sup>.

And, AS8 calcined at quite higher temperatures than the m.p. of Sb<sub>2</sub>O<sub>3</sub> showed lower  $\alpha$  and  $C$  values than those of AS7, and it was considered that the net amount of pyrochlore and spinel phase is decreased by vaporization of a part of Sb<sub>2</sub>O<sub>3</sub> at the condition of 800°C and thus a relatively small amount of the basic varistor structure may be formed.

### 3.2. Samples without Sb<sub>2</sub>O<sub>3</sub>

$C$  and  $\alpha$  values of NS-type samples with several conditions are shown in Fig. 4. The change of  $C$  and  $\alpha$  values for all sintering and calcination conditions was very small. In Fig. 4 it was considered the reason why all the  $C$  values are lowered, was the absence of inhibiting factor for ZnO grain growth, i.e. pyrochlore and spinel phase were not formed with and without Sb<sub>2</sub>O<sub>3</sub>. This was confirmed also by SEM microstructure (Fig. 5) representing ZnO grain size with sintering temperatures. That is, in Fig. 5, the higher the sintering temperature, the larger the ZnO grain size without depending on calcination temperature.

### 3.3. Degree of $C$ -value variation

Sb<sub>2</sub>O<sub>3</sub> behaviour in the calcination process may be appreciated by consideration of the degree of  $C$ -value variation with sintering temperatures. The fractions of  $C$ -value variation for the samples with and without Sb<sub>2</sub>O<sub>3</sub> are shown in Fig. 6, respectively.

In the case of Sb<sub>2</sub>O<sub>3</sub>-added, those values of the samples calcined at below the m.p. of Sb<sub>2</sub>O<sub>3</sub> were very high and the samples calcined at above the m.p. of

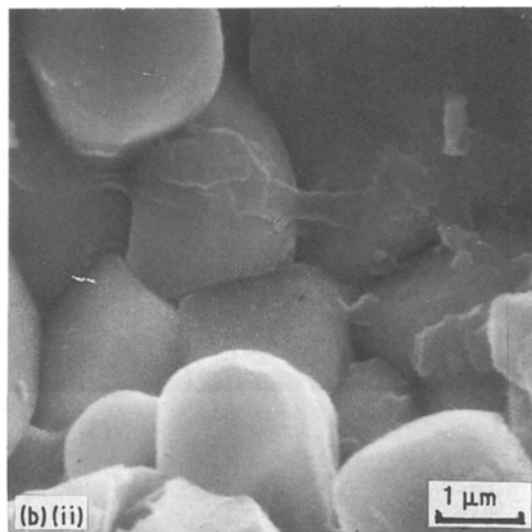
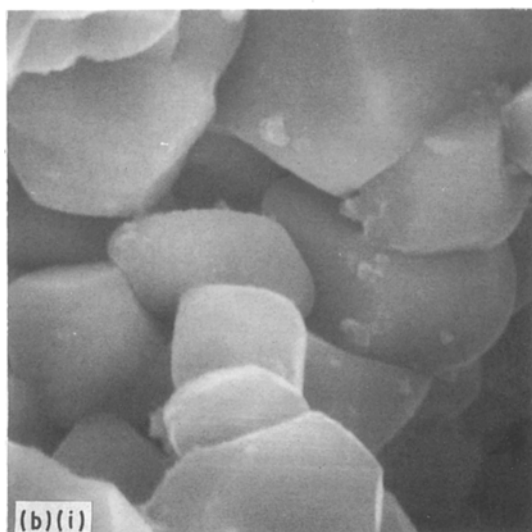
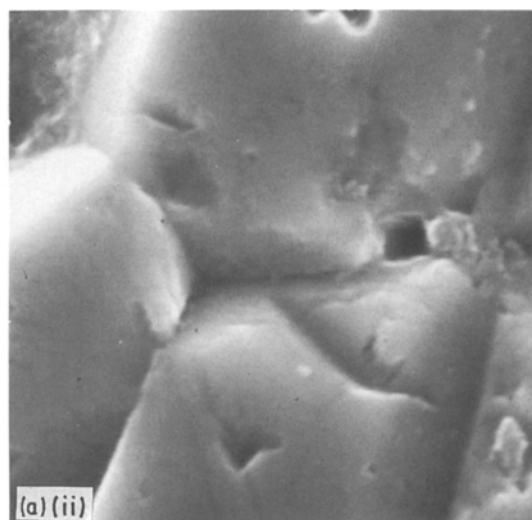
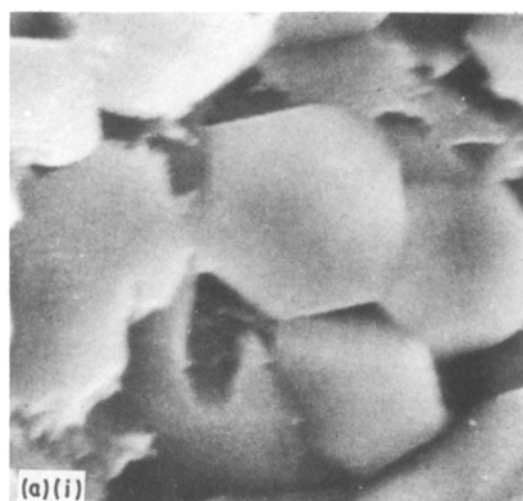


Figure 3 SEM micrographs of (a) ASO and (b) AS7 sintered at (i) 1200°C and (ii) 1300°C.

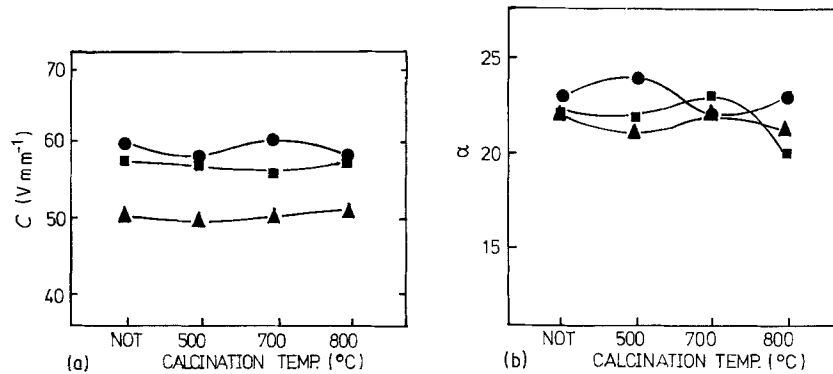


Figure 4 (a)  $C$  and (b)  $\alpha$  values of samples without  $\text{Sb}_2\text{O}_3$ . (●) 1200°C sintered, (■) 1250°C, (▲) 1300°C.

$\text{Sb}_2\text{O}_3$  had relatively low values. It is, as mentioned above, confirmed that the melting of  $\text{Sb}_2\text{O}_3$  should be possible to form the spinel phase which plays an inhibiting role to ZnO grain growth in the subsequent sintering process. In the case of the absence of  $\text{Sb}_2\text{O}_3$ , formation of the spinel phase is impossible and thus ZnO grain growth does not depend on calcination temperature, and the degree of  $C$ -value variation was very small.

And, in the case of the samples without  $\text{Sb}_2\text{O}_3$ ,  $C$ , values were much smaller than that of others with  $\text{Sb}_2\text{O}_3$ , and it revealed the different shape of breakdown characteristics. So, in both cases of  $\text{Sb}_2\text{O}_3$ -added and without- $\text{Sb}_2\text{O}_3$ ,  $I$ - $V$  characteristics of the samples sintered at 1200 after 700°C calcination are shown in Fig. 7. As expected the breakdown point of the sample without  $\text{Sb}_2\text{O}_3$  was quite low, so it seemed to be a low voltage varistor. Therefore, we

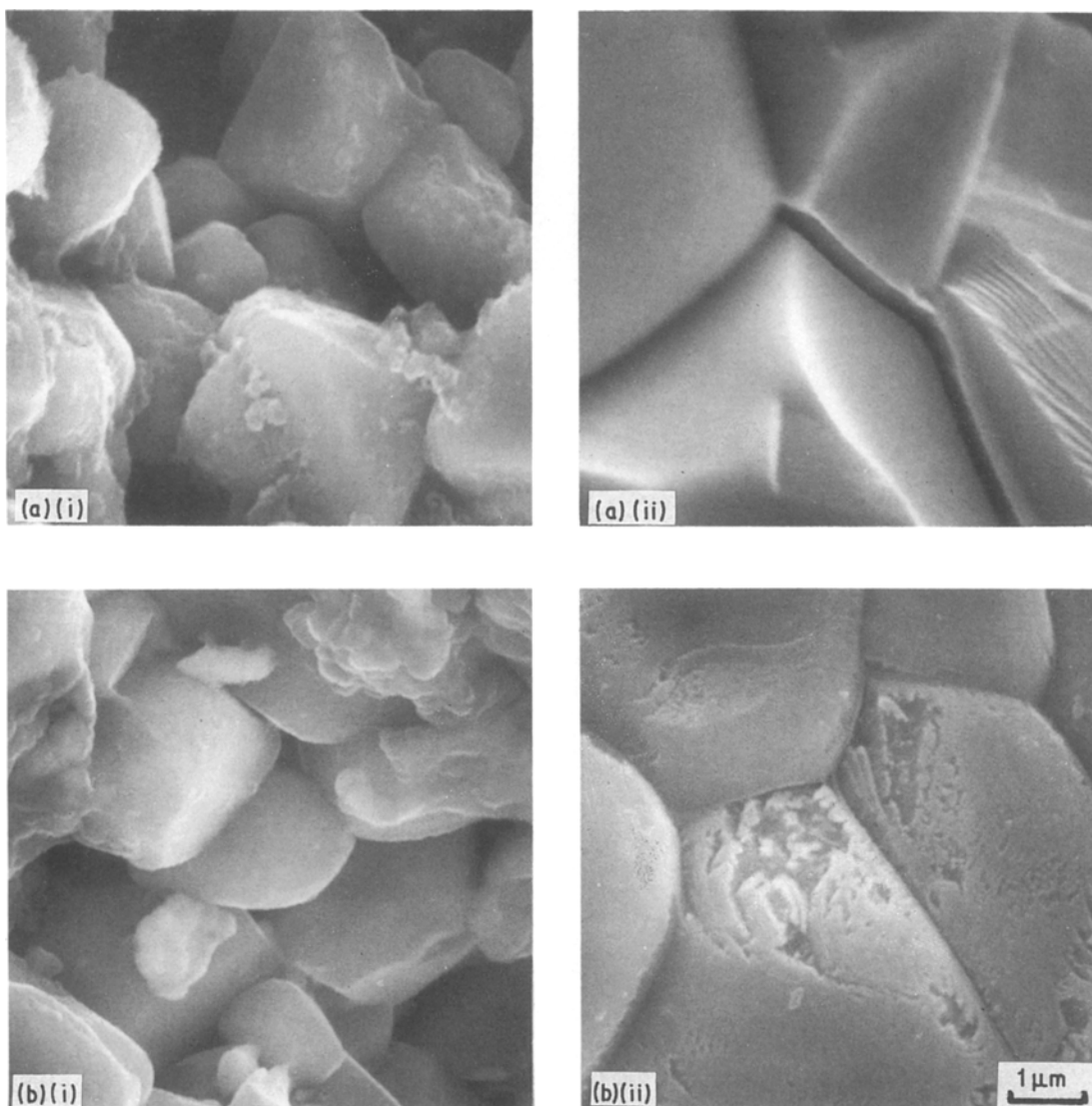


Figure 5 SEM micrographs of (a) NSO and (b) NS7 sintered at (i) 1200°C and (ii) 1300°C.

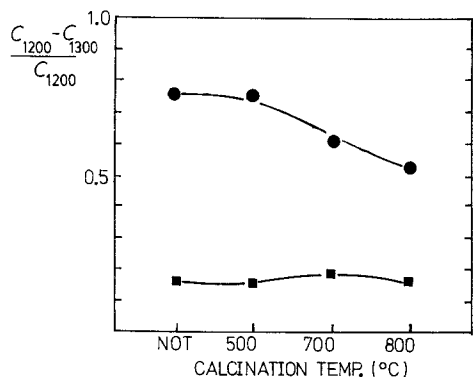


Figure 6  $(C_{1200} - C_{1300})/C_{1200}$  as a function of calcination temperature. (●) With  $\text{Sb}_2\text{O}_3$ , (■) without  $\text{Sb}_2\text{O}_3$ .

reconfirmed that the spinel phase which was formed in the calcination process plays a very important role in the  $C$ -value.

If a low  $C$ -value varistor is required, no  $\text{Sb}_2\text{O}_3$  shown in Fig. 7. As expected the breakdown point calcination process plays an important role in the property of ZnO varistor.

In summary, the ZnO varistor system which could not form the spinel phase in the absence of  $\text{Sb}_2\text{O}_3$  cause active ZnO grain growth and showed low non-linear resistance. And, in the case of the  $\text{Sb}_2\text{O}_3$ -added system, it was found that the pyrochlore and spinel phase forms already in the calcination process. And we found that the primary spinel phase formed in that process and the spinel phase transformed from the pyrochlore phase during sintering inhibit ZnO grain growth and, therefore, strongly affect the nonlinear resistance. By the change of  $\text{Sb}_2\text{O}_3$  behaviour in the calcination condition, the amount of the spinel phase

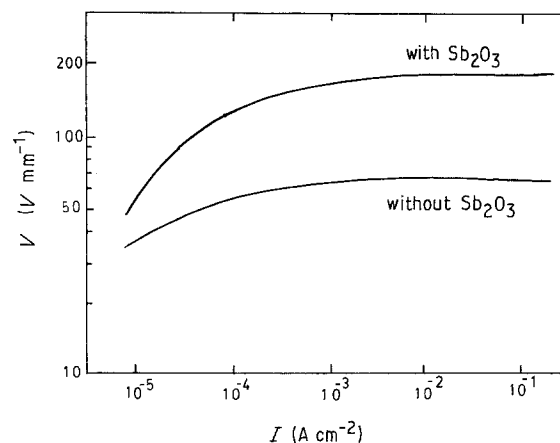


Figure 7  $I$ - $V$  curves of samples sintered at  $1200^\circ\text{C}$ .

was controlled and the base of ZnO grain growth was established. So, we found that the varistors which had the breakdown voltage required for each application could be fabricated.

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