



The Role of Co Ions on the Appearance of Non-linear I-V Characteristics in ZnO based Ceramics

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Abstract. The addition of transition metal elements such as Co is necessary to realize highly non-linear ZnO based varistors. The relation between the oxidation states of Co ions and the appearance and disappearance of the non-linear *I-V* characteristics was studied in ZnO-CoO based compositions. Pressed bodies were sintered at 1430°C in an oxygen atmosphere followed by annealing at various temperatures in air. The *I-V* characteristics of these specimens were then measured. The appearance and disappearance of the non-linear *I-V* characteristics was found to reversibly occur depending on the annealing temperatures and to be closely related to the oxidation states of the Co ions.

Keywords: grain boundary, interface state, non-linear *I-V* characteristics, oxidation state

1. Introduction

Both ZnO-Pr₆O₁₁ and ZnO-Bi₂O₃ based varistors are widely used to suppress transient voltage surges in order to protect electronic devices and instruments. These varistors contain transition metal elements such as Co. Moreover, the role of Co ions has not been clarified. Mukae et al. proposed that Co oxide and Pr oxide released oxygen during the firing process and the oxygen atoms were adsorbed at the grain boundaries to form interface states [1,2]. These interface states are the origin of the double Schottky barriers leading to the non-linear *I-V* characteristics. However, the conditions during firing for release of oxygen and of the formation of the interface states may be different. The release of oxygen occurs during the heating process and the adsorption of oxygen is considered to occur during the cooling process. There are no reasons why the adsorbed oxygen must be released from the Co oxide or Pr oxide.

In this experiment, the relation between the oxidation condition and the appearance and disappearance of the non-linear *I-V* characteristics of sintered bodies of ZnO-CoO based compositions was studied. The *I-V* characteristics of the sintered

bodies fired at 1430°C in an oxygen atmosphere with grain sizes as large as 100 μm were investigated under various annealing temperatures. For comparison, the ones fired at 1280°C in air were also investigated.

2. Experimental

The raw materials of the compositions shown in Table 1 were weighed and mixed in polyethylene pots with nylon-molded steel balls using ion-exchanged water and then dried in porcelain vats. All compositions contained Al₂O₃ as a donor. The dried materials were granulated with PVA and pressed into discs. The pressed bodies were fired at 1430°C in an oxygen atmosphere (about 1013 hPa) for 4 h and then annealed at various temperatures in air for 4 h. Both the heating and cooling rates were 200°C/h. An In-Ga alloy was applied to both sides of the sintered and annealed discs as electrodes. The *I-V* characteristics were measured with constant current pulses using a digital voltmeter. DTA and TGA were performed on the No. 2 composition.

Pressed bodies of the No. 2 and No. 3 compositions were fired at 1280°C in air for 4 h. Some of these

Table 1. Compositions and I-V characteristics of specimens fired at 1280°C in air for 4 h

No.	Components (mol %)				Non-linearity	
	ZnO	Pr ₆ O ₁₁	CoO	Al ₂ O ₃	V _{1mA}	α
1	99.979	0.020	0.000	0.001	0.4	1.0
2	98.479	0.020	1.500	0.001	127	22
3	98.499	0.000	1.500	0.001	84	12

specimens were annealed at 700°C in air for 4 h and their I-V characteristics were then measured.

3. Results

The microstructures of the sintered bodies are shown in Fig. 1. The grain diameters of the specimens having the No. 1 and No. 2 compositions fired at 1430°C in an oxygen atmosphere were about 100 μ m. The non-linear I-V characteristics (non-linear index: α and varistor voltage: V_{1mA}) of each specimen are shown in Table 2. The non-linear index is defined by the following equation. That is, $I = (V/C)^\alpha$, where I is current, V is voltage and C is a constant. The varistor voltage is that at which a current of 1 mA passes. It is clear that specimens without Co ions exhibited no non-linear I-V characteristics. The non-linear indices and varistor voltages of the annealed specimens with the No. 2 composition at various temperatures are

Table 2. I-V characteristics of specimens fired at 1430°C in O₂ for 4 h

Anneal. no.	Non		600°C 4 h		700°C 4 h		1000°C 4 h	
	V _{1mA}	α	V _{1mA}	α	V _{1mA}	α	V _{1mA}	α
1	$\cong 0$	1.0	$\cong 0$	1.0	$\cong 0$	1.0	$\cong 0$	1.0
2	4.5	5	3.0	3	3.5	5	$\cong 0$	1.0
3	62	10	40	8	22	4	4.4	1.4

shown in Fig. 2. Only specimens annealed at temperatures below 900°C exhibited non-linear I-V characteristics. Moreover, the appearance and disappearance of the non-linear I-V characteristics were reversible depending on the annealing temperatures. That is, the specimens annealed at 1000°C exhibited non-linear I-V characteristics after they were annealed again at temperatures below 900°C while the specimens annealed at temperatures below 900°C lost their non-linear I-V characteristics after they were annealed again at 1000°C. The DTA and TGA data of the No. 2 composition powder are shown in Fig. 3. An endothermic peak was found at temperatures of greater than 900°C in the heating process. Simultaneously, a decrease in weight occurred over the same temperature range.

The non-linear I-V characteristics of the specimens having the No. 2 and No. 3 compositions fired at 1280°C in air for 4 h are shown in Table 1. The difference in the non-linear I-V characteristics between the annealed and non-annealed specimens for both the No. 2 and No. 3 compositions was relatively small.

4. Discussion

It has been proposed that adsorbed oxygen atoms at the grain boundaries are the origin of the interface states. Adsorbed oxygen atoms such as O₂⁻, O⁻ and O²⁻ form the states at the levels between 0.8 and 1.1 eV below the conduction band edge. [4] Mukae et al. proposed that these adsorbed oxygen atoms were released from the Co oxide and Pr oxide during the firing process. However, based on this hypothesis, it is considered that the addition of Co oxide and Pr oxide is not necessary to form interface states if the firing atmosphere contains enough oxygen as carried out in

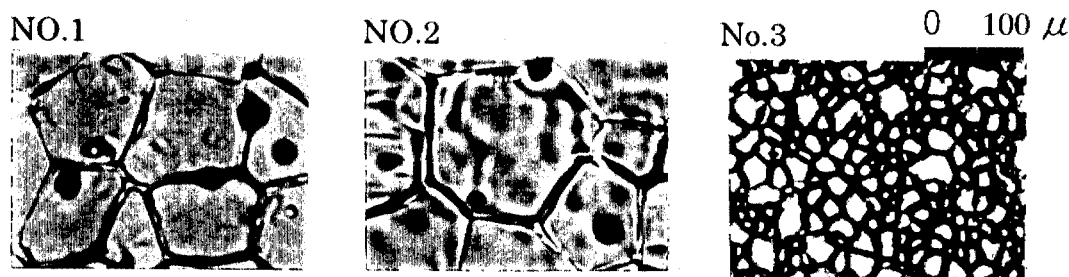


Fig. 1. Natural surfaces of specimens fired at 1430°C in oxygen for 4 h.

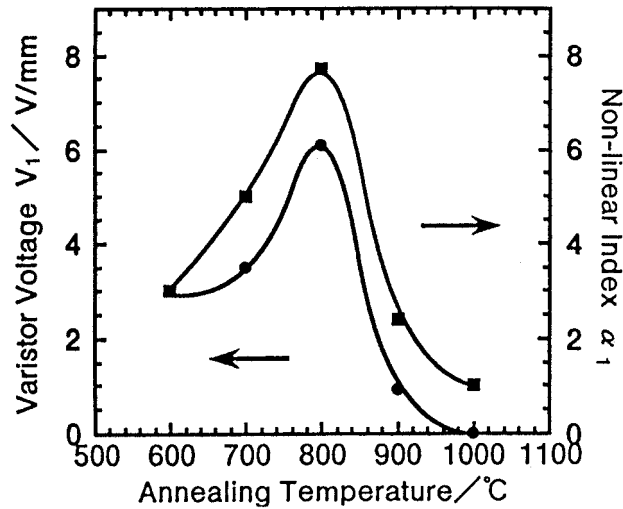


Fig. 2. Annealing temperature and I - V characteristics of specimens with No. 2 composition fired at 1430°C in oxygen atmosphere for 4 h.

this experiment. However, the Table 2 data show that the non-linear I - V characteristics were not obtained without the addition of Co oxide.

The non-linear I - V characteristics did not solely appear with the addition of Pr oxide to ZnO while it did solely appear with the addition of Co oxide. However, the addition of Pr oxide was necessary to obtain the highly non-linear I - V characteristics, especially in the specimens fired at 1280°C in air as shown in Table 1. This fact suggests the difference in the role between the two kinds of metal ions.

Co ions in Co oxide are reduced from trivalent to divalent at temperatures greater than 960°C in air. In the specimens with the No. 2 composition fired at 1430°C in an oxygen atmosphere, the appearance or the disappearance of the non-linear I - V characteristics depended on the fact that the annealing temperature was below or above this temperature, respectively. Therefore, it is considered that the oxidation and reduction of the Co ions near the grain boundaries is closely related to the appearance and disappearance of the non-linear I - V characteristics. That is, the higher oxidation states (trivalent) of the Co ions are considered to be necessary for the adsorption of oxygen atoms or the stability of the adsorbed oxygen atoms at the grain boundaries. These oxygen atoms are considered to form the interface states and trap electrons released from both the donors and Co ions. This is considered to be the role of the Co ions. However, the higher oxidation

states of the Co ions have not been directly confirmed. No ESR signals of Co ions were detected in the ZnO crystals. This is one of the problems to be solved in the future.

ZnO-based compositions containing Pr oxide have second phase melting points at 1380°C [3]. Therefore, due to both the liquid phase and the high oxygen partial pressure, grains grew to the size of $100\ \mu\text{m}$ in the specimens with the No. 2 compositions fired at 1430°C in an oxygen atmosphere. These specimens did not exhibit non-linear I - V characteristics after annealing at 1000°C in air. That is, they were reduced and lost the non-linear I - V characteristics during the annealing at 1000°C . Moreover, this suggests that the oxidation through the grain boundaries during the cooling process after annealing at 1000°C in air did not progress to a sufficient depth to exhibit the non-linear I - V characteristics, that is, to a depth greater than the diameter of at least one grain ($100\ \mu\text{m}$) as conceptually shown in Fig. 4b. Therefore, it is considered that these specimens exhibited the I - V characteristics in the oxidation states at the annealing temperatures even if they were not rapidly cooled. This is considered to be the reason why the reversible appearance and disappearance of the non-linear I - V characteristics were clearly observed.

The large difference between the specimens containing Pr oxide fired at 1430°C in an oxygen atmosphere and the ones fired at 1280°C in air is attributed to whether or not the liquid phase was

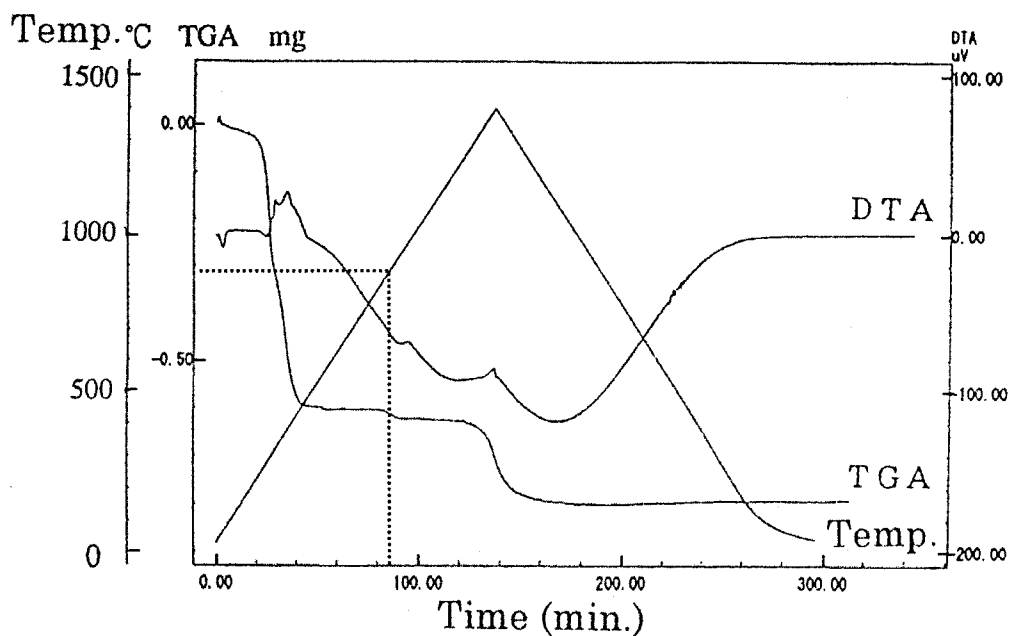


Fig. 3. DTA and TGA curves of No. 2 composition powder.

formed during the firing process and to the difference in the grain size. In the cases of relatively small grain sizes such as the latter ones, the oxidation through the grain boundaries is considered to progress to a sufficient depth to exhibit the non-linear $I-V$ characteristics during the cooling process after sintering or annealing, as shown in Fig. 4a. Most of the previous studies were performed using relatively small grain sizes as already described. This is considered to be the reason why the relation between the oxidation states of transition metal elements such as Co and the

appearance and disappearance of the non-linear $I-V$ characteristics was not found.

5. Summary

1. Non-linear $I-V$ characteristics did not solely appear with the addition of Pr oxide to ZnO while it did solely appear with the addition of Co oxide. However, the addition of Pr oxide was necessary to obtain highly non-linear $I-V$ characteristics.

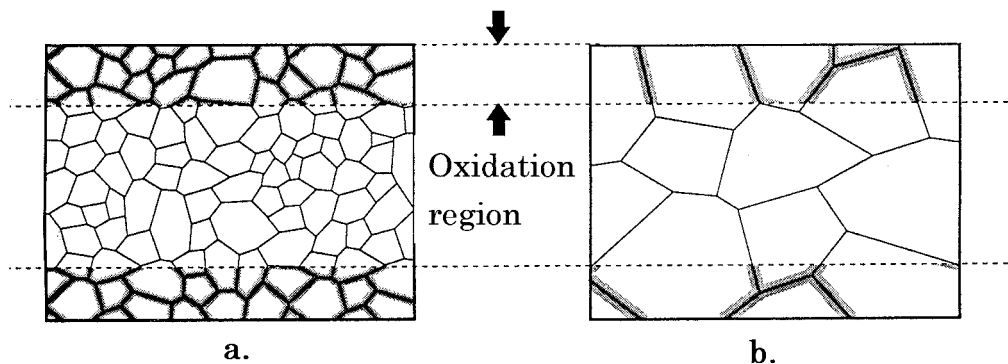


Fig. 4. Progress of oxidation during cooling process. (a) In the case of small grains. (b) In the case of large grains.

2. The specimens of ZnO-Pr₆O₁₁-CoO based ceramics fired at 1430°C in an oxygen atmosphere exhibited the non-linear *I-V* characteristics after annealing at temperatures below 900°C in air and did not exhibit it after annealing at temperatures above 1000°C. These phenomena reversibly occurred.

3. The temperature below or above which the non-linear *I-V* characteristics appeared or disappeared is considered to correspond to that below or above which the Co ions are oxidized or reduced.

4. In the specimens fired at 1280°C in air the oxidation through the grain boundaries during the cooling process progressed to a sufficient depth to exhibit non-linear *I-V* characteristics even after the annealing at 1000°C in air.

5. The large difference between the specimens containing Pr oxide fired at 1430°C in an oxygen atmosphere and the ones fired at 1280°C in air is attributed to whether or not the liquid phase was

formed during the firing process and to the difference in the grain size.

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