Clarifying the Mechanism of High Resistance in Zinc Oxide (ZnO) Elements

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Abstract

With the recent increase in demand for a more compact design for lightning arresters, there is a need to develop higher resistance Zinc Oxide elements (hereinafter referred to as "ZnO elements") for lightning arresters. Rare earth oxides are known as materials that can increase the resistance of elements when added in small amounts. The details of the mechanism, however, have not been clarified until now.

We clarified the mechanism of action of rare earth oxides on increasing the resistance of ZnO elements by applying a new analysis method. We further clarified the conditions under which a high resistance effect can be obtained while maintaining favorable nonlinear resistance characteristics.

By applying these technologies, we achieved an optimal design with high resistance that has an operation start voltage that is 1.5 times higher than our conventional product.

1 Preface

Station class surge arresters protect power equipment from abnormal voltages such as lightning surges and switching surges. Furthermore, the set up of the threshold value with a sufficient margin in the insulation design of station class model contributes to the compact design. In recent years, with the increasing demand for environmental protection requirements, lightning arresters have been required to be more compact and have a lighter design.

Fig. 1 shows the external appearance of a station class surge arrester. The protective function of lightning arresters is performed by ceramic elements whose main component is Zinc Oxide elements (hereinafter referred to as "ZnO elements"). This ceramic exhibits a nonlinear resistance. ZnO elements have a high resistance under grid voltage, but when an overvoltage is applied, their resistance rapidly decreases, allowing an abnormal current to escape. Fig. 2 shows the principle of the ZnO element (water flow model).

As the system voltage increases, the number of elements stacked in a series increases, and the arrester becomes larger. By increasing the resistance of the element itself, the number of layers can, therefore, be reduced and the arrester can be made more compact.

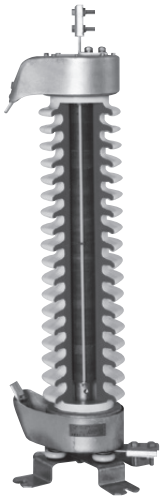


Fig. 1 Station Class Surge Arrester

An external appearance of a station class surge arrester is shown.

We clarified the mechanism that increases the resistance of ZnO elements and developed a high-resistance element with an operating voltage of 600 V/mm or more. This paper introduces the technology for clarifying the mechanism of high resistance.

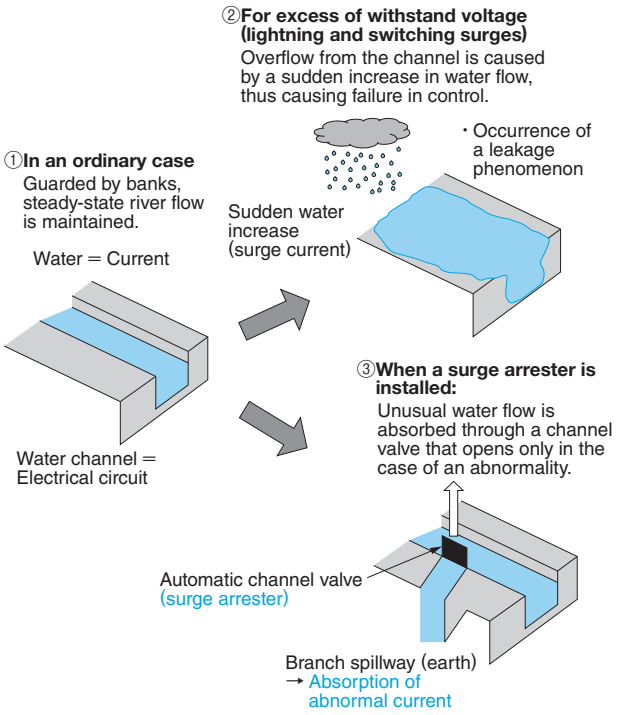


Fig. 2 Principle of ZnO Element (Water-Flow Model)

The role of ZnO element to protect electric equipment by absorbing abnormal currents is conceptually shown.

2 ZnO Element

2.1 Electrical Characteristics of ZnO Element

Fig. 3 shows the current-voltage characteristics of a ZnO element. The basic electrical characteristics of the element are evaluated using the following three parameters.

(1) Reference voltage ($V_{1\,mA}$): "The higher voltage, the higher resistance" → the arrester becomes a more compact design.

(2) Nonlinear resistance coefficient at large currents ($R_L = V_{10\,kA}/V_{1\,mA}$): "The smaller, the better" → Protective performance of surge arresters is improved.

(3) Nonlinear resistance coefficient at small currents ($R_S = V_{1\,mA}/V_{0.01\,mA}$): "The smaller, the better" → Circuit leakage current is lowered.

The higher the operation start voltage, the more compact the arrester can be. In addition, the element development requires maintaining favorable nonlinear resistance characteristics (R_L and R_S values).

2.2 Increasing Resistance of ZnO Elements

The resistance of ZnO elements can be dramatically increased by adding rare earth oxides to the main raw materials. Fig. 4 shows the effect of adding rare earth oxides. The operating start voltage increases in proportion to the amount of rare earth oxide added up to a certain amount. The details of the mechanism behind this increase in resistance, however, have not been clarified until now. As a result, the conditions for maintaining favorable nonlinear resistance characteristics (R_L and R_S values) have not been achieved in high-resistance ZnO elements containing rare earth oxides.

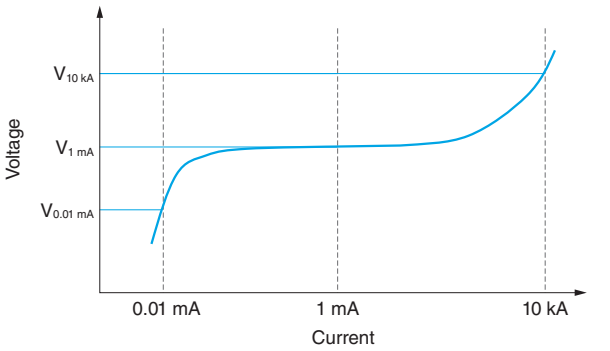


Fig. 3 Current-Voltage Characteristics

This diagram shows that the ZnO element has nonlinear resistance characteristics throughout the small and large current domains.

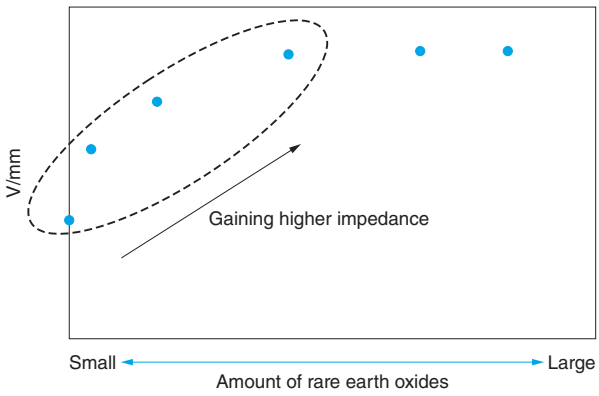


Fig. 4 Effect of Adding Rare Earth Oxides

This diagram shows that the reference voltage (V/mm) increases when rare earth oxides are added.

3 Clarifying High Resistance Mechanism

To solve the above-mentioned problem, we clarified the mechanism by which rare earth oxides cause high resistance in ZnO elements based on analytical research. The technical points are shown below.

3.1 Identification of Rare Earth Containing Phases by FIB-SEM/EPMA (Focused Ion Beam-Scanning Electron Microscope/ Electron Probe Micro Analyzer)

Fig. 5 shows a comparison of the crystal structure and phases of ZnO elements by using X-ray diffraction. It is predicted that a rare earth-containing phase exists in the developed high-resistance element containing rare earth oxides. Conventional analysis using SEM/EDX (energy dispersive X-ray) could not identify, however, the presence of the rare earth-containing phase in the element's microstructure. By controlling the thickness of the evaluation sample to 100 nm or less by using FIB processing, we suppressed the effects of primary electron scattering within the sample. Furthermore, by using the SEM/EPMA, which has better energy resolution than SEM/EDX, we improved the accuracy of elemental quantification. Fig. 6 shows the newly adopted technology FIB-EPMA, and Fig. 7 shows clear presence of rare earth-containing grains by

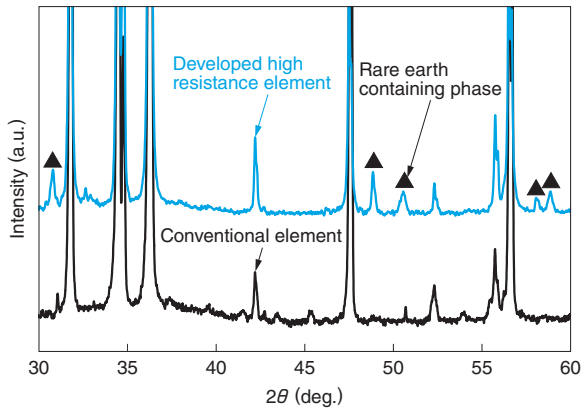


Fig. 5 Comparison of Crystal Structure and Phases of ZnO Elements

A fact is shown that the rare earth containing phase is generated only in the high resistance element (rare earth oxide added system).

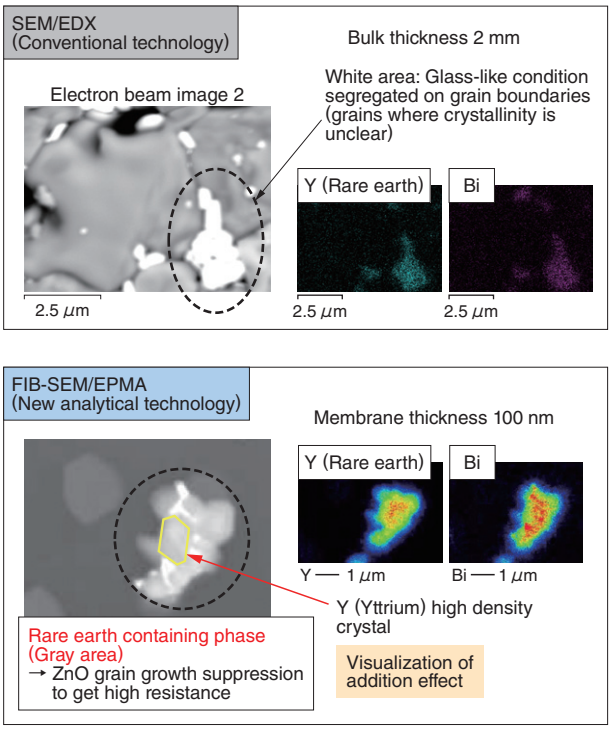


Fig. 7 Clear Presence of Rare Earth-Containing Grains by Using FIB-EPMA

Rare earth containing grains are shown in comparison of conventional and new technologies.

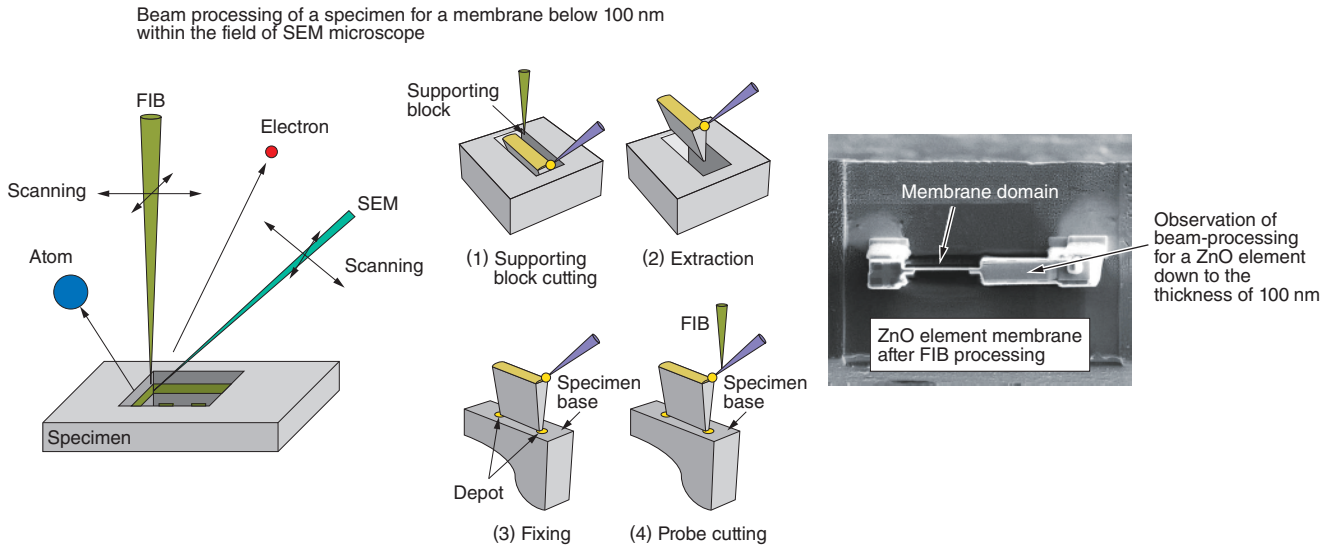
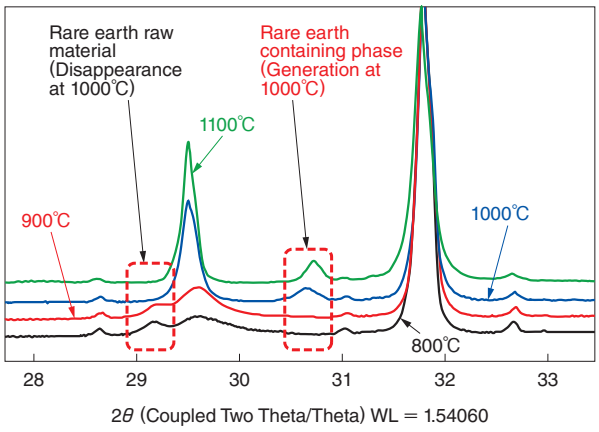
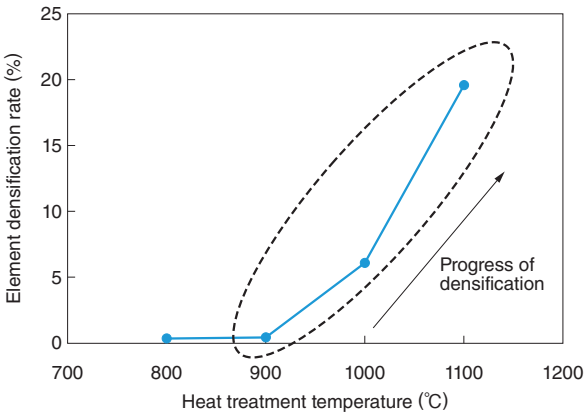


Fig. 6 Newly Adopted Technology FIB-EPMA

The FIB-EPMA concept and a photo of a practical addition process are shown.



(a) Generation of rare earth containing phase at 900℃ → 1100℃



(b) Progress of densification at 900℃ → 1100℃ (Generation of liquid phase)

Fig. 8 **Tracing Reaction Sintering Process**

Generation of rare earth containing phase and progress of its densification are shown.

using FIB-EPMA. The rare earth-containing phase, which was previously difficult to identify, was confirmed as a single grain. These single grains were present in segregated substances between ZnO grains.

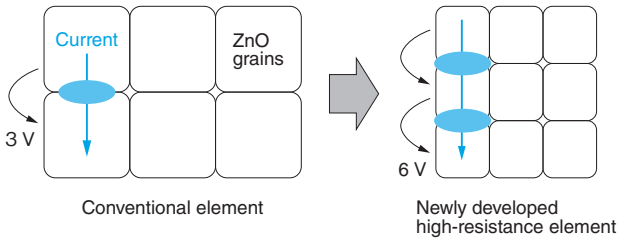
3.2 Tracing Reaction Sintering Process

Fig. 8 shows tracing the reaction sintering process. We investigated changes in the synthesized/disappeared phases and element shrinkage rate with respect to the element heat treatment temperature. The temperature at which the rare earth-containing phase occurs (and the disappearance of the rare earth oxide phase) mentioned above coincides with the densification start temperature. Furthermore, the rapid densification of the element is brought about by liquid-phase sintering, which occurs when the raw material oxide turns into a liquid phase. From the above, a rare earth-containing phase is synthesized along with the generation of a liquid phase as the element is sintered.

3.3 Mechanism of Increasing Resistance

Fig. 9 shows a schematic drawing of increasing element resistance. The operating voltage of a ZnO element is proportional to the number of resistive layers present at the ZnO grain boundaries in the element's microstructure. As ZnO grains become smaller in size, the number of grain boundaries increases, resulting in higher resistance.

As a result of analysis, single grains of rare earth-containing phase exist between ZnO grains during sintering. During sintering and densification,



〈ZnO Grains Densification and High Resistance Model〉

Fig. 9 **Schematic Drawing of Increasing Element Resistance**

A conceptual model of high resistance acquisition is shown.

the single grains mentioned above suppress the grain growth of ZnO grains and increase the number of ZnO grain boundaries. Due to the above effects, it is thought that the resistance of ZnO elements increases dramatically when rare earth oxides are added. Fig. 10 shows a conceptual drawing of grain growth suppression.

Fig. 11 shows the microstructures of a high-resistance element doped with rare earth oxides and a standard element. Compared to standard elements, high-resistance elements have smaller ZnO grains and an increased number of grain boundaries.

4 Improving Performance of High-Resistance Elements

To develop favorable nonlinear resistance characteristics, it is necessary to prevent local concentration of current flowing inside the element. It is,

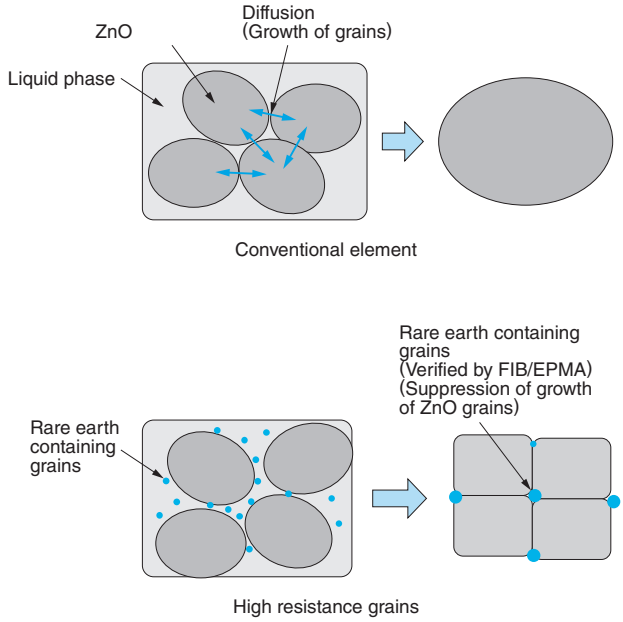
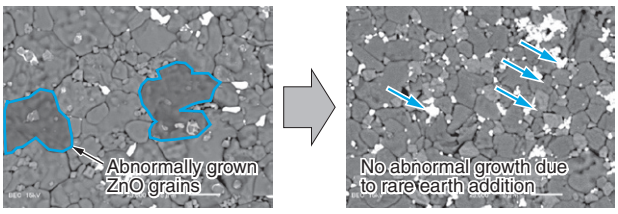


Fig. 10 Conceptual Drawing for Grain Growth Suppression

This conceptual drawing shows that growth of rare earth containing grains is suppressed.



(a) Conventional element (b) High resistance element

Fig. 11 Microstructure of Element

The microstructure of a high resistance element shows that the diameter of each grain is reduced.

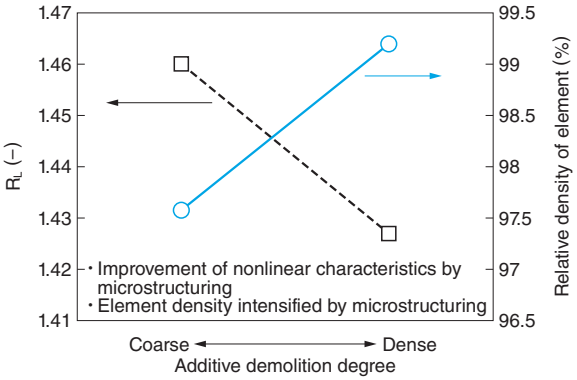


Fig. 12 Relationship between Additive Pulverization and Element Performance

The R_L value is improved because of the pulverization of additives. The resultant dense element is shown.

Table 1 Performance of High-Resistance Element Developed Based on this Mechanism

This table shows that the performance characteristics of the newly developed high resistance varistor elements are superior to those of conventional elements.

ϕ64 element	Standard element	Developed high resistance element
Reference voltage (V/mm)	~400	600~
Value R_L	1.67	1.43
Power loss※1 (Leakage current) (W/kV) [80%-170℃]	1.0	0.4

Note: ※1. Proportional to Value R_S

therefore, necessary to make the ZnO grains size uniform. The grain growth suppressing effect of ZnO grains when rare earth oxides are added is due to the physical inhibition of the bonds between ZnO grains by the rare earth-containing phase in the grain boundaries. Uniformly dispersing co-additives such as bismuth oxide and antimony oxide, which together form the rare earth-containing phase into the compact element, is the key to making the ZnO grain size of the fired element uniform.

By pulverizing additives containing rare earth oxides, we uniformly dispersed them within the molded element. This made the ZnO grain size of the element uniform after sintering. This greatly improved the nonlinear resistance characteristics. Furthermore, by suppressing abnormal grain growth of ZnO, a high-density and strong element was obtained. Fig. 12 shows the relationship between additive pulverization and element performance. Table 1 shows the performance of the high-resistance element developed based on this mechanism.

5 Postscript

This time, by employing the world's first (according to our research) SEM/EPMA by using FIB processing, we clarified the mechanism by which rare earth oxides increase the resistance of ZnO elements. As a result, we achieved an optimal high-resistance design with a start-up voltage that is 1.5 times higher than our conventional product.

By applying the high-resistance elements obtained from this development to lightning arresters for Gas Insulated Switchgear (GIS), the number of elements can be reduced by approximately 30% and the number of sulfur hexafluoride (SF_6) filling for insulation can be reduced due to the compact

design of the lightning arrester. The environmental benefits of the compact design are significant, and social contributions are expected.

Going forward, we will continue to work on making lightning arresters more compact and more efficient, which protect substation equipment and power transmission and distribution systems.

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