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The effect of cooling rate on electrical properties of ZnO varistor for Fire Alarm Circuit

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Abstract

The aim of the present study is to find out the effect of cooling rate on the electrical behavior of ZnO varistors. The microstructure, I-V characteristics and complex impedance spectra were investigated under the change of cooling rates. It is found that at cooling rate 200℃/h, nonlinearity and breakdown voltage reached a maximum value which may show that good intergranular layer is formed as a results of proper cooling rate. Complex impedance spectras were measured as a function of frequency range 100Hz to 13MHz to determine grain and grainboundary resistance. The semicircles were attributed to the dependence of grain and grainboundary resistance on cooling rates.

국문요약

본 연구에서는 화재 감지 회로 등에 사용되는 ZnO바리스터의 제조과정중 냉각 속도가 전기적 특성에 미치는 영향에 대하여 조사한 것이다. 냉각 속도의 변화에 따른 시편의 미세구조, 전압-전류 특성, 복합임피던스 측정을 하였다. 냉각 속도 200℃/h에서 비오옴계수나 바리스터 동작 전압의 최대치를 나타내었다. 이 것은 냉각과정중 형성된 결정입계에 성질에 의존됨을 알았다. 복합임피던스는 100Hz-13MHz의 주파수 범위에서 측정하였으며, 반원의 특성을 검토한 결과 결정립이나 결정입계의 저항이 냉각 속도에 크게 의존되고 있음을 확인하였다.

1. Introduction

ZnO varistors with various additives show an excellent nonlinear behavior in voltage-current characteristics. They are widely used as components that serve protective role against electric surge and transient over voltage of electric power system. Especially ZnO varistor is able to prevent from inflow of switching pulse and temporary overvoltage in the fire alarm circuit[1),2)]. Varistors are directly connected across the power line in parallel with the load to be protected. Electrical

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behavior of ZnO varistor is similar to the diode with double schottky barrier, but with greater current and energy absorption capabilities.

Nonlinear characteristics are found to be highly dependent on the resulting microstructure,. which depends on the sintering temperature and amounts of additives.

For this reason, many studies have been performed to investigate of phase changes during heating, the effect of microstructure and the chemical composition on the electrical properties and nonlinear conduction mechanism[3),4),5)].

Especially sintering procedures are attributed to changes of the crystal structures and the form of the grain and grain-boundary. The microstructure of ZnO varistor consists of conductive grain isolated from each other and grain boundary surrounded by the thin insulating layers.

Many studies have focused on understanding the electrical and physical properties responsible for the sintering conditions. Sintering is one of the principal procedure that has been used extensively for the ceramics products because of the changes of electrical properties during the sintering. Therefore, electrical characteristics of ZnO varistors are directly related to the sintering conditions such as sintering temperature, time, cooling rate and some other factors[6),7)]. It is very important and interesting to find how the microstructure changes to the cooling rate and what manner those microstructures exist and are distributed in the ceramics because the microstructure is responsible for the nonlinear behavior.

However few works have dealt with the resulting electrical properties and microstructure of ZnO ceramics produced by different cooling temperature[8)]. And the explicit role of the cooling rate on the electrical feature of ZnO ceramics is not clearly understood. It is therefore desirable to investigate the influence of cooling rate on the microstructure of ZnO varistor and correlate this to the electrical properties.

The present work is concerned with finding the existence of an intergranular phase relating it's properties and relating the electrical properties of the sintered ZnO ceramics to it's microstructure according to the change of cooling rate. In this study the effect of cooling rate on the electrical properties of ZnO varistor was investigated keeping the composition constant under a fixed manufacturing process.

2. Experimental procedures

2.1 Preparation of Samples

All of the sintered samples of the ZnO-based varistors were prepared by conventional ceramics fabrication techniques. A reagent grade ZnO, Bi_2O_3, Co_2O_3, Sb_2O_3, Cr_2O_3 and Al_2O_3 were used as starting materials. Mixtures were ball milled with the 0.5wt% of PVA binder for 24 hours. After being dried and granulated by 80 mesh sieve, the powders were pressed at the pressure of 1 t/cm^2. The pressed samples were sintered in ambient air at temperature ranges from 1200℃ to 1300℃ for 1.5 hours with a rate of 4 c/min. and cooled to 500℃ with the different rates : 50℃/h, 100℃/h, 200℃/h, 400℃/h and 600℃/h respectively. The surface of sintered samples were lapped, and finally silver electrode were used for the electrical measurement. For microstructure observation, the polished samples were etched thermally.

2.2 Measurement of the Electrical properties

Current-Voltage characteristics of samples were measured by using D.C. voltage supplier in the current range to 30 mA. In order to find the breakdown voltage, curve tracer was introduced. Frequency characteristics of capacitance and dielectric loss were measured by using Impedance Analyzer (HP4192A) in the frequency range from 100 Hz to 13 MHZ. Microstructure of samples were observed by optical microscopy technique. We obtained the nonlinear coefficient in the current range of 1 mA/cm^2 to 10 mA/cm^2 by equation 1[9].

$$\alpha = \delta \log (I) \ / \ \delta \log (V) \qquad (1)$$

Where V is a voltage across the sample and I is a current flowing through the sample

3. Results and discussion

3.1 Microstructure

Fig.1 showd a microstructure of samples with various cooling rates. The grains were observed to be the same size according to the cooling rate changes. ZnO varistors are polycrystalline ceramics materials which are composed of ZnO grains and intergranular regions. All the ZnO grains are completely surrounded by a liquid phases during sintering and remain effectively isolated as third phases solidify during cooling. In the Bi_2O_3 based ceramics, Bi_2O_3 crystal phases can constitute intergranular layers, continuously spreading in the ceramics, because those phases are formed by the crystallization of liquid phases in the cooling processes. On the other hand, the spinel phases can not constitute the continuously spreading inter-

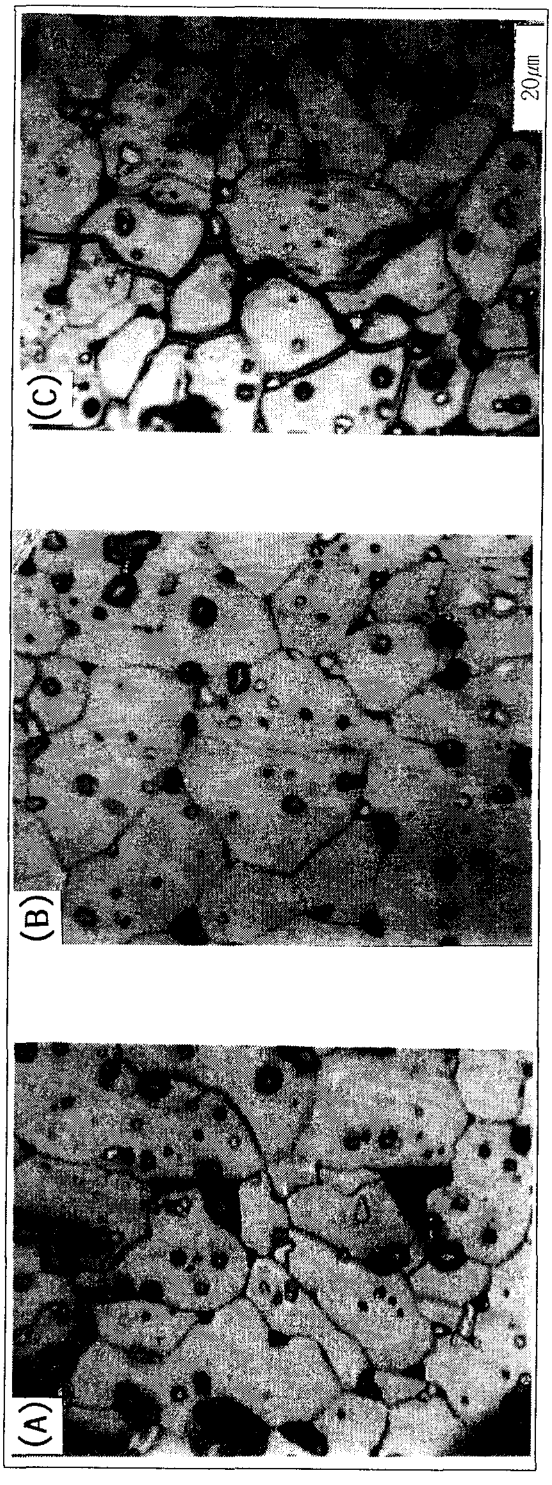

Fig. 1. Microstructure of ZnO varistors with cooling rates (A) 50℃/ h, (B) 200℃/ h and (C) 600℃/ h.

granular layers because it has a melting temperature higher than the sintering temperature of the ceramics[10].

As we can see in this photograph, three phases are present in this samples, namely, ZnO grains, intergranular layers and spinel particles which are compound oxides of zinc and antimony. Spinel phases does not play any electrical role because they are highly resistive. There are spinel phases located at the grainboundary and some pyrochlore phases at the point of grain junctions. At slow cooling rate with 50℃/h and 100℃/h, whichs are only showed in the grainboundary regions. In fast cooling rate above 200℃/h, we found that some materials overflows throughout grains and grain boundaries, and intergranular layers are observed at the grain boundaries but we can not find it at the cooling rates of 50℃/h, 100 ℃/h and 200℃/h. It is seen that a good microstructure of ZnO ceramics can be obtained at a certain cooling rate

3.2 Current-Voltage characteristics

Fig.2 shows current-voltage characteristics of the ZnO varistor which were sintered temperature at 1250℃ at varied cooling rate range from 50℃/h to 600℃/h. In this experiments, sintering temperatures were controlled at 1200℃, 1250℃, and 1300℃ respectively. Sintered temperature of 1250℃ is the best suitable for obtaining the higher nonlinear coefficient of ZnO varistors. At the prebreakdown region, leakage current at constant voltage increases linearly with a decrease in the cooling rate In the nonlinear region the current at constant voltage shows different effect of cooling rate. It indicates that the grain size and the effect of grain boundary states were changed with the cooling rates.

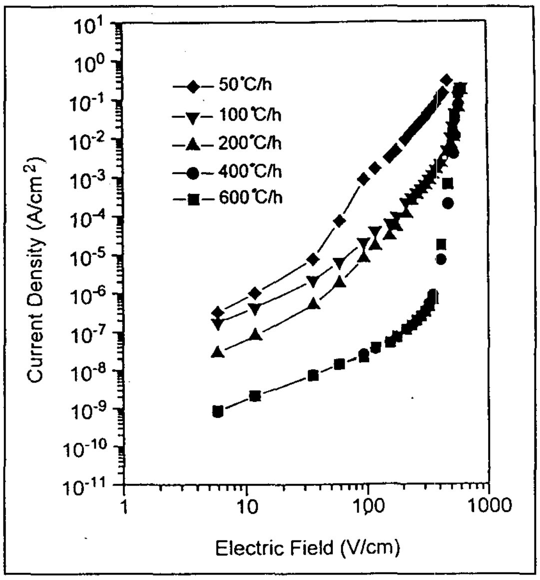

Fig. 2. I-V Characteristics.

Generally leakage conduction is related to the grain boundary rather than ZnO grain itself and it is attributed to the change in the barrier hight due to variation of positive charge density in the depletion region of ZnO grain. The intergranular region of ZnO ceramics has an important effect on the flow of electronic conduction, and grain boundary may contain a large number of point defects and impurities. K. Mukae et al reported that intergranular layer of the ceramics was found to be a rare earth metal oxide compound without ZnO and Co atoms[11]. In fig. 2, it can be seen that leakage current decreases with increasing cooling rate. It may suggest that the number of conducting carriers decreased with the increase of barrier hight of the depletion as the cooling rate increases. This is attributed to the fact that the thick intergranulare layer results in decrease of the currents flowing through the schottky barrier.

In order to find clearly breakdown characteristics, current-voltage curve trace as a function of cooling rate is shown in Fig. 3. In fact, current-voltage curves are symmetrical with respect to the A.C. applied voltage because of double shottky barrier characteristics of ZnO varistors. But this curve was taken in the positive bias voltage. It can be seen that this tendency agree with the results of I-V characteristics in Fig. 2. At the cooling rate of 200℃/h, breakdown voltage shows a significantly larger value than the sample cooled at the other rates. It is attributed to the fact that the sample with a cooling rate 200℃/h has a good grainboundary. At other rates of cooling, spinel particles and pyrochlore phase are observed.

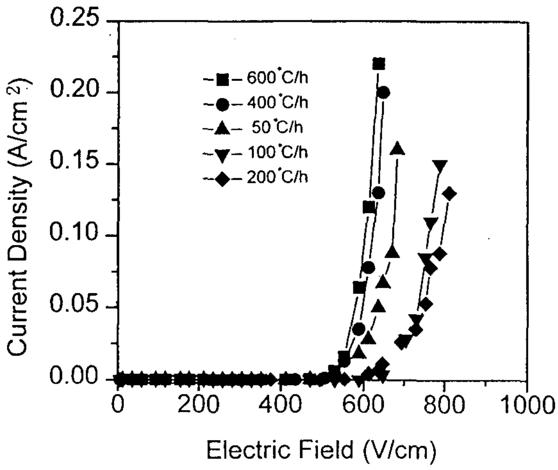

Fig. 3. The breakdown voltage as a function of cooling rates.

Fig4. shows a nonlinear coefficients as a function of cooling rate. It was found that the highest value observed for the nonlinear coefficient was at the cooling rate 200℃/h. After the peak, nonlinear coefficient decreases as the cooling rate increases or decreases and those values were estimated to be in the from 15 to 32 for current density in the interval of $1mA/cm^2$-$10\ mA/cm^2$. Nonlinearity is originated from the grainboundary, and spinel particles decrease the active grainboundary area through which electric conduction flows. As we can see in Fig. 1, there are less spinel particles and more clean grainboundary at the cooling rate of 200℃/h compared at the other cooling rates.

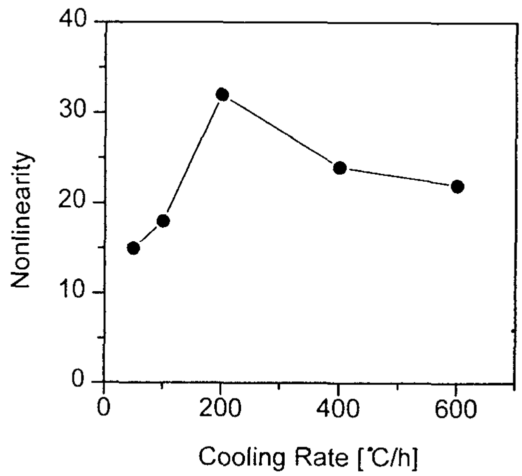

Fig. 4. Nonlinearity as function of cooling rates.

3.3 Frequency characteristics of Capacitance and Dielectric loss

The capacitance of ZnO ceramics is mainly attributed to the grainboundary which have a highly resistance. The capacitance ranges from 1.7 (nF) to 2.1 (nF) at 1KHz according to the cooling rate which is extraordinarily larger than that of ZnO grain. It implied that capacitance is mainly attributed to the grainboundary and entire voltage is sustained the grainboundary because ZnO grains are good conductor and have a lower dielectric constant. ($\varepsilon r=8.5$)

Understanding the electrical behavior of the grainboundary according to cooling rate, variation of capacitance and dissipation factor with cooling rate were examined. Fig.5 and Fig.6 show the capacitance and dissipation factor with cooling rate as a function of frequency range from 100 Hz to 13 MHz. The capacitance of all the samples were

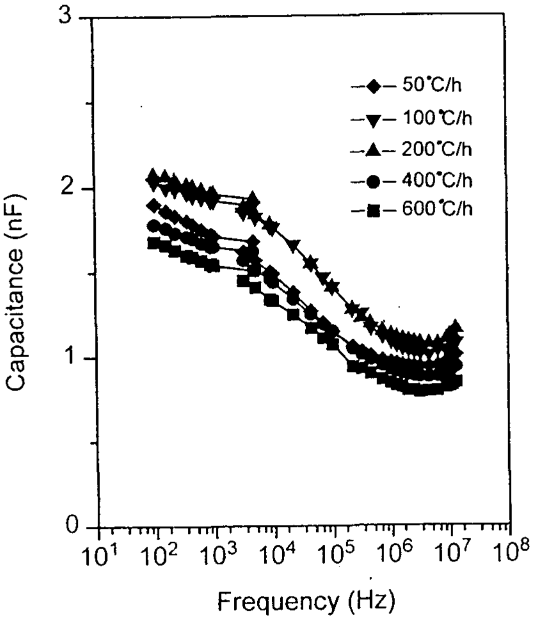

Fig. 5. Capacitance as a function of cooling rates.

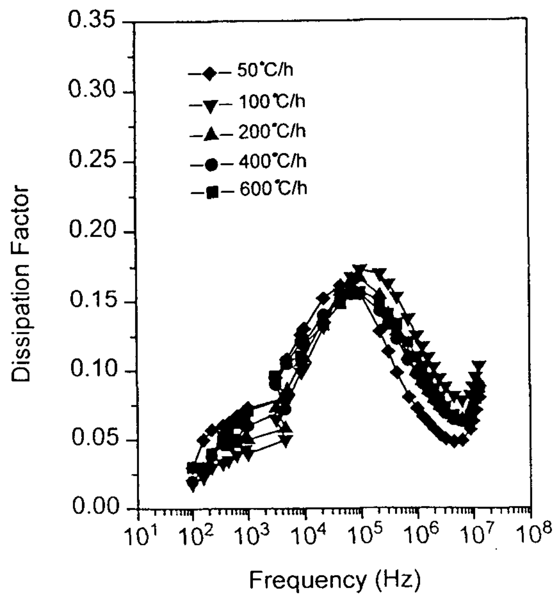

Fig. 6. Dissipation factor as a function of cooling rates.

observed from this figure to decrease continuously as the frequency increases. The facts can be explained as conduction carrier in the depletion region could not follow as a applied frequency increases. which is associated with the dispersion of a dielectrics[12]. And larger capacitance was caused by larger conduction carrier of grainboundary at fast cooling rate. Dissipation factor decreases with increase of frequency up to 105 KHz, then reaches a peak at a frequency about 8MHz and finally increases.

3.4 Complex Impedance

The difficulty with D.C measurement on polycrystalline ceramics is that bulk and grain resistance are lumped together and can not easily be separated. On the other hand, by A.C. method it is possible to resolve both grain and grainboundary components with the aid of complex plane analysis.

Grainboundary impedance be directly identified experimentally. One of the most direct method for probing grainboundary impedance of electrical materials is complex impedance measurements. This method has been used on intermediate resistance ceramics based on the fact that on RC network produces a semicircles. And this plots useful for determining an appropriate equivalent circuit for system and for estimating the values of the circuit parameters[13]. Semicircular arc corresponds to a lumped R-C combination. The resistance values are derivable from the circular arc intercepts on the R-axis and capacitance values can be derived from repressions involving the frequencies at the peaks of the circular arc.

The method is perhaps best illustrated by specific examples of simple circuit (Fig.7).

The interpretation of frequency-dependent conduction and capacitance can be greatly facilitated by the combined use of complex plane diagrams and equivalent circuit.

The impedance of this circuit is given by

$$Z(\omega)=R_1+\frac{R_2}{1+\omega^2C_2^2R_2^2}-j\frac{\omega R_2^2C_2}{1+\omega^2C_2^2R_2^2} \quad (2)$$

where R_1 is grain bulk resistance, R_2 is grainboundary resistance, C_2 is capacitance of grainboundary and is angular frequency.

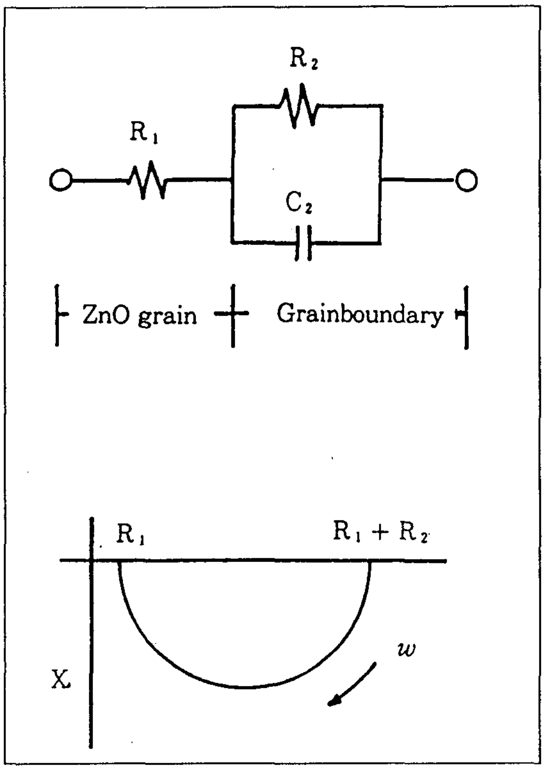

Fig. 7. (a)Electrical equivalent circuit of ZnO varistor, (b) Complex impedance spectra.

In high frequency region, it is expected to become $Z(\omega) = R_1$. From the intercepts of the semicircle, it is possible to determine the values of the resistance in the equivalent circuit and from the maxima of the semicircle to obtain the capacitance value C_2.

Complex impedance measurements were performed over 100Hz-13MHz frequency range. The complex impedance plots with the various cooling rate are shown in Fig. 8. All semicircle plots with the additives agree with principle with the diagram in Fig. 1. And we are able to obtain data with the single semicircle, At the same frequency range, we can see on the interesting variations are taking place. Complex impedance plots dependence of frequency show difference shape due to grainboundary resistance.

In the Fig. 8. the first intercept of real resistance gives the bulk resistance(R_1). and the second intercept gives the sum of grain and grainboundary resistance (R_1+R_2). It is possible to obtain reasonable values of the grainboundary capacitance (C_2) by using $\omega R_2 C_2 = 1$ (at the peak of semicircle).

The sample having a cooling rate of 200℃/h shows a particular semicircle different from that other cooling rates. At cooling rate of 200℃/h, low frequency resistance (R_1+R_2) from the complex impedance spectra was about 60KΩ, but at other cooling rate that value were not exactly estimated in this spectra because those are out of data. We can suggest that the sample cooled at 200℃/h has a lower grain boundary resistance than others.

4. Conclusion

The microstructure, I-V characteristics and complex impedance spectra were observed in this study to find the electrical behavior by the cooling rate of the ZnO varistors. As the cooling rate increases, leakage current decreases. The breakdown voltage and nonlinearity have a highest

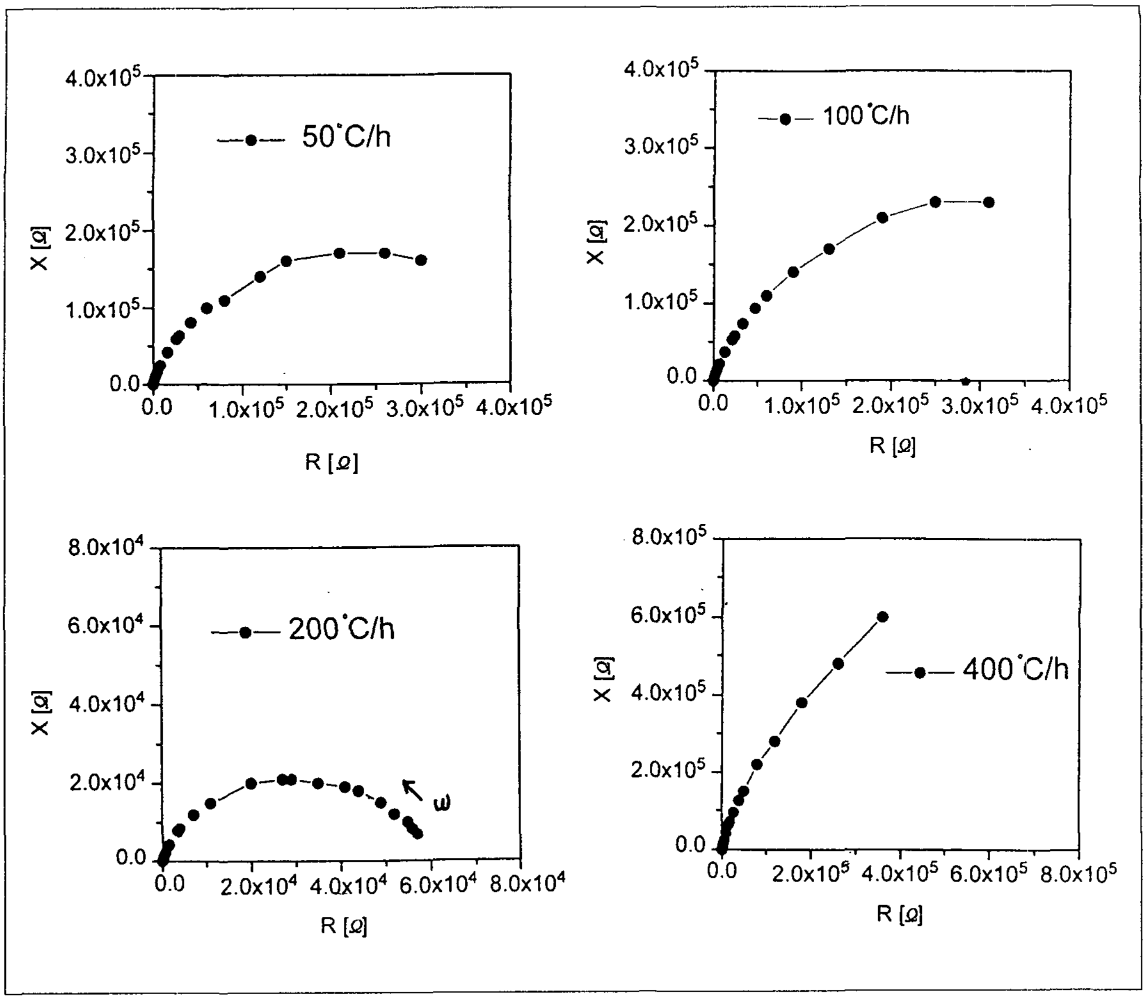

Fig. 8. Complex impedance spectra measured at various cooling rate.

value at the cooling rate of 200℃/h. It is attributed to the fact that the that cooling rate of 200℃/h has a less spinel and pyrochlore phase than other cooling rates. By a complex impedance spectra, it was found that the cooling rate seriously affects the formation of grainboundary resistance.

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