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Microstructures and positive temperature coefficient resistivity (PTCR) characteristics of high silicon addition barium-strontium titanate ceramics

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Ferroelectric barium titanate ($BaTiO_3$) shows a high intrinsic resistivity of more than 10^{10} Ω-cm when prepared in an oxidizing atmosphere [1, 2]. When polycrystalline $BaTiO_3$ ceramics are doped with higher valence cations such as La^{3+}, Y^{3+}, Nb^{5+} or Ta^{5+}, semiconducting properties and the positive temperature coefficient of resistivity (PTCR) effect can be obtained [1–5]. These effects involve a nonlinear change in the resistivity with temperature occurring around 120–130 °C which is known as the Curie temperature (T_C) [6, 7]. The T_C of $BaTiO_3$ can be shifted to lower temperatures by substituting barium with strontium [8–10]. The solid solution of $(Ba,Sr)TiO_3$ materials has, therefore, been widely used for fabrication of positive temperature coefficient (PTC) thermistors with various Curie temperatures [8]. The most acceptable model to explain the temperature dependent conduction mechanism in the PTCR barium titanate ceramics was proposed by Heywang and Jonker [7, 8, 11–13]. Above the Curie temperature, Heywang suggested that the formation of a Schottky barrier is caused by the presence of electron traps. Below the Curie temperature, Jonker proposed that the highly conductive semiconductor results from the charge compensation due to the polarized charges at the grain boundaries [11, 13].

In recent PTCR processing, excess titanium and silicon are commonly used to create a liquid phase and reduce the sintering temperature [14]. The eutectic temperature resulting from excess titanium is around 1320 °C. After addition of silicon, this temperature decreases to approximately 1260 °C [15]. Cheng *et al.* [11] prepared $Ba_{0.8}Sr_{0.2}TiO_3$ ceramics by adding 12.5 mole percent aluminum, silicon, and titanium (so called AST) with a ratio of 4:9:3. After sintering at 1350 °C for 1.5 h, a uniformly small granular structure was obtained with an increase in resistivity of 5 orders of magnitude (from 10^3 to 10^8 Ω-cm) at the Curie temperature. Many investigations have been

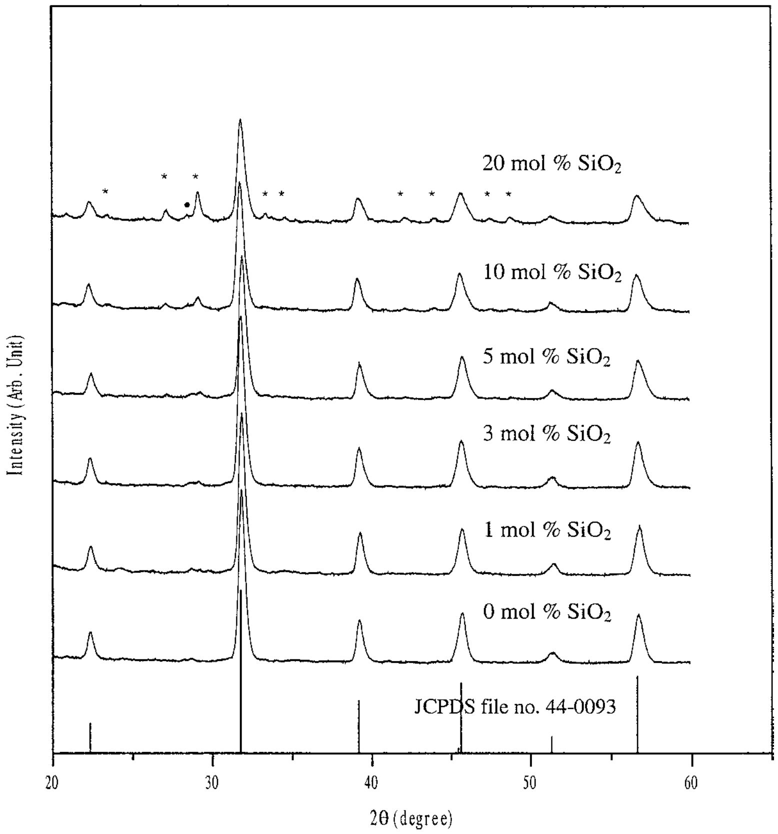

Figure 1 X-ray diffractograms of powders with various silicon content when calcined at 1100 °C. * = $Ba_2TiSi_2O_8$; · = $Ba_6Ti_{17}O_{40}$.

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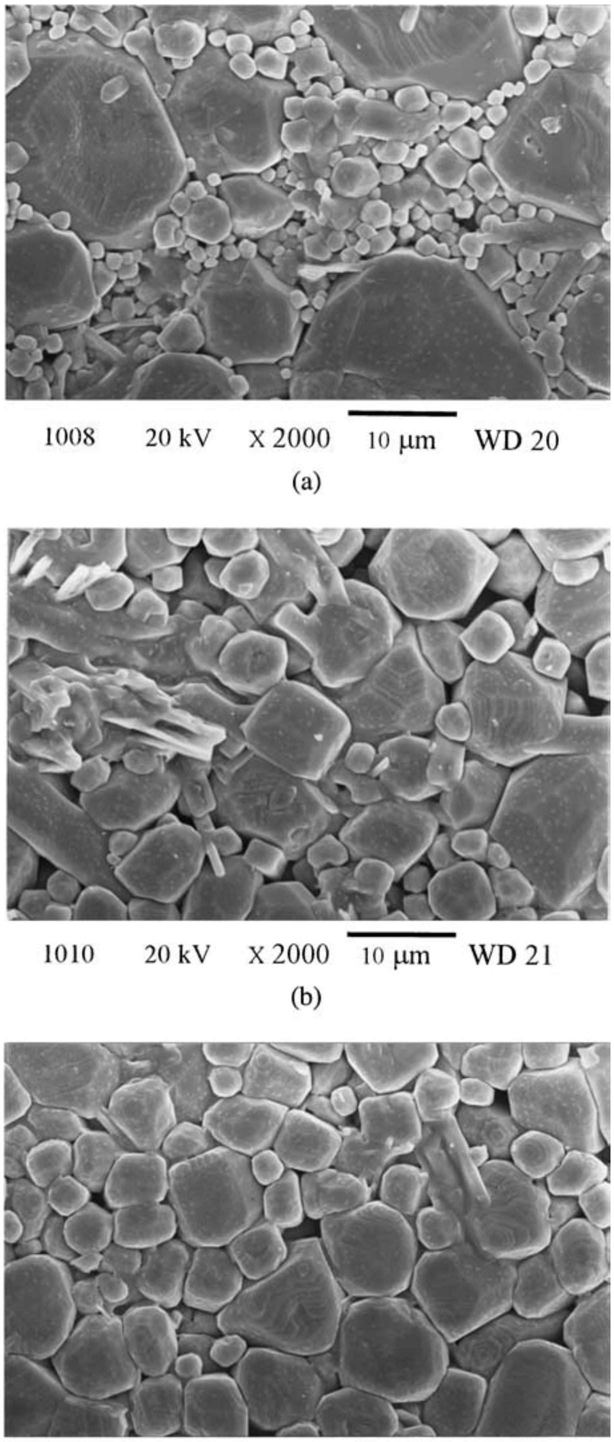
undertaken to study the effects of silicon additions to the PTCR ceramics [2, 14, 16]. However, the microstructures were found to be inhomogeneous due to the considerable difference in the densities of barium titanate and silicon [16]. Most of the investigations were performed with small (1–4 mol%) silicon additions [2, 14, 16]. The microstructural evolution might be significantly different when the liquid phase is incorporated in a larger proportion. The aim of the present investigation is, therefore, focused on studying the sintering behavior, microstructures and PTCR characteristics of antimony-doped $Ba_{0.8}Sr_{0.2}TiO_3$ materials with high levels of silicon addition.

Ceramic specimens in this work were prepared by the conventional mixed oxide process. The starting materials ($BaCO_3$, TiO_2, $SrCO_3$, Sb_2O_3, SiO_2, Aldrich Chemical Company, Inc.) were weighed according to the composition $Ba_{0.8}Sr_{0.2}TiO_3 + 0.15$ mol% $Sb_2O_3 +$ 1 mol% $TiO_2 + xSiO_2$ where x varied from 0 to 20 mole percent. Antimony was used in order to form an *n*-type semiconductor and the amount of 0.15 mole percent was found to be optimum in these experiments. The excess of TiO_2 (1 mole percent) was added as a sintering aid to create a liquid phase during sintering so as to reduce the sintering temperature. The mixed powders were ball milled for 24 h and calcined at 1100 °C for 2 h in an alumina crucible using heating and cooling rates of 10 °C/min. In order to obtain compact pellets, the calcined powder was mixed with a small amount of polyvinyl alcohol (PVA) before being pressed into pellets and the specimens were sintered in air at 1275, 1285, 1300, 1350, 1400 and 1450 °C, for 2 h using heating and cooling rates of 5 °C/min. X-ray diffraction (Siemens D500) was employed to characterize the samples. The microstructures of the as-sintered surface were observed by scanning electron microscopy (Jeol JSM-840A). The resistivity change of the specimens as a function of temperature from room temperature to about 285 °C was measured using a digital multimeter (Agilent 34401A) and a D.C. power supply, after both sides of specimens were painted with silver paste.

Fig. 1 shows the X-ray diffractograms of the specimens with various silicon contents. Traces of fresnoite ($Ba_2TiSi_2O_8$) and $Ba_6Ti_{17}O_{40}$ are found, in addition to the major tetragonal barium-strontium titanate ($Ba_{0.77}Sr_{0.23}TiO_3$) phase. Peaks were identified on the basis of Joint Committee on Powder Diffraction Standards (JCPDS) data (card number 44-0093, 84-0924, 35-0817). Furthermore, it was found that the amount of the $Ba_2TiSi_2O_8$ increased with increasing silicon content. The presence of $Ba_2TiSi_2O_8$ and $Ba_6Ti_{17}O_{40}$ in these results is in agreement with those obtained by Abicht *et al.* [16] and Felgner *et al.* [17].



(a)
(b)
(c)

Figure 2 Microstructures of the specimens containing 5 mole percent of SiO_2 after sintering at various temperatures: (a) 1285 °C, (b) 1300 °C, and (c) 1350 °C.

The developments of the microstructures of the specimens with various amounts of silicon are shown in Figs 2 and 3. It is obvious that the specimens show an abnormal grain growth and the size of the abnormally growing grains decreases with increasing sintering temperature as shown in Fig. 2. The grain structures of all the specimens when sintered above 1300 °C become rather uniform with sizes of 3–12 μm. The grain structures in the specimens with various amounts of silicon are shown in Fig. 3. It can be concluded that the grain size tends to decrease with increasing silicon contents, although the grain size of the sample with 5 mole percent of silicon (Fig. 2c) is slightly larger than that of the sample with 3 mole percent of silicon (Fig. 3b). In the specimen without silicon, the grains are irregularly sized and roughly equiaxed. However, in the specimens with higher silicon content (up to 20 mole percent) they

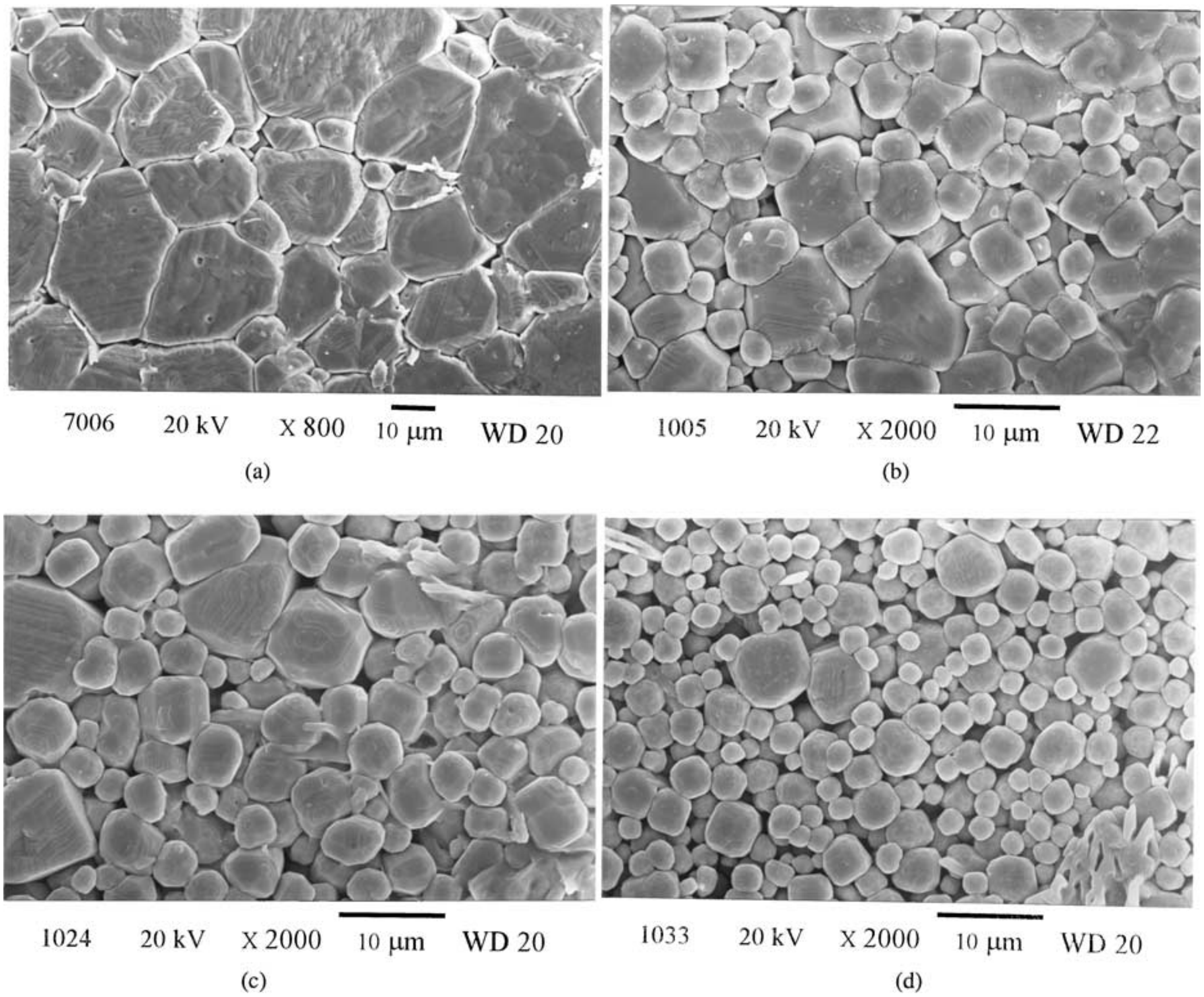


Figure 3 Microstructures of the specimens with various SiO_2 contents sintered at 1350 °C: (a) 0 mole percent SiO_2, (b) 3 mole percent SiO_2, (c) 10 mole percent SiO_2, and (d) 20 mole percent SiO_2.

become rounder and smaller with a grain size of about 2–5 μm as shown in Fig. 3d. The decrease in grain size with increasing silicon content is most probably caused by the large amount of liquid phase formed during sintering. Subsequently, the solid grains dissolve and become rounder in shape and smaller.

Porosity of the samples was also measured. It is found that porosity increases with decreasing sintering temperature but increases with increasing silicon content (Tables I and II).

The resistivity-temperature characteristics of the specimens prepared at various sintering temperatures and silicon contents are shown in Fig. 4. The Curie temperatures of these specimens are around 60 °C. It is also found that the room temperature resistivity (ρ_{RT}) varies as a function of silicon content and sintering temperature. The specimens without silicon cannot be sintered at temperatures lower than 1350 °C. The specimens sintered at 1350 °C show high resistivity. According to Liu and Roseman [14], however, low resistivity can be achieved by the addition of silicon to $Ba_{0.8}Sr_{0.2}TiO_3$. The resistivity at room temperature decreases to 10^1–10^4 Ω-cm in the specimens containing 1–20 mole percent silicon. The lowest room-temperature resistivity of about 25 Ω-cm can be obtained in the specimens containing 3 mole percent silicon when sintered at 1300 °C (see Fig. 5). The change in ρ_{RT} to higher values with decreasing sintering temperature is due to the coexistence of very large and very fine grains, as seen in Fig. 2a, As the silicon content increases so does the amount of $Ba_2TiSi_2O_8$ second phase (see Fig. 1). Consequently ρ_{RT} increases and there is a decrease in the magnitude of the PTCR characteristics (see Fig. 4d). Abicht *et al.* [16] found that the silicon containing second phases affect the electrical properties in an indirect manner. The resistivity changed over five orders of magnitude for the samples with 8–13% porosity (samples with 5–10 mole percent of silicon content, sintered at 1300 °C). Change of resistivity reduced to 2–3 orders

TABLE I Porosity, grain size and magnitude of PTCR effect in the specimens containing 5 mole percent SiO_2 sintered at various temperatures

Sintering temperature (°C)	% Porosity	Grain size (μm)	Order of magnitude of change in resistivity
1285	10.3	3.0–29.0	2.8
1300	8.6	3.5–12.0	4.7
1350	7.6	4.0–11.0	4.5

TABLE II Porosity, grain size and magnitude of PTCR effect in the specimens with various SiO_2 contents sintered at 1300 and 1350 °C

SiO_2 contents (mole %)	% Porosity		Grain size (μm)		Order of magnitude change in resistivity	
	1300 °C	1350 °C	1300 °C	1350 °C	1300 °C	1350 °C
0	–	5.2	–	10.0–30.0	–	–
3	8.4	5.8	3.0–11.0	3.1–10.0	3.8	3.3
10	13.2	11.1	3.2–10.0	3.6–7.0	5.0	3.1
20	20.8	16.9	2.7–5.5	2.3–5.5	3.2	2.0

if the porosity was less than 8%. It can be noted that the appropriate silicon addition brought a considerable enhancement of the PTCR characteristics. However, grain size, sintering temperature, porosity, and other second phases still affect the PTCR properties.

In conclusion, antimony-doped $Ba_{0.8}Sr_{0.2}TiO_3$ positive temperature coefficient resistors can be prepared below 1300 °C by the conventional mixed oxide process using silicon addition. The grains of the specimens sintered with a large addition of SiO_2 become rounder and smaller. However, $Ba_2TiSi_2O_8$ appeared as a second phase resulting in a decline in the electrical properties. The lowest room temperature resistivity of about 25 Ω-cm was obtained in the specimens containing 3 mole percent silicon, sintered at 1300 °C and the highest magnitude change in PTCR characteristics of

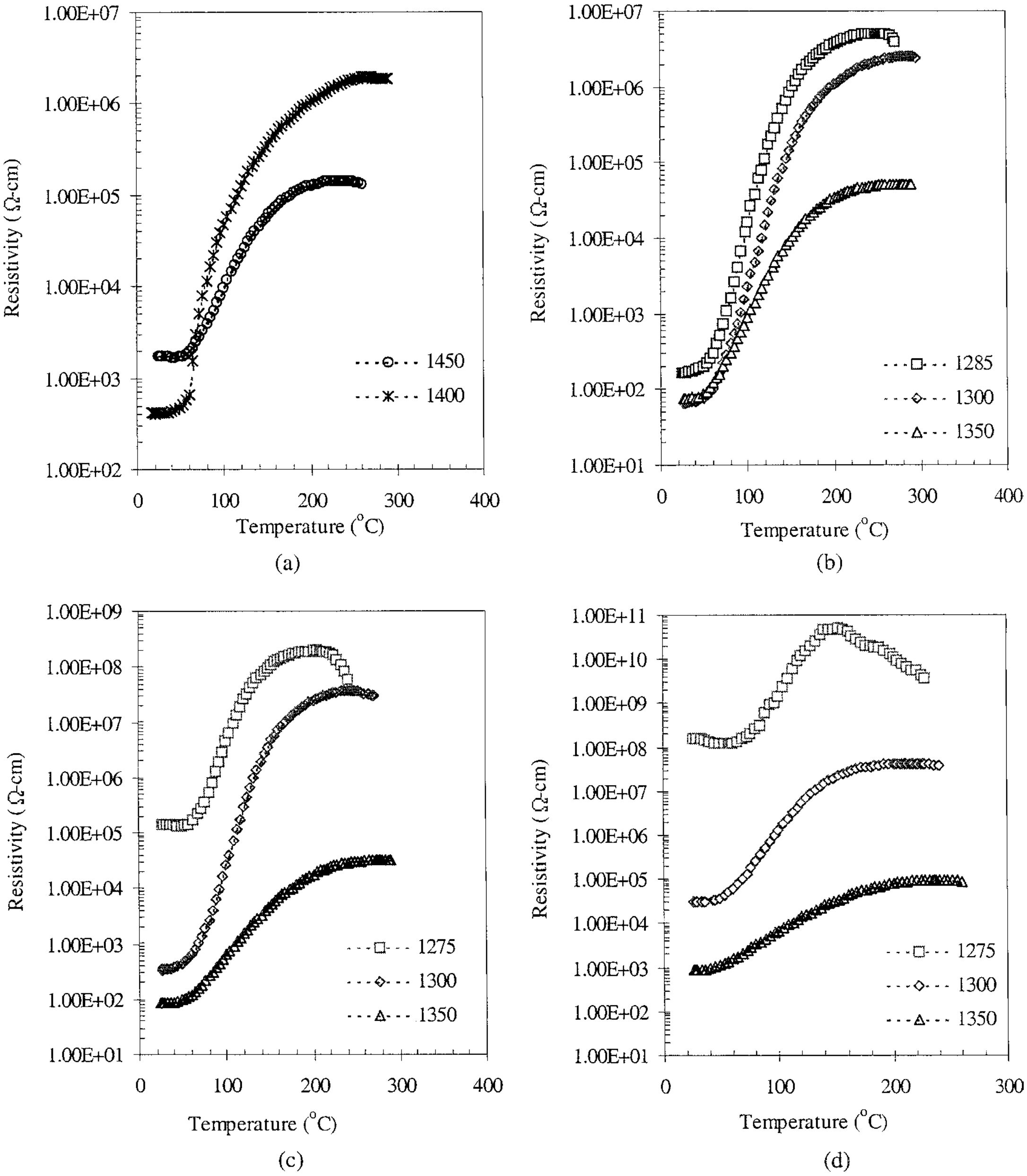


Figure 4 The resistivity-temperature (ρ-T) characteristics of the specimens with various sintering temperatures and SiO_2 contents: (a) 0 mole percent SiO_2, (b) 5 mole percent SiO_2, (c) 10 mole percent SiO_2, and (d) 20 mole percent SiO_2.

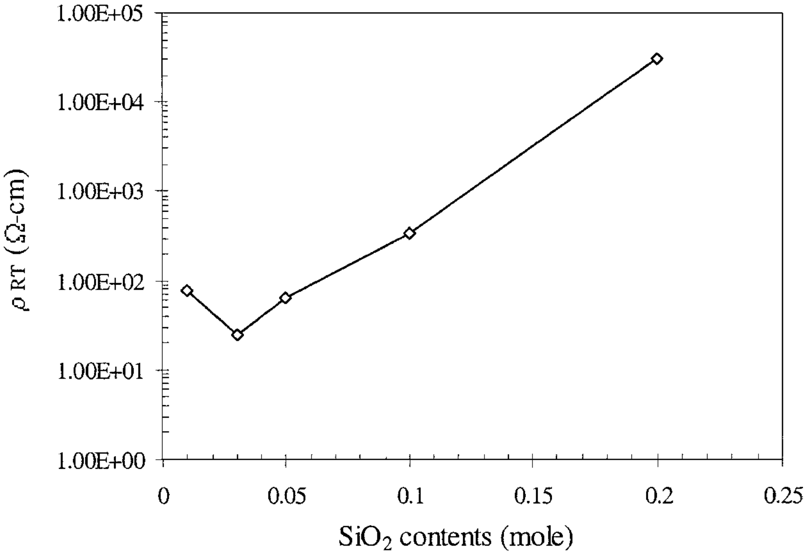


Figure 5 The room temperature resistivity of specimens with various amounts of SiO_2 sintered 1300 °C.

about 5 orders of magnitude was found in the specimens containing 5–10 mole percent silicon.

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