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The influence of silicon on microstructure and electrical properties of La-doped $BaTiO_3$ ceramics

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$BaTiO_3$ positive temperature coefficient of resistance ceramics were prepared with the general composition $(La_{0.002}Ca_xBa_{0.998-x})(Ti_{1.01-y}Mn_y)O_3 \cdot zSiO_2$ and sintered in air. The Ca content as well as the amount of doped Mn were varied ranging from 4–20 mol% and 0.02–0.04 mol%, respectively. Up to 4 mol% Si was added using a new method as well as by the classical means as solid silica. In the new method, the desired quantity of $Si(OC_2O_5)_4$ ($Si(OEt)_4$), contained in dry tetrahydrofurane (THF), was dropped under a slight stream of inert gas into the vigorously stirred aqueous slurry which was manufactured after the calcination process. The addition of Si by this technique was found to result in a homogenization of the microstructure and an improvement in electrical properties. The effect of Si on electrical properties is explained by the influence of the observed second phase on the equilibrium of Ba vacancies. The results of further variation of Ca and Mn contents are presented.

1. Introduction

The positive temperature coefficient of resistance (PTCR) effect in $BaTiO_3$ ceramics is the basis of numerous technical applications which use the material as, for example, self-regulating heating elements, television degaussers, and current limiters. One condition necessary for making devices for use at high voltages is a uniform ceramic microstructure with an average grain size in the range 3–5 μm and a narrow grain size distribution. On the basis of such a microstructure the electrical properties (PTCR effect, room-temperature resistivity (ρ_{25}), withstand voltage) can be deliberately adjusted by variation of the intergranular barrier layers which are determined by additional dopants, sintering regime, and sintering atmosphere. However, the microstructure formation is also influenced because both the processes occur simultaneously during sintering.

In the field of PTCR thermistors, $BaTiO_3$ is usually sintered with a small titania excess from 1–4 mol %. This excess forms a liquid phase and promotes anomalous grain growth, which is controlled by a solution–diffusion–reprecipitation process. The number and distribution of the nuclei involved in this process determine the average grain size of the subsequent microstructure. Hitherto many efforts have been made to find suitable methods of controlling the discontinuous grain growth. For example, it has been proposed to add "seed grains" to the starting powder [1, 2] or to realize a temporary and local melting phase during sintering [3]. In addition, numerous sintering additives are known which modify the intergranular phase and which form a liquid phase together with the matrix powder. The subsequent eutectics decrease the sintering temperatures to a greater or lesser degree.

A large number of investigations have been undertaken to study the manner and the effect of silicon addition. Many years ago it was recognized that the influence of silicon exceeds a microstructural effect [4–8]. However, the results were partially contradictory. More recently, some papers have been published which deal with the problem in detail [9, 10]. Here silicon addition was achieved by using solid SiO_2. However, the microstructure formed was inhomogeneous because of the considerable difference in the densities of $BaTiO_3$ and SiO_2. Admixtures of silicon containing substances with higher densities (see Table I) did not improve the microstructural properties substantially.

The aim of the present investigation was to search for an effective way of adding silicon and to elucidate its role in the microstructural and electrical properties.

2. Experimental procedure

Two different types of sample, both with a composition of $(La_{0.002}Ca_xBa_{0.998-x})(Ti_{1.01-y}Mn_y)O_3 \cdot zSiO_2$, were prepared from reagent-grade $BaCO_3$, $CaCO_3$, TiO_2, $La_2(C_2O_4)_3 \cdot 9H_2O$, $Mn(CH_3CO_2)_2 \cdot H_2O$, and SiO_2 (only type B samples). The Ca content, as well as the amount of doped Mn were varied ranging from 4–20 mol % and 0.02–0.04 mol %, respectively. Up to 4 mol % silicon, contained in two different agents, was added.

The starting materials were mixed in appropriate molar proportions in distilled water with agate balls in rolling polyethylene bottles for 24 h. The powder was

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TABLE I Densities of some Si sources

	Si source	Density (g cm^{-3})
$BaTiO_3$		~ 6.0
	SiO_2 (quartz)	2.65
	SiC	3.17
	$Ba_2TiSi_2O_8$	4.44

calcined at 1100 °C for 2 h and fine-milled. After addition of 5% polyvinylalcohol as a binder, discs (diameter 12 mm, height 3 mm) were pressed uniaxially with a green density of 3.1 g cm^{-3}.

The only difference between type A and B specimens consists in the manner of silicon addition. In the case of type A samples the desired quantity of $Si(OEt)_4$, having been contained in dry tetrahydrofurane (THF), was dropped under a slight stream of inertgas into the strongly stirred aqueous slurry which had been manufactured after the calcination process. For a realistic valuation of the results using this new method for silicon addition, type B samples were produced classically, i.e. appropriate amounts of solid SiO_2 were milled together with the mixture of the starting materials.

Sintering was performed in air in an Al_2O_3 crucible at linear heating and cooling rates. In the standard firing programme (SFP) the discs were heated at 10 K min^{-1} to the desired sintering temperature (T_s). After soaking for 1 h the compacts were cooled to room temperature also at 10 K min^{-1}. Samples for electrical measurements were prepared by applying an In/Ga alloy to the slightly ground surfaces of the disc. Resistivity–temperature characteristics were recorded analogously by an automatic measuring device [11].

Microstructures of polished and etched specimens were examined by optical microscopy or occasionally scanning electron microscopy (SEM), whereas as-fired surfaces were inspected by SEM only. The average grain size was determined by linear intersect measurements on optical micrographs.

3. Results and discussion

3.1. Effect of the new method of adding silicon

Generally there was a significant difference between type A and B samples. Although the addition of SiO_2 (type B) improved microstructural homogeneity, anomalous grain growth was not avoided. In contrast, added $Si(OEt)_4$ (type A) definitely hindered discontinuous grain growth, as illustrated in Fig. 1.

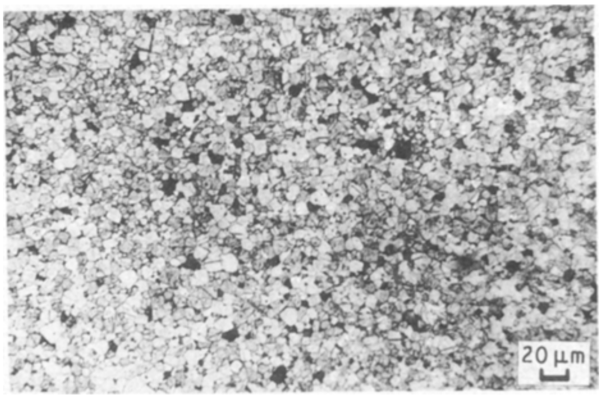

Figure 1 Optical micrograph of a polished and etched type A sample with a composition of $(La_{0.002}Ca_{0.16}Ba_{0.838})(Ti_{1.0096}Mn_{0.0004})O_3 \cdot 0.0125\,SiO_2$.

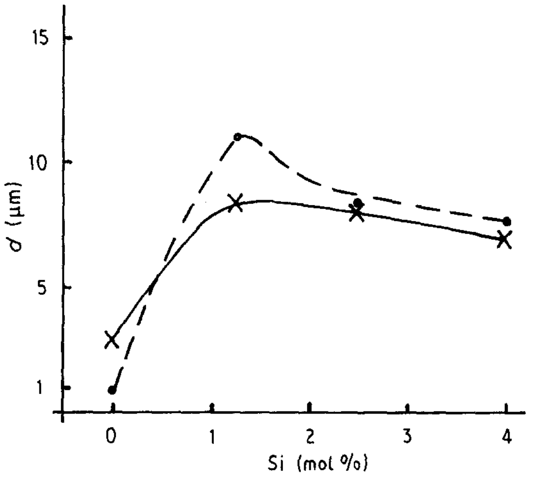

Figure 2 The dependence of the mean grain size on the amount of added Si at a fixed Ca content. T_s = (●) 1300 °C, (×) 1350 °C; series A, $x = 0.16$, $y = 0.0004$, z.

Type A samples with no silicon addition (there is no difference between the two sample types in this case) and 0.5 mol % Si addition exhibited a bimodal particle-size spectrum whereas admixtures in the range 1.25–4 mol % Si led to average grain sizes of 7–11 µm (Fig. 2). Apparently, a certain minimum amount of silicon (about 1 mol %) is required to prevent discontinuous grain growth. This can be interpreted as follows. The $Si(OEt)_4$ addition, having been dropped in without catalysing admixtures, hydrolyses rather slowly. Therefore, it is supposed that a fine-distributed "SiO_2 precursor" is developed which quickly sticks to the matrix powder by strong adhesive forces and is transformed into SiO_2 on heating. Under favourable conditions (a sufficient amount of SiO_2 and a small degree of agglomeration) the precursor can involve each grain of the matrix powder and the subsequent SiO_2 material should also involve grains of the sintering body. In this way a homogeneous distribution of silicon should be obtained in spite of the considerable difference in the densities between $BaTiO_3$ and SiO_2.

At least part of the excess TiO_2 transforms into $Ba_6Ti_{17}O_{40}$ (B6T17) during calcination [12], thus the sintering body contains $BaTiO_3$ grains, B6T17 spheroids [12] and SiO_2. If the temperature exceeds about 1250 °C, melting will occur at points where all three materials, or at least SiO_2 and $BaTiO_3$, are in contact. The number of contact points or regions would be larger if the other components of the sample were surrounded by an SiO_2 film (series A) than in the case of type B specimens. Consequently, the number of melting phases developing microregions increases, and the melt should embed the microcrystals of the ceramic substantially, without penetrating the crystals [13]. However, it should be noted that the exact role of the added Si in the subsequent Ostwald ripening process is not clear. During the liquid-phase sintering process the eutectic melt decomposes into $BaTiO_3$ and the second phase. This second phase segregates in the grain interstices, whereas all the $BaTiO_3$ apparently separates on the grains.

The nature of the second phase in excess Ti- and Si-containing PTCR ceramics is still not understood. For excess Ti samples only, the existence of the exclusive second phase B6T17 was evinced and accepted, whereas in the presence of Si as second phase, $BaTi_3O_7$ and/or "$BaTiSiO_5$" [14–16], $Ba_2TiSi_2O_8$ (fresnoite) [17, 18], and B6T17 have been discussed.

A type A powder ($x = 0.16$, $y = 0.0004$, $z = 0.04$) sintered at 1300 °C was examined by X-ray diffraction (Philips powder diffractometer PB 1710) which revealed the presence of $Ba_2TiSi_2O_8$ as a crystalline second phase, in addition to the major tetragonal $BaTiO_3$ phase (see Fig. 3). Presumably, the B6T17 phase could not be detected because its content lies below the detectable limit of about 5 wt % as discussed below. According to Bast [17], the Ti-rich B6T17 develops in Si-containing $BaTiO_3$ ceramics due to the formation of the Ba-rich fresnoite, because of the balance of stoichiometry. The process can be summarized as

$$28BaTiO_3 + 22SiO_2 \rightarrow 11Ba_2TiSi_2O_8 + Ba_6Ti_{17}O_{40} \quad (1)$$

i.e. the B6T17 content of Si-containing samples should be higher than that of corresponding Si-free ones. Analogously, the formation of B6T17 in excess Ti samples can be represented by

$$6BaTiO_3 + 11TiO_2 \rightarrow Ba_6Ti_{17}O_{40} \quad (2)$$

From these relations the concentration of second phase can be estimated roughly in the examined powder (1 mol % excess Ti, 4 mol % Si addition) to about 2.6 and 4.3 wt % for B6T17 and fresnoite, respectively.

Type A powders showed a higher sinterability resulting in significant changes in the electrical properties, as discussed below. It is seen from Table II, that the temperature of maximum resistivity (T_{max}) increases with increasing Si content, whereby this effect appears more distinctly at $T_s = 1300\,°C$ than at $T_s = 1350\,°C$. We observed the well known decrease in T_s if silicon is added, in which case the results are again different for the two series. From $z = 0.005$ (0.5 mol % Si), all type A compositions exhibited a good conductivity from $T_s = 1300\,°C$ (SFP), whereas corresponding type B samples were semiconducting at the same T_s with $z \geq 0.015$.

It was also found that the plot ρ_{25} versus silicon addition shows a maximum which is placed at $z = 0.005$ for type A samples and at $z = 0.015$ for type B samples (see Fig. 4). The change in ρ_{25} with Si content to the maximum can tentatively be explained by a decrease in the average grain size and homogenization of the microstructure, whereas the slope of ρ_{25} cannot be interpreted in terms of the microstructure. It is assumed that the Si-containing second phase affects the electrical properties in an indirect manner; in the case of Si-free specimens the required Ba vacancies for the adjustment of defect equilibrium can be formed by

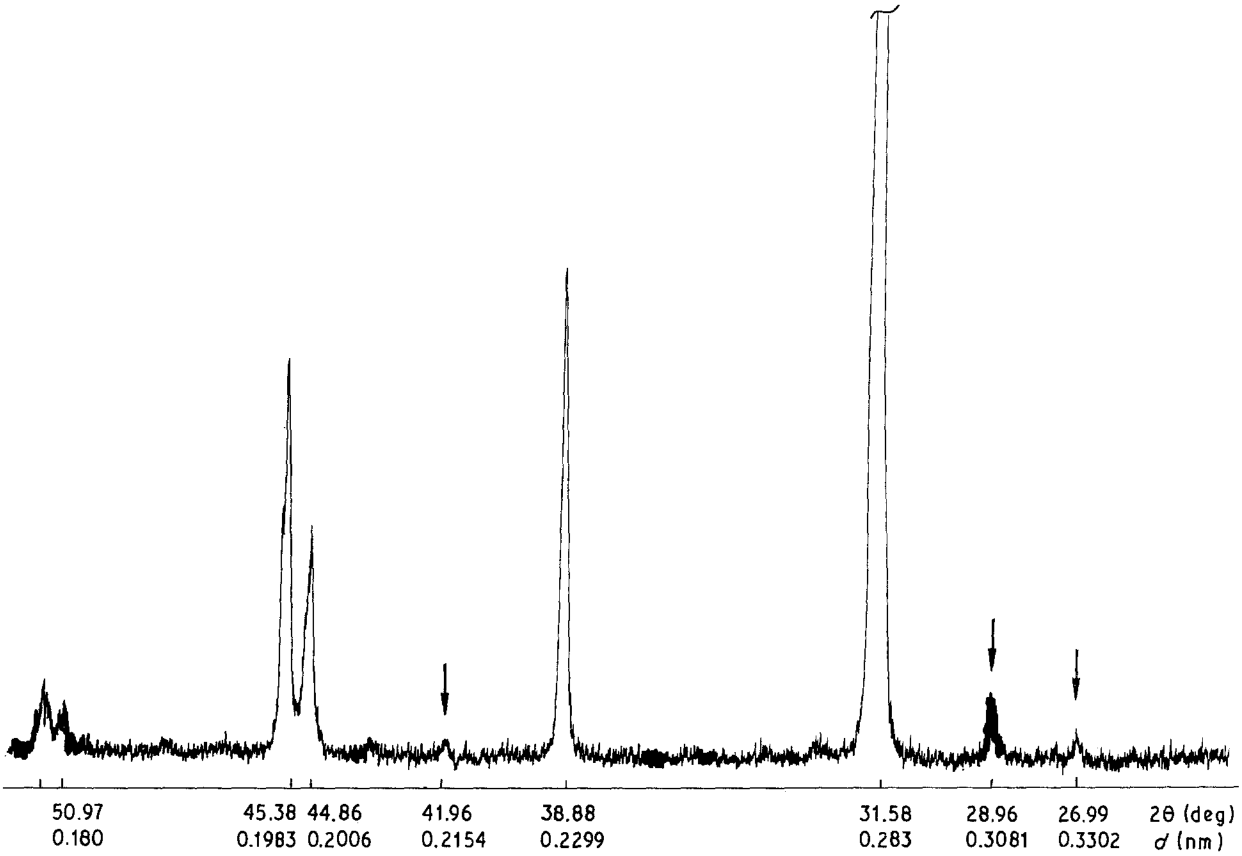

Figure 3 The X-ray diffraction pattern of a type A powder sintered at 1300 °C; $x = 0.16$, $y = 0.0004$, $z = 0.04$; (↓) $Ba_2TiSi_2O_8$.

TABLE II T_{max} and magnitude of PTCR effect as a function of the sintering temperature, cooling rate, Ca and Si contents. Series A; $(La_{0.002}Ca_xBa_{0.998-x})(Ti_{1.0096}Mn_{0.0004})O_3 \cdot zSiO_2$

Ca content (mol %)	Si content (mol %)	Cooling rate (K min^{-1}) at sintering temperature, T_s		$\frac{\rho_{max}}{\rho_{min}}$	T_{max} (°C)
		1300 °C	1350 °C		
16	1.25	1		4.7×10^5	246
16	1.25	10		5.0×10^3	332
16	1.25		1	3.8×10^5	231
16	1.25		10	3.4×10^3	310
16	2.5	1		4.9×10^5	255
16	2.5	10		4.2×10^2	325
16	2.5		1	2.0×10^6	237
16	2.5		10	1.3×10^3	310
16	4.0	1		3.8×10^5	275
16	4.0	10		1.7×10^3	360
16	4.0		1	3.6×10^5	245
16	4.0		10	5.4×10^3	345
20	1.25	1		1.2×10^4	260
20	1.25	10		2.4×10^2	320
20	1.25		1	1.8×10^5	235
20	1.25		10	7.7×10^3	270
20	4.0	1		4.6×10^4	255
20	4.0	10		1.1×10^4	360
20	4.0		1	2.0×10^5	240
20	4.0		10	6.7×10^3	310

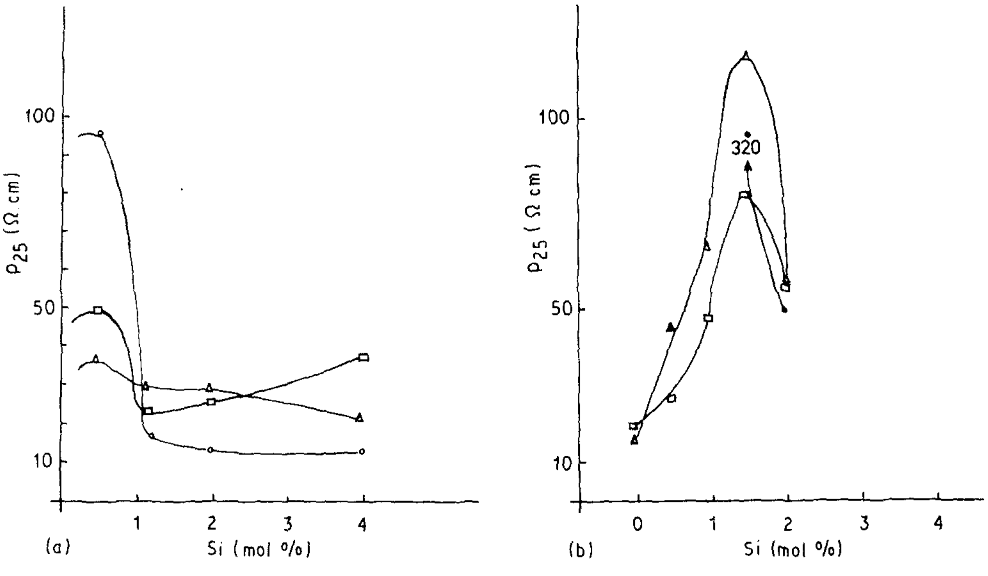

Figure 4 The dependence of the room-temperature resistivity, ρ_{25}, on Si content for samples with a composition of $(La_{0.002}Ca_{0.08}Ba_{0.918})(Ti_{1.0098}Mn_{0.0002})O_3 \cdot zSiO_2$. (a) Series A, (b) Series B. T_s = (○) 1300 °C, (□) 1350 °C, (△) 1400 °C.

a reaction of BaO which steps out the grain boundary with the intergranular B6T17 phase according to [19]

$$11BaO + Ba_6Ti_{17}O_{40} \rightleftharpoons 17BaTiO_3 \quad (3)$$

Such a reaction does not seem to be possible with the Ba-rich $Ba_2TiSi_2O_8$ phase. On the other hand, the second phase is segregated at the interstices adjoining three or more grains, as mentioned above, whereby a distinct phase boundary separates the two phases into two continuous microregions [13]. Thus the fresnoite phase diminishes the area of direct contact between the $BaTiO_3$ grains and the B6T17 phase as a source of Ba vacancies. In this way the formation of Ba vacancies inside the perovskite grains should be hindered and the concentration of Ba vacancies in the intergranular barrier layer should decrease. As a consequence, the electrical resistivity of the compact is reduced, as observed.

3.2. Variation of Ca content

The microstructural effect of adding Ca to $BaTiO_3$ ceramics has been reported by Kolar *et al.* [20]. We found, in Si-free samples, a nearly linear decrease in the mean grain diameter ($\bar{d}$) with increasing Ca content (up to 20 mol %) in agreement with the appearance of a narrow grain size distribution (Fig. 5). This plot is modified with increasing Si content. From

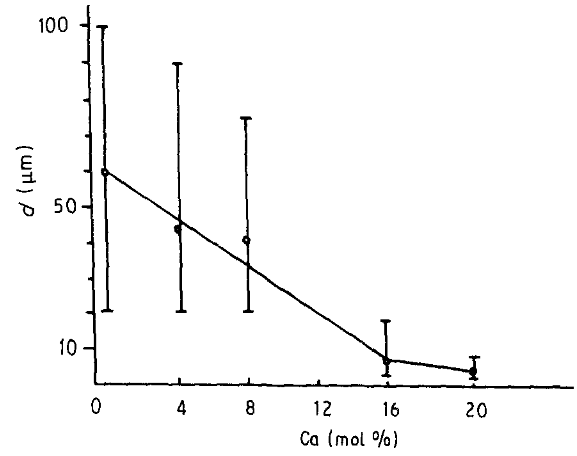

Figure 5 The dependence of the mean grain size on Ca content, a $T_s = 1350\,^{\circ}\mathrm{C}$, for $(\mathrm{La_{0.002}Ca_{x}Ba_{0.998-x}})\mathrm{Ti_{1.01}O_3}$.

1.25 mol % Si (series A) the grain diameter decreases sharply in the region of small amounts of Ca, reaches a minimum at 4 mol % Ca, and decreases slightly up to 16 mol % Ca. Increasing amounts of Si again cause a microstructural homogenization. However, from $x = 0.2$ (20 mol % Ca) the microstructure becomes inhomogeneous and that tendency increases if the Si content is increased to 4 mol %. Obviously, this behaviour may be attributed to a changed mechanism of nucleation, whose effect is intensified at larger Ca contents [21]. In addition, at higher concentrations of added Ca and Si, larger amounts of second phase should be present in the compacts, because the limit of Ca solubility in $\mathrm{BaTiO_3}$ is exceeded. Its value was determined to be $\sim$ 16 mol %; this in contradiction to published [22, 23]. Additionally, the ratio between the maximum ($\rho_{\max}$) and the minimum ($\rho_{\min}$) resistivity of the resistivity–temperature characteristics decreases if the amount of added Ca reaches 20 mol %, especially in the case of slow cooling rates, as seen from Table II.

3.3. Variation of Mn content

Mn acts in regions near the grain boundaries [24, 25] and, depending on temperature, it represents singly and doubly ionized acceptors, respectively [26]. According to Al-Allak *et al.* [24] the Mn ions, which are located inside a thin Mn-rich boundary layer, are partially compensated due to the formation of ionized oxygen vacancies. During continued sintering (and also at higher sintering temperatures) in air, more of these vacancies are filled resulting in an increase in the number of Mn ions acting as acceptors. Thus a slow cooling rate ($1\ \mathrm{K\,min^{-1}}$) causes, in addition to an increase in the intergranular barrier layer (gradient of Ba vacancies), a rising acceptor concentration near the grain boundaries. The consequence is that both ρ_{25} as well as the slope and the maximum of the resistivity (ρ) – temperature (T) plot are affected, as illustrated in Fig. 6. Curve 1 shows a typical ρ–T plot for a type A sample with $x = 0.16$, $y = 0.0002$, and $z = 0.125$ sintered at $T_s = 1300\,^{\circ}\mathrm{C}$ with SFP. Curve 2 shows one for a sample with twice the Mn addition ($y = 0.0004$) sintered with the same firing regime, whereas the only difference between the specimens plotted in curves 2 and 3 consists in the cooling rate, which was $1\ \mathrm{K\,min^{-1}}$ for the latter. Additionally, the influence of the cooling rate on both the slope of the ρ–T plot and the magnitude of the PTCR effect is exhibited by the values listed in Table II.

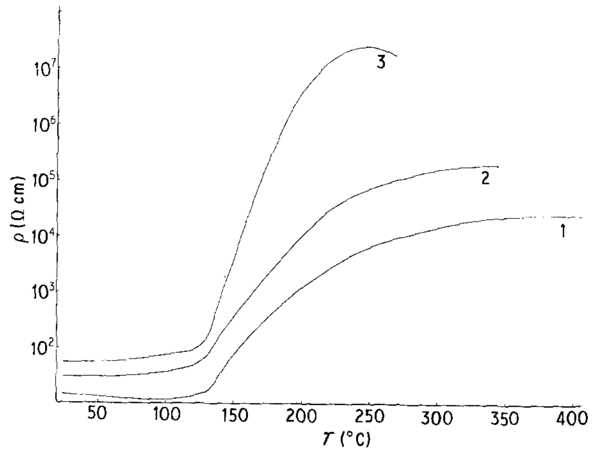

Figure 6 Resistivity–temperature plot of type A samples.
Curve 1: $x = 0.16$, $y = 0.0002$, $z = 0.125$, cooling rate $= 10\ \mathrm{K\,min^{-1}}$.
Curve 2: $x = 0.16$, $y = 0.0004$, $z = 0.125$, cooling rate $= 10\ \mathrm{K\,min^{-1}}$.
Curve 3: $x = 0.16$, $y = 0.0004$, $z = 0.125$, cooling rate $= 1\ \mathrm{K\,min^{-1}}$.

4. Conclusions

A study of the effects of a new method for adding silicon on the microstructural and electrical properties allows the following conclusions to be drawn:

1. Under suitable conditions, anomalous grain growth is definitely avoided and the microstructure appears homogeneously.
2. Si added by the new method affects the properties in a more effective manner than that added classically, i.e. a smaller amount of Si is required to obtain the same or better effects. The consequence is a decreasing portion of second phase in the sintered body.
3. The discussion suggests application of this means of adding Si in those cases in the field of ceramics where silicon-containing agents are used as sintering aids.

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