

Effects of aluminium on the electrical and mechanical properties of PTCR BaTiO₃ ceramics as a function of the sintering temperature

Part 1 *Electrical behaviour*

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The effect of Al additions on the electrical behaviour of positive temperature coefficient of resistance (PTCR) BaTiO₃ ceramic sintered in air at temperatures ranging between 1220 and 1400°C have been investigated. Two batches of material, both showing a PTCR effect, were prepared identically except that additions of Al₂O₃ (0.55 mol %) were made to one of them. It has been confirmed that the presence of aluminium results in an increase in the temperature at which the maximum resistivity, ρ_{\max} , occurs as well as reducing the sintering temperature, in the presence of silicon, to 1240°C. Additionally, direct comparisons between the two materials have demonstrated that such additions result in an increase of ~100% in the minimum resistivity, ρ_{\min} , at sintering temperatures beyond 1280°C. A similar increase in ρ_{\max} for sintering temperatures below 1360°C and a five-fold reduction in the ratio of ρ_{\max}/ρ_{\min} in samples sintered above 1320°C have also been attributed to the presence of aluminium. It was further found that aluminium increases the average grain size by ~30% and promotes the formation of a liquid phase.

1. Introduction

It is well known that donor-doped BaTiO₃ ceramics sintered in air show a large increase in resistivity near the ferroelectric transition temperature. The overwhelming evidence in the literature suggests that this behaviour (commonly referred to as the positive temperature coefficient of resistance or simply the PTCR effect) is a grain-boundary related phenomenon. The essential features of this effect have been explained successfully by a barrier layer model [1, 2].

PTCR materials capable of withstanding mains voltages of 240 V a.c. have considerable commercial value because they can be used in industry as motor starters or in domestic appliances as self-regulating heating elements, e.g. in food warmers, hair dryers, etc. In order to obtain useful ceramics it is essential to minimize the decrease in their resistance with applied voltage (arising from the barrier layer nature of the PTCR effect) to avoid thermal run away. Their mechanical performance will also have to be such that they will be able to endure the mechanical stresses resulting from the initial thermal shock when switching on the electric supply. As the fracture strength depends inversely on the square root of the average grain diameter [3] and the voltage dependence of resistivity is reduced for smaller grains [4], it is necessary to ensure that such ceramics have a uniform grain structure composed of small grains. As reported by Ueoka and Yodogawa [5], PTCR devices consisting of small grains were found to have higher withstand voltages (defined as the voltage corresponding to the minimum

current at a steady state power) than those with a non-uniform grain structure.

It is now established that the use of a liquid-phase sintering process for the production of barium titanate ceramics is important in the control of grain growth. The additives commonly employed to provide a liquid phase during sintering include TiO₂, SiO₂ and Al₂O₃ [6-9] which form a eutectic reaction with BaTiO₃. If a slight excess of TiO₂ is present then a eutectic with barium meta-titanate provides a liquid phase at 1322°C [10]. On the other hand, the addition of small amount of SiO₂ reduces the temperature at which the liquid phase appears to 1260°C [11]. This further reduces the possibility of non-uniform grain growth. The eutectic temperature obtained in the presence of SiO₂ is further lowered to about 1240°C by the addition of a small amount of Al₂O₃ [12]. However, the effect of aluminium on the characteristics of PTCR ceramics is rather complex. In a recent review article, Kulwicki [13] noted that authors who just used aluminium with pure n-doped BaTiO₃ reported a detrimental effect, while those who introduced aluminium together with silicon to modify the liquid phase found it to be less detrimental or even beneficial. Other recent investigations were found to be in agreement with the above conclusion. Using raw materials not containing silicon, Chan *et al.* [14] showed that aluminium acts as an acceptor, while Atsumi and Wada [7] reported the advantageous effects of aluminium if added together with silicon. However, Fleming *et al.* [15] claimed that aluminium is beneficial even if added without silicon,

although they stated that it is preferable to add silicon as well. Nevertheless, it was not clear in this case if silicon was introduced with aluminium as an impurity during the fabrication process. The claimed advantages of aluminium when added with silicon are: (i) to lower the sintering temperature, (ii) to shift the temperature T_{\max} , at which ρ_{\max} occurs, to a higher value, and (iii) to suppress the influence of harmful impurities such as potassium, sodium, etc. which are commonly found in the raw materials and hinder the conversion of the ceramic composition into a semiconductor [7].

In the present work a comprehensive study of the effects of aluminium on the sintering and electrical behaviour of BaTiO₃ ceramics has been carried out. This was done by comparing two types of ceramic which were prepared in the same way from the same mix except that 0.55 mol % Al₂O₃ was added to one of them. The effect of aluminium on the mechanical properties will be the subject of a subsequent paper.

2. Experimental method

2.1. Sample preparation

Two types of PTCR ceramic (subsequently referred to as types A and B) were prepared using commercial BaTiO₃. Except for the addition of Al₂O₃ to type A devices, the two kinds of ceramic had the same composition and were processed identically. These were both prepared with the following composition: (Ba_{0.89}Ca_{0.107}Ho_{0.003})TiO₃. Small amounts of excess TiO₂ (0.45 mol %) and SiO₂ (0.8 mol %) were also added to improve the sintering characteristics. With mix A the amount of Al₂O₃ added was 0.55 mol %. The raw materials of each formulation were first mixed independently with water using agate milling balls in a polyethylene vessel for 12 h. The slurry was then dried and mixed with a small amount of binder solution. After further drying, the material was granulated and compressed into small pellets by means of a hydraulic press using a forming pressure of 300 MPa. During sintering the green pellets were placed inside a tunnel furnace very close to the control/monitoring thermocouple. A slow flow of air, $\sim 0.5 \text{ l min}^{-1}$, was maintained throughout the entire firing process. Initially the samples were heated at a rate of $400^\circ \text{ C h}^{-1}$ to 500° C for 2 h to ensure effective burning off of the binder. The temperature was then increased at a rate of $900^\circ \text{ C h}^{-1}$ to the sintering temperature which was varied between 1220 and 1400° C for different batches. After sintering for 30 min the samples were annealed at 1220° C for a further 30 min during cooling to improve their PTCR behaviour. Following the sintering and annealing processes the cooling rate was maintained at $300^\circ \text{ C h}^{-1}$ down to 800° C below which the furnace was allowed to cool naturally.

2.2. Measuring procedure

Ohmic contacts to the BaTiO₃ ceramics were made by using an In/Ga alloy in the ratio of 2 to 1. Resistivity measurements were then carried out under d.c. conditions at different temperatures, at approximately 10° C intervals. Between readings, the sample was heated at a rate of $3^\circ \text{ C min}^{-1}$ in the temperature range 30 to 330° C . The temperature was always maintained at a

constant level for 4 min before measurements were recorded to ensure that the specimen temperature was uniform. These measurements were made under micro-processor controlled conditions.

3. Results

3.1. Effect of aluminium additions on the grain structure at different sintering temperatures

The grain structure of the as-sintered surfaces of specimens of both ceramics was examined using a Cambridge Instrument (S600) scanning electron microscope. The variation of the average grain size with the sintering temperature for both types of ceramic is shown in Fig. 1 and was determined from scanning electron micrographs using a linear intercept technique. It is immediately obvious that the addition of aluminium leads to an increase in the average grain size. Major grain growth in both types A and B samples is completed when sintering is carried out at about 1280° C . Ceramics from both types of material fired at 1220° C were found to be insulating, yellow in appearance and to have very small grain size ($< 1 \mu\text{m}$) i.e. not sintered. Both type A and B ceramics showed grain growth when sintered at 1240° C , because their grain size had increased to $\sim 2 \mu\text{m}$. These ceramics were also insulators and had a greenish yellow colour. The variation of the grain structure of type A and B specimens with higher sintering temperatures is shown in Figs 2 and 3, respectively. A wide grain-size distribution was found when firing at 1260° C (see Figs 2a and 3a). The grains of type A ceramic were generally flat and have straight edges especially for sintering temperatures below 1360° C , while those of ceramic B were of a boulder shape.

Numerous fibrous features were observed generally near the grain boundaries at the free surfaces of the aluminium-containing specimens when sintered at 1360° C . However, the number of these fibres decreased in samples sintered at other temperatures. One such fibre is shown in detail in Fig. 4, but others can also be seen clearly at F in the micrograph in Fig. 2c. The chemical composition of a number of these fibres was investigated using the EDX technique. The results revealed that the individual fibres had different compositions, possibly resulting from imperfect mixing of

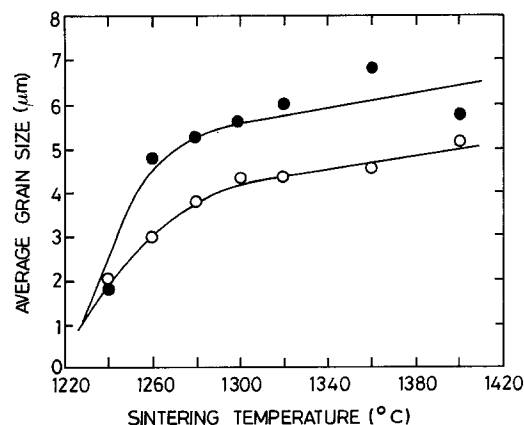


Figure 1 Dependence of average grain size on the sintering temperature (●) type A ceramic (○) type B ceramic.

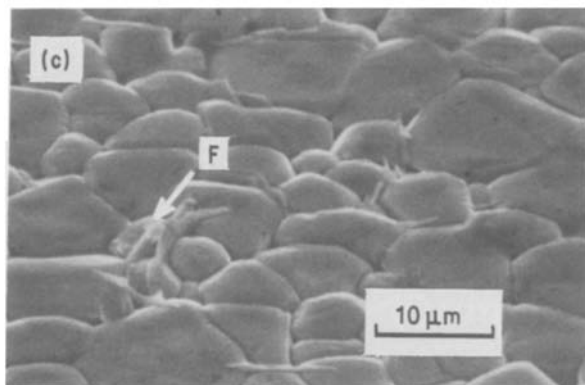
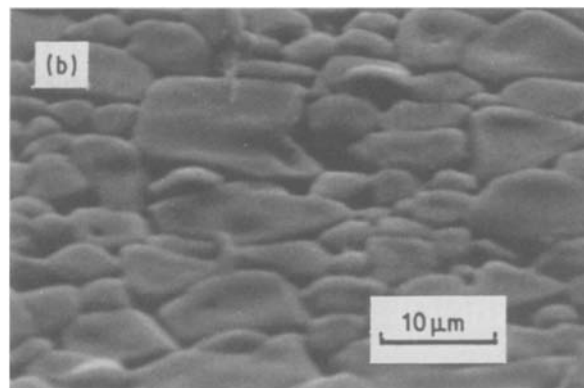
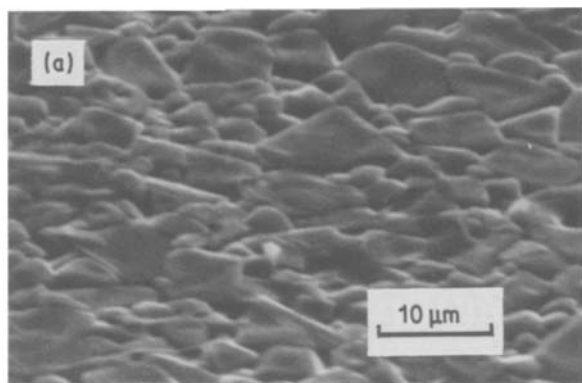
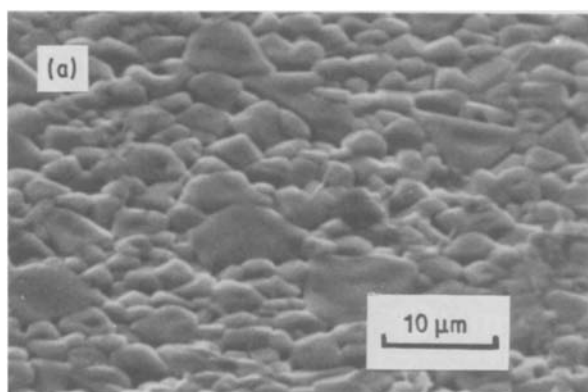


Figure 2 Dependence of grain structure of type A ceramic on the sintering temperature, (a) 1260°C, (b) 1300°C and (c) 1400°C. (F = Fibres).

the additives. Typical EDX spectra of a fibrous feature and one recorded from mid-grain (included for comparison) are presented in Fig. 5. Clearly this fibre contained both silicon and aluminium. Furthermore, since the Ba $L3$ and $L4$ lines are of the same height for both the mid-grain and the fibre, the difference in the heights of the $TiK\alpha/BaL1$ lines for the two spectra indicates an excess of titanium in the fibre. Other fibres showed different levels of aluminium, silicon

and excess titanium while some were found to be deficient in calcium or titanium and in others the presence of aluminium, silicon or excess titanium was not detected. This does not necessarily mean that these elements were completely absent in the fibres, because the EDX technique is typically only capable of revealing such elements if they are present at a level of at least 1 wt %.

In contrast, only very few fibrous features were observed in samples made from type B ceramics and these were generally smaller and thinner than those of type A. Again these fibres showed a large variation in their composition. The majority of the EDX spectra demonstrated that these fibres were mainly rich in titanium, while silicon lines were less frequently detected, indicating that silicon was either absent or present in very small quantities (< 1 wt %). Fig. 6 shows the spectrum of a fibre with a large silicon peak, it can also be seen that this fibre is deficient in calcium and titanium.



3.2. Resistivity against temperature plots

A series of plots of ρ against T were obtained for both materials sintered at various temperatures investigated. However, those samples fired at 1220 and 1240°C could not be measured as they were found to be insulating, as mentioned earlier. Specimens sintered between 1260 and 1400°C showed normal PTCR behaviour. A typical example is presented in Fig. 7

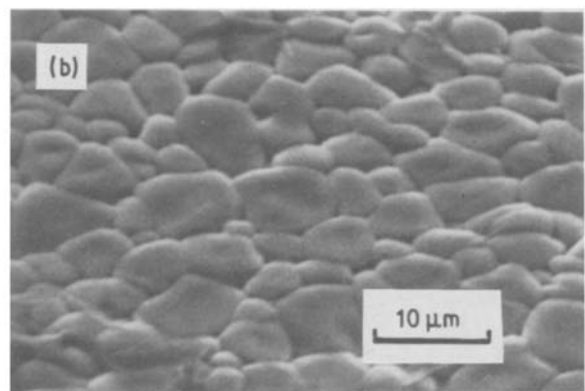
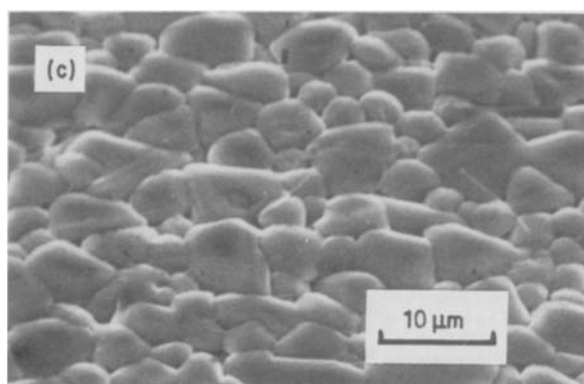


Figure 3 Dependence of grain structure of type B ceramic on the sintering temperature (a) 1260°C, (b) 1300°C and (c) 1400°C.



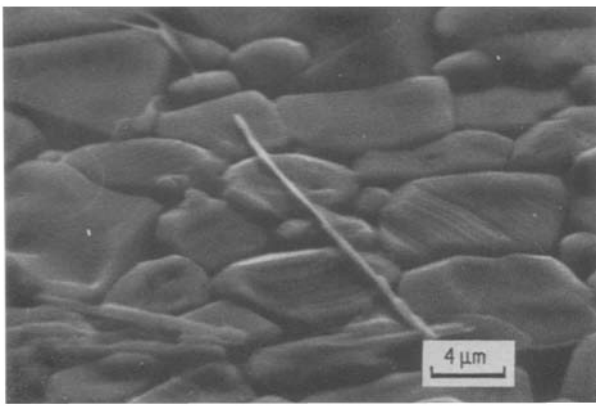


Figure 4 A representative fibrous feature observed on as-fired surface of type A ceramic.

which corresponds to a type A ceramic. Each experimental point is an average of measurements taken from nine nominally identical samples. Obviously T_{max} is reduced by a small amount ($\sim 20^\circ\text{C}$) when the sintering temperature is increased from 1260 to 1400°C. A similar decrease in T_{max} was also observed in type B specimens. For the same sintering temperature, it is also apparent from Fig. 7 that ϱ_{max} occurs at higher temperature when aluminium is added.

The dependence of ϱ_{max} , ϱ_{min} and the ratio of $\varrho_{max}/\varrho_{min}$ (which determines the magnitude of the PTCR effect) on the sintering temperature for both materials is presented in Figs 8, 9 and 10, respectively. With type A material both ϱ_{min} and ϱ_{max} increase with sintering temperature; however, the increase in ϱ_{max} is less pro-

149 CNT

3440 eV

Link Systems 860 Analyser

4K FS: B
10 eV / CHAN

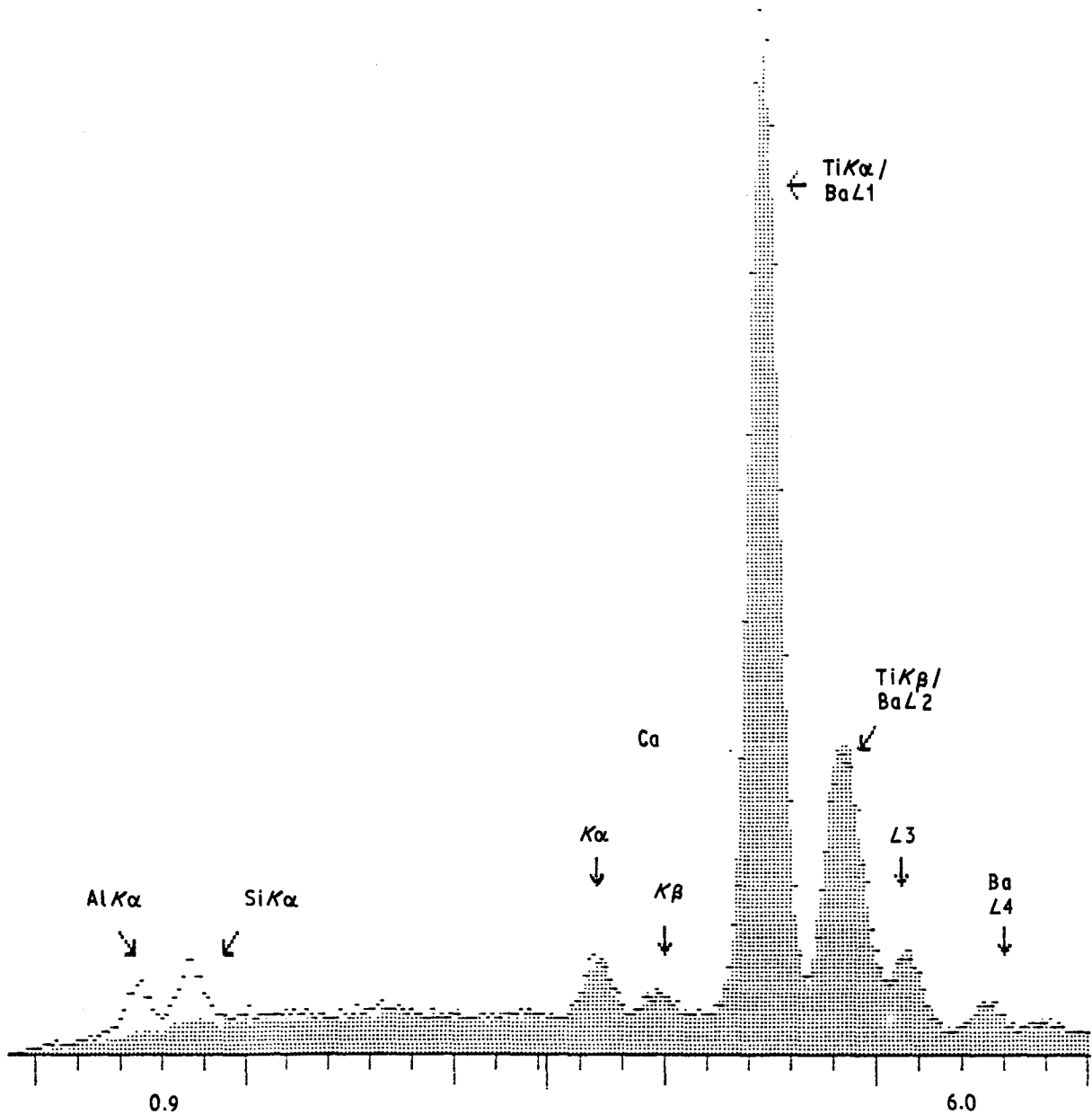


Figure 5 EDX spectra for type A ceramic recorded from a fibrous feature (—) and the mid-grain (---).

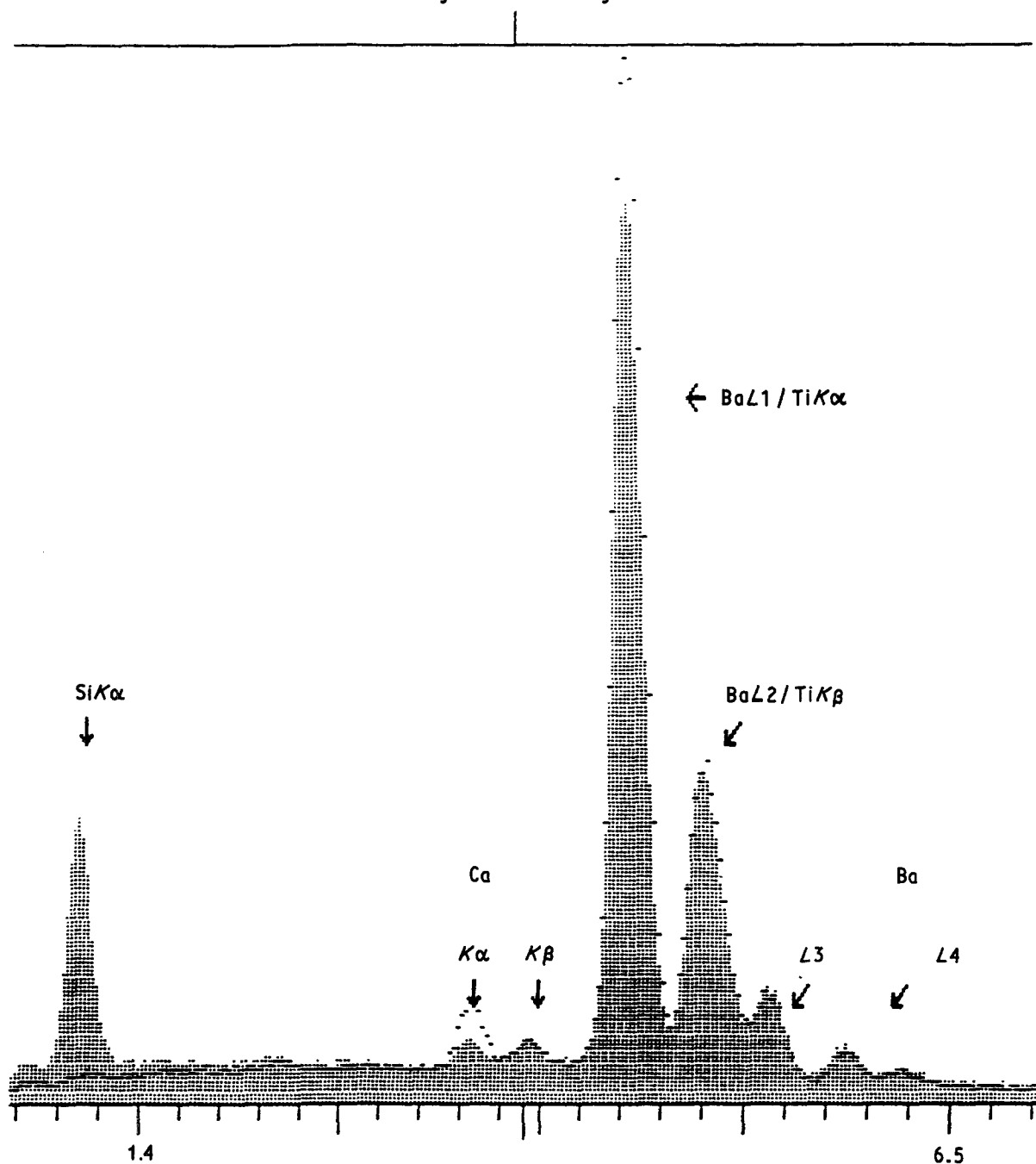


Figure 6 EDX spectra of a sintered specimen of type B ceramic taken from a fibrous feature (---) and the mid-grain (---).

nounced when sintering below 1300°C . On the other hand, for type B specimens, both q_{max} and q_{min} show an initial decrease with sintering temperature, but then start to increase at sintering temperatures above 1300°C . In both ceramics, the ratio $q_{\text{max}}/q_{\text{min}}$ shows an initial decrease with sintering temperature. However, with type B specimens, $q_{\text{max}}/q_{\text{min}}$ starts to increase again on sintering above 1280°C up to 1360°C , and thereafter remains almost constant. In type A ceramics $q_{\text{max}}/q_{\text{min}}$ exhibits a small peak on sintering at about 1320°C and then decreases again as the sintering temperature is increased. It is apparent from Figs 8, 9 and 10 that the addition of aluminium leads to an increase in q_{min} when sintering above 1280°C , an increase in q_{max} in samples sintered below 1360°C and a reduction

in the magnitude of the PTCR effect when sintering above 1320°C .

4. Discussion

Matsuo *et al.* [16] and Matsuo and Sasaki [12] who both used aluminium, silicon and titanium to achieve liquid-phase sintering did not report the presence of fibrous features. In contrast, Drofenik *et al.* [17], using excess titanium to obtain the liquid phase, observed that when the sintering temperature was maintained constant for several hours, the amount of liquid phase which originally existed between the triple points, was gradually reduced, and simultaneously a large number of needle-like fibrous features were observed to grow on the outer surface of the specimens as well as on the

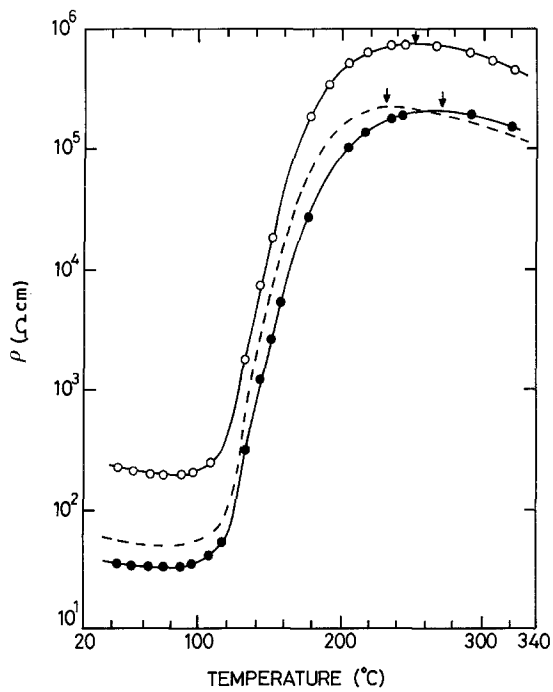


Figure 7 Dependence of resistivity on temperature. The continuous solid lines correspond to type A material sintered at 1260°C (●) and at 1400°C (○), while the dotted line is for type B material sintered at 1260°C. Arrows indicate T_{max} .

surface of large pores. These fibrous features were identified as single crystals of monoclinic $Ba_6Ti_{17}O_{40}$ [17]. The fibrous features reported in the present work are also thought to be formed from the liquid phase, but they cannot be directly associated with those observed by Drogenik *et al.* because of the large variation in their chemical composition. The addition of aluminium also seems to result in an increase in the amount of the liquid phase, as indicated by the fact that the fibres in the aluminium-containing specimens (type A) were both more numerous and generally

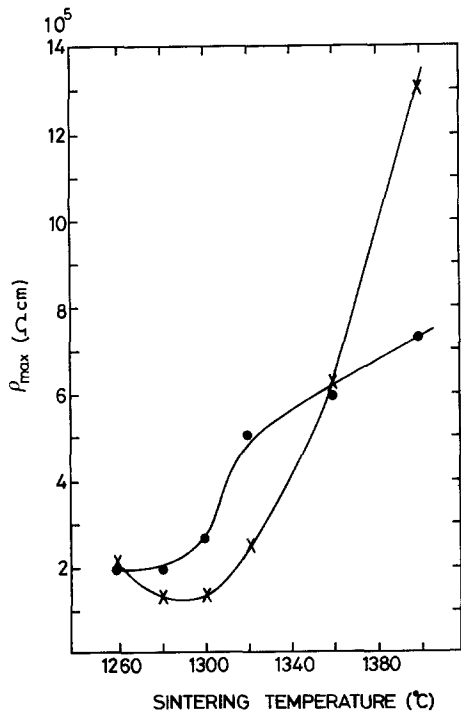


Figure 8 Comparison of the effect of sintering temperature on ρ_{max} for type A (●) and type B (×) materials.

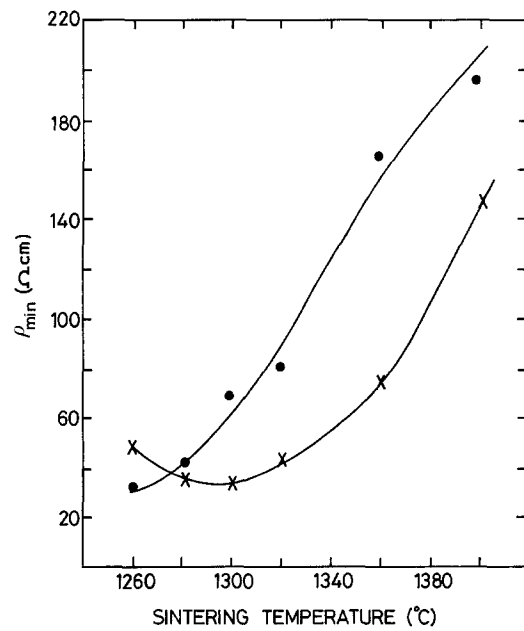


Figure 9 Comparison of the dependence of ρ_{min} on sintering temperature: (●) type A and (×) type B materials.

larger in size than those observed in type B material. This is consistent with the results of Fulson and Rutt [18] who reported that aluminium has a solubility limit of less than 0.1 at % in $BaTiO_3$. This observation also supports a suggestion made by Kulwicki [13] that the addition of aluminium in the presence of silicon favours the formation of a liquid.

It has been reported [19] that more of the n-dopant is depleted if the amount of the liquid phase is increased. Thus, the increase in the grain size of the aluminium-containing samples may be attributed to the fact that more of the inhibitors to grain growth (e.g. the n-dopant and other impurities) are leached into the liquid phase, the volume of which was increased by the addition of aluminium. Samples sintered near the liquid-phase melting point were found to have non-uniform grain growth, Figs 2b and 3b. It is suggested that at this temperature the liquid phase, which absorbs the inhibitors to the grain growth, is not present in sufficient quantity to wet all the grains

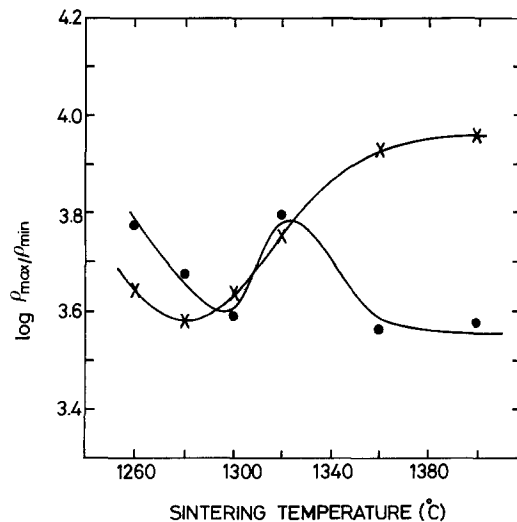


Figure 10 Comparison of the behaviour of ρ_{max}/ρ_{min} with sintering temperature (●) for type A and (×) for type B materials.

uniformly. Irregular grain growth then results from the uneven distribution of these inhibitors. The fact that grain growth commenced at 1240°C indicates that aluminium lowers the eutectic temperature of the Si–BaTiO₃ system as suggested previously (see Section 1). Aluminium was present only as an impurity in type B ceramics.

The increase in ρ_{\max} and the decrease in T_{\max} with sintering temperature, after major grain growth has been completed, indicate an increase in the surface state density at the grain-boundary region [20]. The slope of the rising parts of the ρ – T plots should also increase as a consequence of the enhancement of the surface state density. However, this was not observed experimentally, probably because the increase in the surface state density was not particularly large as evidenced by the fact that the changes in ρ_{\max} and T_{\max} were rather small. On the other hand, the increase in ρ_{\min} may be attributed to the increase in the surface state density and, additionally, the formation of a resistive layer rich in barium vacancies at the grain boundary in series with the barrier layer [21]. Both ρ_{\max} and ρ_{\min} are also expected to be reduced by the increase in the grain size with sintering temperature, because this leads to a decrease in the number of grain boundaries per unit length. This effect is thought to be most significant at the lower sintering temperature where major grain growth was still taking place.

The effect of aluminium on the electrical behaviour of the ceramic is rather complicated. This is because the changes in the structure and composition of the ceramic caused by the addition of aluminium can influence the electrical properties of the material in different ways. As explained above the increase in the grain size results in a decrease in both ρ_{\max} and ρ_{\min} . On the other hand, the suppression of the impurities such as potassium and sodium leads to an improvement in the PTCR behaviour. The reduction in the effective concentration of the n-dopant by the addition of aluminium (due to leaching out of more of the dopant or alternatively aluminium may act as an acceptor) will also affect ρ_{\min} , ρ_{\max} , the magnitude of the PTCR effect and the switching temperature [22]. Furthermore, the increase in the volume of the liquid phase may also affect the electrical performance of the material [23].

In conclusion, these results have demonstrated some of the effects of aluminium on the properties of the PTCR BaTiO₃ ceramics as a function of the sintering temperature. This has been achieved by making direct comparisons between two ceramics which have been produced identically except for the fact that aluminium was added to one of them. Aluminium has

been found to (i) increase ρ_{\min} , (ii) increase ρ_{\max} (when sintering below 1360°C), (iii) decrease ρ_{\max}/ρ_{\min} at sintering temperatures higher than 1320°C, and (iv) shift T_{\max} to higher values. The results have also shown that aluminium reduces the sintering temperature, increases the grain size and favours the formation of liquid phase with silicon.

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