Effect of secondary-phase segregation on the positive temperature coefficient in resistance characteristics of n-BaTiO$_3$ ceramics

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Modifications in the positive temperature coefficient in resistance (PTCR) of n-BaTiO$_3$ ceramics are brought about by specific additives such as Al$_2$O$_3$, B$_2$O$_3$ or SiO$_2$, leading to the segregation of secondary phases such as BaAl$_6$Ti$_4$O$_{19}$, Ba$_5$Ti$_4$O$_{17}$ or BaTiSi$_{3}$O$_8$ at the grain boundaries. Segregation of barium aluminititanates resulted in broad PTCR curves, whereas B$_2$O$_3$ addition gave rise to steeper jumps and SiO$_2$ addition did not result in much broadening compared with donor-only doped samples. Microstructural studies clearly show the formation of a structurally coherent epitaxial second phase layer of barium aluminititanate surrounding the BaTiO$_3$ grains. Electron paramagnetic resonance investigations indicated barium vacancies, $V_{Ba}$, as the major electron trap centres which are activated across the tetragonal-to-cubic phase transition according to the process $V_{Ba}^\ominus + e^\ominus \rightarrow V_{Ba}^\ominus$. The grain size dependence of the intensity of the $V_{Ba}$ signal indicated the concentration of these trap centers in the grain-boundary layer (GBL) regions. Further, the charge occupancy of these centres is modified by the secondary phases formed through grain-boundary segregation layers. BaAl$_6$Ti$_4$O$_{19}$ gave rise to Al-O$^-$ hole centres whereas no paramagnetic centres corresponding to boron could be detected on B$_2$O$_3$ addition. Such secondary phases, forming epitaxial layers over the BaTiO$_3$ grains, modify the GBL region, rich in electron traps, surrounding the grain core. The complex impedance analyses support this three-layer structure, showing the corresponding contributions to the total resistance which can be assigned as $R_{gb}$, $R_{ep}$ and $R_{secondary}$ phase. The epitaxial second phase layers bring about inhomogeneity in the spatial distribution of acceptor states between the grain boundary and the grain bulk resulting in extended diffuse phase transition characteristics for the GBL regions in n-BaTiO$_3$ ceramics. This can cause the GBL regions to have different transition temperatures from the grain bulk and a spread in energy levels of the associated GBL trap states, thus modifying the PTCR curves. An attempt has been made to explain the results based on the vibronic interactions applied to the mid-band-gap states in n-BaTiO$_3$. © 1998 Kluwer Academic Publishers

1. Introduction
In semiconducting polycrystalline ceramics, the bulk characteristics are intricately related to the composition and structure of grains as well as grain boundaries. The electrical behaviour of the boundaries is associated with the charge-transfer process. The segregated impurities, the precipitated second phase and the distribution of the frozen-in point defects at the grain boundaries play major roles in determining the overall electrical properties. The well-known grain-boundary phenomenon in donor-doped semiconducting BaTiO$_3$, namely the positive temperature coefficient in resistance (PTCR), has been attributed to the formation of electrical barriers at the grain boundaries across the tetragonal-to-cubic phase transition [1]. These barriers are reported to arise from acceptor states near the grain boundary which trap electrons. A more recent review by Huybrechts et al. [2] showed that the PTCR effect cannot be explained by assuming only one kind of electron trap. Native defects such as barium vacancies, $V_{Ba}$, titanium vacancies, $V_{Ti}$, adsorbed gases at the grain boundaries, or 3d transition-metal ion impurities can act as electron traps, with experimental evidence supporting one or the other [3–16]. This has kindled renewed interest in the subject of PTCR. The differential distribution of these electron traps as well as the formation of new electron traps by the alien constituents segregating at the grain boundaries can significantly alter the PTCR in BaTiO$_3$. Segregation studies on BaTiO$_3$ have been made previously by Lewis et al. [6]. From calculations of the bulk and surface defect energies, they proposed that there is a strong tendency for segregation of acceptor states in low-charged states. Also, the activation energy for the migration of acceptors in the titanium sublattice is very high and hence donors will deplete the
grain-boundary area, leaving behind an acceptor-rich layer, which leads to n-i-n junctions responsible for the PTCR effect. However, according to the segregation studies made by Chiang and Takagi [15], the spatial distribution of the acceptor defects at the grain boundary can be neglected compared with the electron depletion layer width. Therefore the acceptor layer caused by segregation is assumed to be one dimensional in the Heywang [1] model, but the acceptor levels in the samples of Chiang and Takagi [15] were much higher (0.3–1.0 mol%) than PTCR doping levels. Through similar segregation studies, Desu and Payne [16] proposed an n-i-n model; contrary to the calculations of Lewis et al. [6], the donors are said to be segregated at the grain boundaries, creating an insulating layer through vacancy compensation and forming the grain-boundary barriers. Again, the donor (10 mol% Nb) and the acceptor levels (0.6 at% Fe) used by them were much higher than the PTCR doping levels, namely 0.1–0.3 at% donor and 0.01–0.05 at% acceptor, and hence the model is questionable vis-à-vis the PTCR effect. Further, the experimental techniques used by them (scanning Auger electron spectroscopy and scanning transmission electron microscopy) yielded results which were specific to a few grains or grain boundaries and were not the average over all the grains or grain boundaries in the specimen. Experimental evidence exists in the literature [17–19], by way of electron paramagnetic resonance (EPR) measurements on single crystals and polycrystalline BaTiO₃ ceramics, to show that the acceptors do not segregate at the grain boundaries but dissolve within the grain bulk at the concentration levels used for PTCR. Both single crystals and polycrystals showed the same set of EPR signals arising from the acceptor ions (mostly 3d transition-metal ions). Apart from the bulk dopants, segregation of grain-boundary modifiers such as Al₂O₃, SiO₂ and TiO₂ in BaTiO₃ polycrystalline ceramics, owing to limited solid solubility, is known [13, 20–26]. They form segregated layers at grain boundaries and also randomly distributed secondary phases when present in higher concentrations (greater than 1 mol%). These have been used as aids to lower the sintering temperature but their effect on the PTCR of BaTiO₃ has not been dealt with in detail. No reports exist on the possible formation of alumino-titanates or silicotitanates of barium along the grain boundaries, nor on the polytitanates of barium. These secondary phases can modify the distribution of grain-boundary electron traps, thus directly influencing the electrical characteristics of n-BaTiO₃ ceramics. Unlike acceptor dopants, these segregated species can have a higher tolerance limit (up to a few per cent) of addition without increasing the room-temperature resistivity. Furthermore, no report exists on the difference in behaviour when these modifiers are bulk doped in raw material BaTiO₃ powder, in comparison with the heterogeneous addition during the ceramic fabrication. In view of the lack of detailed studies on the segregation effects of grain-boundary modifiers on PTCR of BaTiO₃ and to understand the role of these in modifying the grain-boundary electrical barriers, we have investigated the changing effects in PTCR brought about by specific grain-boundary modifiers such as Al₂O₃, B₂O₃ or SiO₂ in donor-doped BaTiO₃. The resulting grain-boundary segregation or second-phase formation can affect the electrical conduction possibly through the formation of new types of defect state and their differential distribution between grain boundary and grain bulk. EPR spectroscopy has been used as a tool, as in the previous studies by our group [17, 18, 27], for investigating the grain-boundary trap states in donor-doped BaTiO₃. Impedance spectroscopy studies were carried out to monitor the contributory components from the grain-boundary layers (GBL’s), leading to an explanation for the drastic change in PTCR with different grain-boundary modifiers.

2. Experimental procedures

Preparation of fine powders and the processing of ceramics have been described elsewhere [17, 28, 29]. The starting material was obtained by the thermal decomposition of BaTiO₃(OC₃H₇)₂·H₂O (BTO). In order to observe the changing pattern of trap centres associated with native defects by EPR, the BaCl₂ to TiOCl₂ ratio was varied from 0.9 to 1.1 following the method adopted in [17, 30]. Although the resulting BaTiO₃ has a correspondingly small deviation in stoichiometry leading to possible enhancement in V_Ba X-ray powder diffraction showed phase singularity. The background impurities in the starting material were kept as low as possible (Mn, less than 0.1 μg g⁻¹; Fe, less than 1μg g⁻¹) by the procedure described in [17]. Nb (0.2–0.4 at%, i.e., (3.1–6.3) × 10¹⁹ ions cm⁻³) was used as the donor and separately, Mn (25–200 ppm, i.e., (0.16–1.17)×10¹⁸ ions cm⁻³) was used as the acceptor. Donor concentrations greater than 0.4 at% resulted in smaller grain sizes. The grain boundary modifiers (Al₂O₃, B₂O₃ or SiO₂) were added heterogeneously, i.e., by mixing the preheated donor doped BaTiO₃ powder with the modifier and pressing into green discs. The addition of Al₂O₃ resulted in the formation of secondary phases such as BaAl₂TiO₅ and Ba₂Al₂TiO₇ along the grain boundaries. B₂O₃ addition did result in the formation of distinct secondary phase but was not detectable by X-ray diffraction. It is possible that B₂O₃ can form a glassy phase having the composition Ba₂B₂O₅TiO₂. SiO₂ led to the formation of second phases such as BaTiSi₂O₆ (benitoite).

The powder mixtures were mixed with an organic binder and pressed at 200 MPa to obtain green ceramics of 65–70% compaction. The binder was subsequently burnt off at 1100 K in air. The discs were then sintered in static air at 1630 K to obtain ceramics of 1–25 μm grain size. The sintering density of the ceramic discs ranged from 92 to 97% of the single-crystal value. Ceramics of different grain sizes were obtained by varying the sintering conditions for a given composition or by increasing the donor concentration to more than 0.4 at%. The ceramic discs were polished after sintering so that layers of 20–30 μm on both the sides were removed, in order to ensure that the measured characteristics did not correspond to those of