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Polytype induced exaggerated grain growth in ceramics

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Abstract

In polycrystalline materials we frequently observe exaggerated growth of some grains. One of the reasons for such growth irregularity, which we describe here, is the formation of polytypic sequences within the affected grains. We present an atomic-level study of the polytypic faults that are found in sintered perovskite ceramics with various oxide additions. Grains containing polytypic faults grow preferentially along the direction of fault planes. Results from this study indicate that both the local structure and chemistry of these faults are intimately related to the host crystal and the secondary phase that exists between the main phase and the additive. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

It is commonly recognised that any crystallisation process may, under specific conditions, lead to exaggerated grain growth. Such conditions are observed during the formation of polycrystalline bodies when the crystal grains are in mutual contact throughout a common medium. During the coarsening process some predetermined crystallites are enabled to grow rapidly at the expense of other grains, violating the uniform texture of the polycrystalline body. A number of possible reasons for this abnormal grain growth have been proposed,[1,2] these include: an initial bimodal distribution of grain sizes, a non-uniform pore pinning, and a preferential wetting. However, we find situations where none of these effects are operative, particularly when exaggeratedly grown grains show an anisotropic character, and segregation of impurities to specific crystallographic planes may be responsible for anisotropic growth. This fails to explain the anisotropic growth in the case of isometric crystals, where segregation of impurities to any favoured family of planes would, in effect, constrain the growth of the whole crystallite.[3] In such cases where we find no extrinsic feature that could lead to anisotropic grain growth the only possible reason for growth anomalies is a presence of intrinsic faults within these grains. While, qualitatively, it is accepted that particular impurities can lead to the formation of polytypic planar faults,[4] the driving force for polytype induced exaggerated grain growth has not been studied so far. In different ceramic systems we observed exaggerated anisotropic growth of grains containing polytypic faults such as twin,[5,6] antiphase,[7,8] or inversion boundaries.[9,10] These types of faults are regularly confined to low-index crystallographic planes. Regardless of the material where they are observed the faults extend parallel to the elongation of the crystal, implying that the origin of the crystal anisotropy must be related to the formation and growth of the two-dimensional polytypic structure within. Structure and chemistry of these planar faults are closely related to the nearest stable polytypic compound that exists in the corresponding matrix-additive phase system. The formation of these two-dimensional polytypic faults having typical widths of about one atomic monolayer will be referred as *nanostructural polytypism*, and its effect to crystal growth will be called as *polytype induced exaggerated grain growth*. To illustrate this concept of abnormal grain growth we used $CaTiO_3$–BaO system, where the crystal morphology clearly depends on the presence of either random polytypic faults or partially ordered polytypic layers within the affected grains.

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2. Experimental

In our study we used the samples of $CaTiO_3$ with 10 mol% excess of BaO. The samples were sintered above the temperatures of cubic modification of $CaTiO_3$.[11] The samples were examined by optical and transmission electron microscopy (TEM). For high-resolution TEM we used 400 kV TEM (Jeol, 4000EX) with point resolution of 0.17 nm. The HRTEM images were recorded close to first reverse passband of the contrast transfer function, where atomic columns appear as white dots. A scanning transmission electron microscope (STEM, VG HB301) equipped with an annular dark-field (ADF) detector and an electron energy-loss (EEL) spectrometer (Gatan, 666) was used to trace the distribution of Ba, Ca, and Ti across the planar faults. The estimated spectral resolution was 0.7 eV.

3. Results

The samples sintered at 1350°C exhibit pseudo-cubic exaggeratedly grown grains. These grains are idiomorphic with no apparent anisotropy (Fig. 1a). At higher sintering temperatures crystal morphology is completely deteriorated. At 1550°C the microstructure is dominated by larger sandwich-like grains that are strongly anisotropic with the longer axis parallel to the imbedded secondary-phase layers (Fig. 1b). To study the intrinsic structure and chemistry of both types of exaggeratedly grown grains we used various TEM techniques. HRTEM images of the large isotropic grains grown at 1350°C reveal a high concentration of planar faults that form square networks along $\{100\}_{cub}$ planes (Fig. 2a), similar to those observed in SrO doped $CaTiO_3$.[7] These faults have a rock-salt layer sequence produced by two consecutive $(002)_{cub}$ perovskite planes of AO composition (A = Ca, Ba) translated by an antiphase 1/2·[110] shift. The faults are similar to AO layers of $n(ATiO_3)\cdot AO$-type polytypic phases.[12] In the anisotropic grains grown at 1550°C we observe a high density of parallel faults (Fig. 2b) which exhibit a one-dimensional disorder along $[001]_{cub}$. In some regions these faults are ordered into simple polytypic sequences where every fault in the polytype layer is followed by either two or three perovskite blocks. The local chemistry of faulted regions was assessed by HAADF-STEM imaging combined with EELS. Both random faults and polytypic layers have composition CaO while the perovskite blocks in between comprise $(Ca_{1-x}Ba_x)TiO_3$ (Fig. 3), indicating a similar origin of the faults within high-temperature polytypic layers and the low-temperature isolated polytypic faults.

As a result of Ba replacement on Ca sites in the perovskite lattice the surplus of CaO segregates on planar faults along the lowest energy planes in the host crystal. Oxides like BaO are virtually insoluble in $CaTiO_3$[13] and the non-stoichiometry introduced by the addition of barium oxide is compensated by the formation of oxide-rich faults in the matrix perovskite crystal. Faulting can be easily avoided by equimolar addition of TiO_2. This, together with BaO excess, produces $BaTiO_3$ that has wide solid solubility range with $CaTiO_3$,[13] and consequently, no planar faults or polytypes are formed, and we no longer observe any exaggerated or anisotropic grain growth.

4. Discussion

Several good examples of *nanostructural polytypism* are known from the literature. One of these is the cubic-hexagonal phase transition in $BaTiO_3$ that occurs under

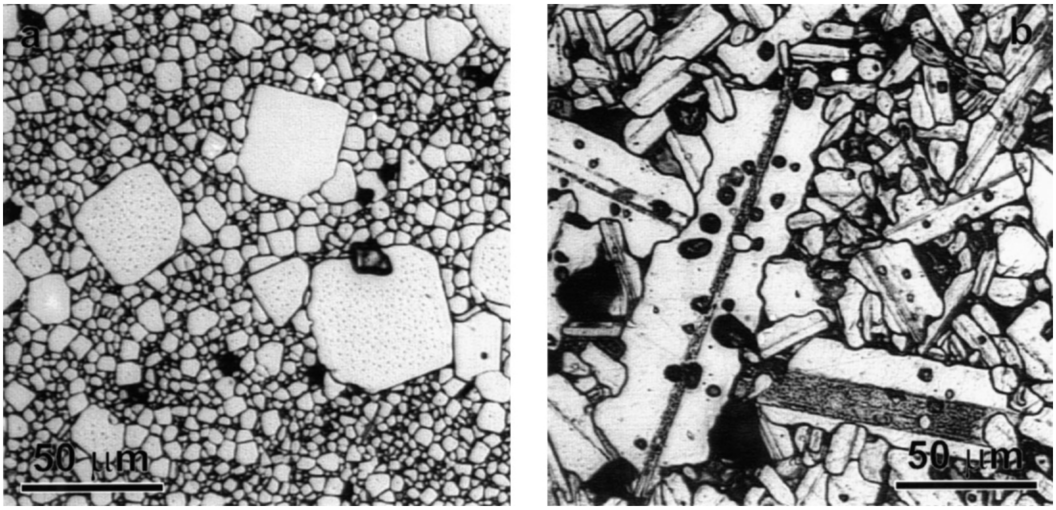

Fig. 1. Exaggerated grain growth in BaO doped $CaTiO_3$. (a) Large isometric grains formed at 1350°C display no apparent faulting. (b) Anisotropic grains developed at 1550°C show distinct polytypic lamellae stretching out of the grains in the direction of preferential growth. As soon as these grains collide their anisotropic growth is stopped and they start to thicken.

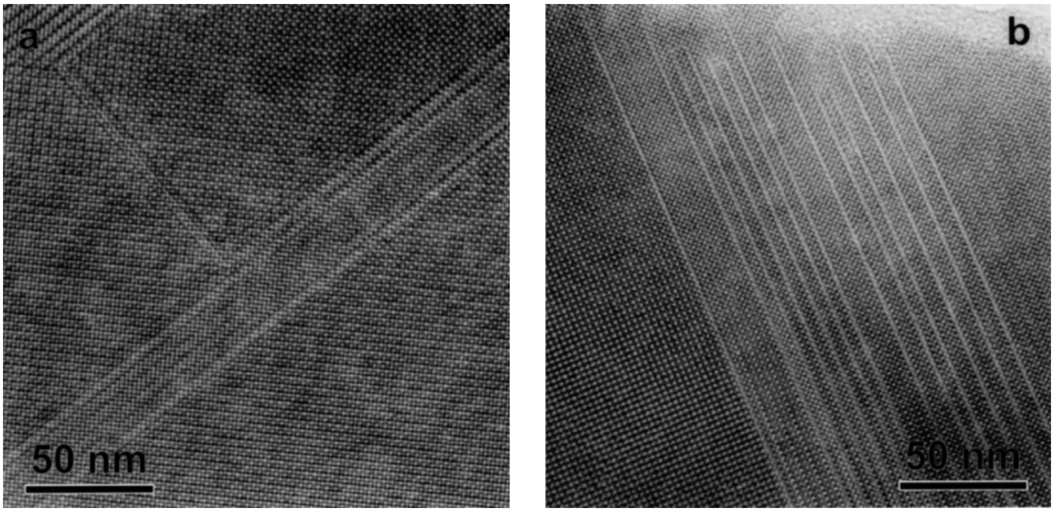

Fig. 2. Lattice images of the polytypic faults in (Ca,Ba)TiO_3 crystals. (a) Preparatory stage of nanostructural polytypism — random antiphase boundaries found in the large isometric crystals. (b) Final stage of nanostructural polytypism — ordered polytypic layers as found in anisotropic crystals. The faulting in the polytype layer occurs at a distance of two or more perovskite cells.

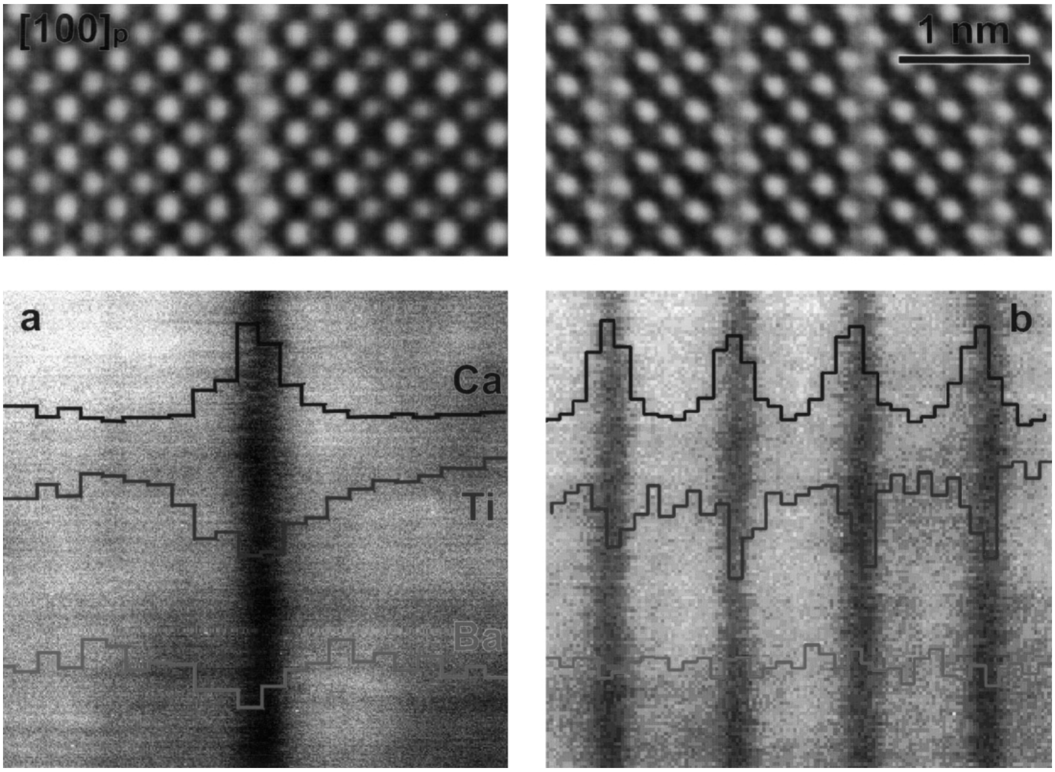

Fig. 3. Phase-contrast and annular dark-field images of the polytypic faults with elemental profiles. (a) Single antiphase boundaries found in large isometric crystals show an increase of Ca at the fault (dark band in the Z-contrast image) and a decrease in Ba and Ti concentration. (b) Multiple faults show a similar structural pattern and composition as single faults.

reducing sintering conditions. At lower formation temperatures we find {111} twin boundaries with local hexagonal stacking in an otherwise cubic crystal, while at higher sintering temperatures hexagonal polymorph forms about 100 K below the normal cubic-hexagonal transition temperature.[6] The cause for this early phase transition is the presence of Ti^{3+} at the fault.[5] During the sintering process faulted grains undergo anisotropic growth.[3,6] Normal grains without twin boundaries show no anisotropy. Another example of *polytype induced anisotropic grain growth* are AO-doped ABO_3 perovskite materials, like $CaTiO_3$ and $SrTiO_3$.[7,8] At sintering temperature these materials are cubic and no anisotropic growth occurs unless the grains are infected with AO-type planar faults along the $\{100\}_p$ planes. Only then is crystal growth dictated by the growth direction of faulted sequence within the host cubic crystals. Polytypism as the reason for abnormal grain growth is not limited only to perovskite materials. One of the well known polytypic materials is silicon carbide. Many of the SiC polytypes do not exist as stand-alone phases and are found imbedded in the matrix α-SiC in a form of *sandwich* layers.[14] A phase transformation into longer-period polytypes of SiC and subsequent anisotropic growth is enhanced by adding Al. Analytical electron microscopy studies of SiC polytypes have proven the presence of Al_4C_3 layers along the basal planes of α-SiC, implying that these phase transitions are impurity induced.[15] Impurity induced faulting is also known in wurtzite materials such as ZnO. Small additions of SnO_2 cause the formation of inversion boundaries in ZnO, and consequently these grains undergo anisotropic grain growth parallel to the fault plane. Using the effects of this phenomenon one can control a microstructure development of varistor ceramics.[10] Several other materials exist that are prone to polytypism and polytypic faulting. In all these cases the solubility of the additive in a host material is very low and it rather forms polytypic faults within the host crystal than exist as a stand-alone phase. The general implication from these studies is that small deviations from stoichiometry, produced by specific dopants or impurities, can lead to the nucleation of singular or multiple polytypic faults in host crystals. Intrinsic polytypic sequences introduce an anisotropic character to these grains, and under specific thermodynamic conditions they will undergo exaggerated growth.

Let us take a closer look what kind of dopants may be critical for producing polytypic faults and cause an abnormal grain growth. The initial stage of nanostructural polytypism, i.e. single polytypic sequences imbedded in the host crystal, can be found in a group of phase systems that tend to form secondary polytypic phases. The special topotactic relation of polytypic faults with host crystal and their specific chemistry implies that they are syngenetic with the main phase. These faults nucleate during the growth of the host crystal at moderate sintering temperatures and low concentrations of the additive and are never produced by deformation. They form when the solid solubility of a particular additive in a major phase is low or non-existent, and there exists at least one thermodynamically stable phase between the major phase and the additive. The formation of single polytypic sequences can be understood as a preparatory stage of a polytype formation, or its special case, a polymorphic phase transformation as described by Cahn.[16] Independent of the phase system and the faulting type there are some crystallographic rules that are always obeyed. In the preparatory stage of polymorphism the local structure of the twin is, according to the rules of Aminoff and Broomé,[17] related to the existing polymorph. Similarly, in the preparatory stage of polytypism, the structure and chemistry of planar faults, such as twin, antiphase, or inversion boundaries, so often termed as *special grain boundaries*, are closely related to the structure and chemistry of the existing secondary phase, i.e. polytype. The faults form preferentially in such planes of the host crystal that have the closest crystallographic relationship with the polytype. The atomic stacking across the fault plane will be such that it closely conveys the structural pattern that can be found in the polytype.[4] If the fault lies parallel to close-packed planes of the host crystal then it will occupy those planes rather than any other lower density planes. There are very few matching planes where all these rules can be obeyed. Therefore faults are generally bound to not more than one type of low-index lattice planes in the host crystal. In addition to primary faults we often observe secondary faults.[5] These typically occupy planes perpendicular to the primary fault plane and result from impingement of the two oppositely growing domains formed by faulting the host crystal in two parallel primary planes. Secondary faults are never observed in the absence of primary faults. Multiple faulting and consequential ordering takes place at higher concentrations of dopants and elevated sintering temperatures.[6] Crystallography of multiple faults adheres to same rules as validated above for isolated faults, but what has been stated before for a singular situation, now repeats intermittently throughout the host structure with occasional one-dimensional disorder.[7] The final stage of multiple faulting is the formation of polymorphs or closely related structures, such as polytypes. Polytype layers, like the single faults, intersect the host crystal at its centre. In polytype, blocks of the main phase interchange topotactically with monolayers of a foreign structure resembling that of the single faults. One dimensional ordering (in the direction normal to the fault planes) of the monolayers increases with the reaction temperature, whilst their density increases with the concentration of the additive.[8]

During early stages of sintering, the nucleation of polytypic sequences introduces an element of anisotropy in the host crystallite, and within more or less narrow band of processing conditions this dictates an anisotropic growth. Such conditions are met below the temperature of normal polymorphic phase transformations or the temperature of secondary phase (polytype) formation. Anisotropic growth will be most pronounced under liquid phase sintering conditions where all crystallites are in better contact through a liquid phase medium compared to a slow solid-state diffusion regime. A low solid solubility of additives triggers the formation of a reactive surface diffusion layer and nucleation of polytypic faults in the grains of the major phase. The formation of a reactive layer occurs as soon as the solid solubility range is surpassed, and the ions of the additive cannot find appropriate structural sites for their incorporation in the crystal lattice of the major phase and therefore they remain in a diffusion band. At elevated temperatures the quantity of ions that find no thermodynamically plausible site in the surrounding phases is increased, and this leads to thickening of the surface diffusion layer. The only way to reduce the energy of the system is for ions in the diffusion layer to form a new structure that is energetically favourable for both the major phase and the additive. The best solution for accommodation of the ions from a diffusion band is the formation of polytype layers that comprise structural patterns of both competing phases and hence the energy of the system is massively decreased. Under these conditions growth of such composite crystals is favoured, and grains grow preferentially in the direction of fault planes at the expense of the fault-free grains. As soon as faulted grains collide, anisotropic growth is stopped and from that point on faulted grains undergo normal coarsening until they dominate the entire microstructure. The driving force responsible for the formation of nanostructural polytypic sequences in effect controls the growth of the whole crystallite.

5. Conclusions

The nucleation of the polytypic sequences along special planes of the host crystal introduces anisotropy to the affected grain which tends to follow the growth direction of the polytype. In the environment of normal grains of either the main phase or the additive, the faulted grains are superior as they lower the energy of the system by re-crystallisation of both competing phases. The faulted grains soon become larger than the surrounding normal grains which gives rise to exaggerated growth. Generally we may expect this effect in any phase system where polytypes exist between the main phase and a particular additive. Systems with no polytypes will not be prone to polytypism and hence to polytype-induced anisotropic growth. It is often advantageous to avoid exaggerated grain growth, however many situations exist where it is possible to exploit this effect in order to design textures with specific morphologies and crystal orientations. The phenomenon described here is of wide ranging interest as exaggerated growth of faulted crystals is known not only in ceramics, but is also common in metals, biomaterials, and is repeatedly observed in the realm of naturally grown crystals.

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