Journal of the European Ceramic Society 21 (2001) 2141–2144
www.elsevier.com/locate/jeurceramsoc

Nucleation and growth of planar faults in SrO-excess $SrTiO_3$

Sašo Šturm *, Aleksander Rečnik, Miran Čeh

Jožef Stefan Institute, Ceramics Department, Jamova 39, 1000 Ljubljana, Slovenia

Received 4 September 2000; received in revised form 16 October 2000; accepted 30 October 2000

Abstract

A SrO-excess $SrTiO_3$ polycrystalline ceramic was sintered at 1450°C for different times in order to study the anisotropic growth induced by the formation of SrO-rich planar faults inside the perovskite matrix. In the early stage of sintering the microstructure consisted of anisotropic perovskite grains containing polytypic lamella and a fine perovskite, which was free of planar faults. Further treatment caused a decrease in the anisotropy: elongated grains, due to the coarsening effect, developed into equiaxed perovskite grains containing polytypic lamellae. In order to study the preference for polytypic growth we used a $SrTiO_3$ single crystal sintered in a SrO-rich atmosphere. We found that in the initial stage, fault-rich platelets were formed as discrete nuclei that had no crystallographic relation to the $SrTiO_3$ single crystal. These platelets provided nucleation sites for a fault-free perovskite, forming sandwich-like composite grains. The single crystal acted as a source of $SrTiO_3$ for the recrystallisation of these composite grains.

Keywords: Defects; Grain growth; Interfaces; Perovskites; Varistors

1. Introduction

The protection of electronic devices is provided by various semiconductive materials with varistor properties. $SrTiO_3$ grain boundary layer ceramics are attractive for varistor applications as they exhibit very high permittitivity and good varistor properties.[1–3] In other words, $SrTiO_3$ ceramics possess both capacitor and varistor characteristics, which suggests that the material could be used in applications where the varistor component compensates for the high-frequency and high-amplitude pulses that are often generated in electric motors and are not efficiently suppressed by a varistor alone.

The experiments performed by Yamaoka et al.,[1] have shown that the nonlinear coefficient and the breakdown voltage are controlled by the grain size of the $SrTiO_3$ ceramics. Recent studies of $CaTiO_3$ and $SrTiO_3$ ceramics with small additions of SrO have shown that the preferential growth of planar faults embedded in the perovskite matrix causes anisotropic growth of the perovskite grains.[4,5] These planar faults can be considered as layers of SrO having rock-salt structure, which are coherently intergrown with the host perovskite matrix.[6] In addition, Balachandran and Eror[7] have found that an excess of SrO, which is accommodated in the $SrTiO_3$ by the formation of planar faults did not alter the electrical properties of the ceramic. While at low sintering temperatures the planar faults are organised into polytypic lamellae within the highly anisotropic perovskite grains, at higher firing temperatures two discrete phases are observed and comprise equiaxed polytype-rich grains in fault-free $SrTiO_3$ grains.[5] Anisotropic growth occurs only when polytypic lamellae are embedded in the host $SrTiO_3$ grains.

In the present work we have studied microstructures of a SrO-doped $SrTiO_3$ ceramic which was exposed to elevated temperatures for different time periods. The aim of our research was to investigate how the growth of the grains was affected by the formation of planar faults. To study the nucleation of planar faults, we used a $SrTiO_3$ single crystal fired in a SrO-rich atmosphere.

2. Experimental procedures

As the starting material we used $SrTiO_3$ (Kyorix, ST-HP1, Sr/Ti = 0.9998). In order to achieve dense sintered polycrystalline ceramic bodies, mixtures of $SrTiO_3$ with additions of 3 and 5 mol% SrO were prepared by conventional ceramic procedures. The appropriate mixtures

* Corresponding author. Tel.: +386-1-4773418; fax: +386-1-5263126.
E-mail address: saso.sturm@ijs.si (S. Šturm).

PII: S0955-2219(01)00189-3

of SrO (Alfa) and $SrTiO_3$ powders were homogenised in a planetary ball mill filled with absolute ethanol and dried at 110°C in air. The mixtures were pressed into pellets and sintered at 1450°C for different time periods: 10 min, 1 h, 5 h and 15 h. Heating and cooling rates were 10°C/min. To study the nucleation and growth of planar faults in a perovskite matrix we used a $SrTiO_3$ single crystal (Mateck) that was cut parallel to the (001) plane. The $SrTiO_3$ crystal was sintered in the presence of a pure SrO pellet at 1450°C for 4 days, which provided enough SrO to trigger the nucleation and growth of SrO-rich planar faults on the surface of the perovskite crystal. Sintered samples were then polished and chemically etched to expose the microstructural features. The samples were examined in a scanning electron microscope (SEM) (Jeol, JSM5800) equipped with an energy-dispersive X-ray spectrometer (EDS) (Oxford Instruments, Link ISIS300).

3. Results

3.1. The evolution of polytype-rich grains

In order to show that planar faults influence the grain growth of $SrTiO_3$ crystallites we fired $SrTiO_3$ with the addition of 3 mol% SrO at 1450°C for between 10 min and 15 h. The resulting microstructures are shown in Fig. 1. The microstructure of the sample sintered for 10 min reveals a bimodal grain size distribution. The microstructure consists of anisotropic perovskite grains rich in planar faults and a fine matrix consisting of small isotropic fault-free perovskite grains. In the samples sintered for longer time periods, 1–5 h, elongated grains with planar faults dominate the microstructure, while the amount of small isotropic fault-free perovskite grains is significantly reduced (Fig. 1b and c). The final microstructure of ceramic samples sintered for 15 h shows only fault-rich perovskite grains. The anisotropy of these grains is less pronounced. The resulting microstructure reveals a uniform grain size distribution of nearly isotropic fault-rich perovskite grains (Fig. 1d). Due to the amount of excess SrO, which has to be accommodated in the perovskite matrix, the concentration of planar faults in the perovskite grains increases with larger additions of SrO. The resulting morphology of these $SrTiO_3$ grains changes from highly anisotropic to an equiaxed appearance (Fig. 2). Although the morphology of the elongated grains changes, due to different amounts of embedded planar faults, the microstructural features remain similar; i.e. abnormal perovskite grains rich in planar faults situated in a fine matrix of fault-free equiaxed $SrTiO_3$ grains.

3.2. Nucleation and growth of planar faults

Because polytypic layers form along any available {100} plane in the host perovskite,[8,9] the nucleation and

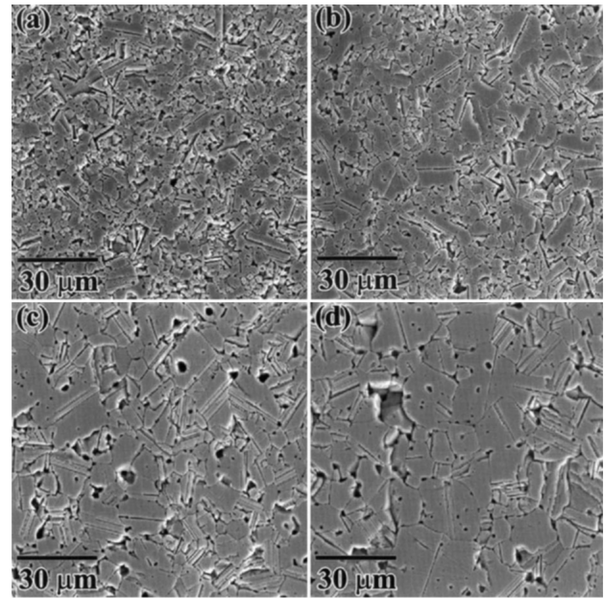

Fig. 1. Microstructures of $SrTiO_3$ with 3 mol% SrO sintered at 1450°C for 10 min, 1 h, 5 h and 15 h. (a) The micrograph reveals abnormal growth of anisotropic grains containing polytypic lamellae in a fine fault-free $SrTiO_3$ matrix. (b) The exaggerated growth of elongated grains is promoted, while the fine $SrTiO_3$ matrix is reduced. (c) Elongated grains grow excessively, while the fine fault-free matrix dissolves. (d) Due to final coarsening effects the dense microstructure consists only of uniform perovskite grains containing polytypic faults, no fine $SrTiO_3$ matrix is observed.

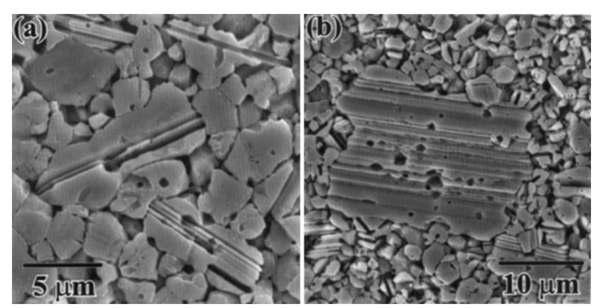

Fig. 2. Microstructures of $SrTiO_3$ with (a) 3 mol% SrO and (b) 5 mol% SrO, sintered at 1450°C for 10 min. The anisotropy of the fault-rich $SrTiO_3$ grains depends on the amount of imbedded planar faults in the perovskite matrix.

growth of planar faults can be studied by using a $SrTiO_3$ single crystal fired in a SrO-rich atmosphere.

An SEM micrograph of a $SrTiO_3$ monocrystal shows a recrystallisation zone, approximately 300 µm wide, containing various SrO-rich phases (Fig. 3). Near the edge of the crystals, discrete polytypic grains are observed. According to the EDS analysis, this single crystal completely recrystallise in the presence of SrO to form $Sr_4Ti_3O_{10}$ and $Sr_3Ti_2O_7$ polytype phases. This is consistent with the highest SrO concentration near the surface of the single crystal. The transition zone consists of tabular grains, that are very rich in planar faults. According to the analysed Sr/Ti ratios, the composition

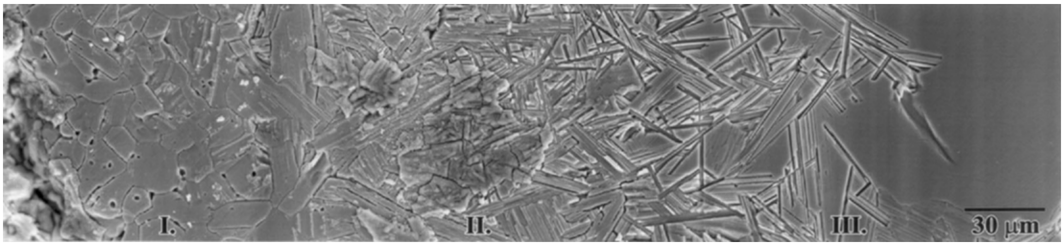

Fig. 3. SEM image of the recrystallisation zone of the $SrTiO_3$ crystal fired in a SrO-rich atmosphere. The edge of the crystal recrystallises to discrete homologue phases $Sr_4Ti_3O_{10}$ and $Sr_3Ti_2O_7$ (Region I). The transition zone reveals tabular $SrTiO_3$ grains (Region II) rich with planar faults. The recrystallisation front is terminated by highly anisotropic grains containing polytypic lamella (Region III).

of these grains is below the value of the first stable polytype phase $Sr_4Ti_3O_{10}$, indicating one-dimensional disorder, where the average spacing of the planar faults within the analysed grains is higher than that in $Sr_4Ti_3O_{10}$. The recrystallisation front is characterised by highly anisotropic grains with fault-rich lamellae penetrating the host perovskite matrix. Fig. 4 reveals that the growth direction of the planar fault-rich lamellae is independent of the single-crystal orientation. Another interesting phenomenon is revealed at the frontier of the recrystallisation zone, where each lamella is covered by a thin layer of recrystallised perovskite, thus forming a *sandwich-like* structure in the shape of platelets, similar to those of polycrystallite SrO-excess $SrTiO_3$ ceramics. The single crystal acts only as a source of perovskite for the formation of highly anisotropic *sandwich-like* grains, rather than being a nucleation site for polytypic layers.

4. Discussion

Our investigation has shown that the amount of excess SrO and the sintering conditions of $SrTiO_3$ ceramics significantly influence the final microstructure. Anisotropic grain growth is most pronounced during the initial firing stage. The microstructure consists of elongated grains containing polytypic lamellae and a fine matrix of uniform equiaxed grains which are free of planar faults. The growth of elongated grains is promoted as a result of a preferential growth of the planar faults, due to the presence of excess SrO. Planar faults are combined into lamellae that are surrounded by the perovskite matrix, forming *sandwich-like* grains. Although the morphology of elongated perovskite grains in the initial firing stage is influenced by the number of embedded planar faults, the growth mechanism remains unchanged. Elongated grains with embedded planar faults exhibit rapid growth by dissolving smaller matrix grains. Also, the fault-rich elongated grains grow excessively compared to the fault-free $SrTiO_3$ grains. The microstructure of SrO-excess $SrTiO_3$ sintered at 1450°C for 15 h suggests that the excess SrO was already used up for the growth of planar faults and in the absence of any additional SrO the anisotropic grain growth is stopped. In the final stage of sintering, elongated grains grow further as a consequence of coarsening effects. The anisotropy of the fault-rich perovskite grains is reduced due to thickening of the platelets, leading to nearly equiaxed large perovskite grains.

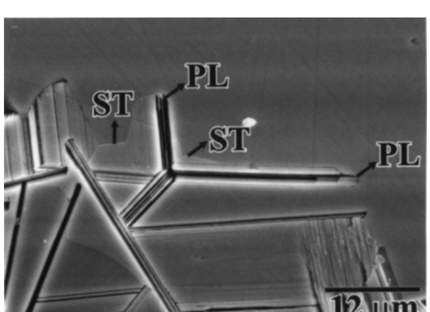

Fig. 4. Close-up of recrystallisation front in $SrTiO_3$ crystal reveals polytypic lamellae (PL) covered with a thin layer of perovskite (ST) that has recrystallised from the $SrTiO_3$ crystal. The direction of growth of these platelets is controlled by the formation of polytypic layers within, which grow independently of the $SrTiO_3$ crystal orientation.

The $SrTiO_3$ monocrystal experiment supports the idea of a polytype-induced growth[10] mechanism of the perovskite matrix as a result of the preferential growth of polytypic lamellae. The increasing anisotropy of the grains with embedded planar faults in the interior of the single crystal implies that the conditions which occur when growth of lamellae is promoted are probably achieved at the lowest SrO-excess concentration. Higher amounts of excess SrO cause the formation of discrete equiaxed polytypic grains, similar to $SrTiO_3$ polycrystalline samples with high SrO excess. Although the structural accommodation of planar faults in a perovskite matrix is a well-known phenomenon, the nucleation of planar faults has never been investigated in detail. In a previous study the origin of locked-in rectangular polytypic loops consisting of disordered polytypic faults was investigated.[5] The topotaxial relation between $SrTiO_3$ and the planar faults indicates that the nucleation of these planar faults could start on the internal $SrTiO_3$ surface along one of the $\{100\}$ perovskite planes. In contrast, polytypic lamellae located in the $SrTiO_3$ crystal show no crystallographic relation with respect to the monocrystal. In the initial stage, discrete fault-rich platelets are formed. Both sides of these platelets, in the direction of the one-dimensional ordering, are available for coherent growth of fault-free perovskite, while the excess SrO is structurally accommodated along the planar-fault layers and this causes preferential growth of the whole grain. The resulting *sandwich-like* grain may be considered as a composite made of a fault-rich platelet overgrown by fault-free perovskite matrix. The experimental evidence that fault-rich grains grew into the $SrTiO_3$ single crystal clearly shows the preferential growth of polytypic lamellae. In spite of a much larger $SrTiO_3$ monocrystal, where growth at the expense of smaller grains would be expected, the formation of polytypic nuclei induce recrystallisation of the $SrTiO_3$ monocrystal to form numerous smaller perovskite fault-rich grains. Due to the fact that no additional charged defects[7] are induced by the formation of planar faults, the properties of the whole composite should be similar to the fault-free perovskite grains.

This phenomenon can serve as a mechanism to control the final microstructure of a SrO-excess $SrTiO_3$ ceramic where an appropriate distribution in grain sizes could be achieved by selecting a proper amount of SrO and the sintering conditions to tailor the electrical properties of the $SrTiO_3$-based varistor.

5. Conclusions

We have shown that small additions of SrO to $SrTiO_3$ ceramics trigger the formation of planar faults that significantly modify the growth of the whole perovskite matrix. The preferential growth of the SrO-rich planar faults, embedded in the perovskite, affects the anisotropic growth of the whole perovskite grain. Anisotropy is induced in the early stage of sintering. When all the SrO is accommodated by the formation of planar faults, elongated grains undergo coarsening. The final microstructure consists of nearly uniform $SrTiO_3$ grains containing polytypic lamellae. The experiment with the single crystal has shown that the formation of planar faults is related to the discrete fault-rich nuclei that act as growing sites for the perovskite matrix. This mechanism is so powerful that a large $SrTiO_3$ monocrystal in the presence of surplus SrO recrystallises to much smaller fault-rich perovskite grains. The preferential growth of planar faults significantly alters the morphology of perovskite grains, thus influencing the microstructural evolution and the final properties of the ceramic.

Acknowledgements

We acknowledge the financial support by the Slovenian Ministry of Science and Technology for this work under grant No. S23-106-003-19030/98, project No. P2-0509-0106/00.

References

1. Yamaoka, N., Masuyama, M. and Fukui, M., $SrTiO_3$-based boundary layer capacitor having varistor characteristics. *Am. Ceram. Soc. Bull.*, 1983, **62**, 698–700.
2. Shiojiri, M., Isshiki, K., Nishio, K., Saijo, H., Nomura, T., Hitomi, A. and Sato, S., Microscopy of $SrTiO_3$-based ceramic varistors and capacitors. In *Proceedings of the 14th International Congress on Electron Microscopy*, ed. H. A. C. Benavides. Institute of Physics Publishing, Bristol and Philadelphia, 1998, pp. 683–684.
3. Laurent, M. J., Desgardin, G., Raveau, B., Haussonne, J. M. and Lostec, J., $SrTiO_3$ based type III dielectric materials sintered at low temperature. *Science of Ceramics 14*. Institute of Ceramics, Stoke-on-Trent, UK, 1988, pp. 1031-1036.
4. Čeh, M. and Kolar, D., Solubility of CaO in $CaTiO_3$. *J. Mater. Sci.*, 1994, **29**, 6295–6300.
5. Šturm, S., Rečnik, A., Scheu, C. and Čeh, M., Formation of Ruddlesden–Popper faults and polytype phases in SrO-doped $SrTiO_3$. *J. Mater. Res.*, 2000, **15**, 2131–2139.
6. McCoy, M. A., Grimes, R. W. and Lee, W. E., Phase stability and interfacial structures in the SrO-$SrTiO_3$ system. *Philos. Mag. A*, 1997, **75**, 833–846.
7. Balachandran, U. and Eror, N. G., On the defect structure of strontium titanate with excess SrO. *J. Mater. Sci.*, 1982, **17**, 2133–2140.
8. Tilley, R. J., An electron microscope study of perovskite-related oxides in the Sr–Ti–O system. *J. Solid State Chem.*, 1977, **21**, 293–301.
9. Hawkins, K. and White, T. J., Defect structure and chemistry of $(Ca_xSr_{1-x})_{n+1}Ti_nO_{3n+1}$ layer perovskites. *Philos. Trans. R. Soc. London, A*, 1991, **336**, 541–569.
10. Rečnik, A., Čeh, M. and Kolar, D., Polytype induced exaggerated grain growth in ceramics. *J. Eur. Ceram. Soc.*, 2001, **21**, this issue.