MICROSTRUCTURE EVOLUTION IN SrTiO$_3$ WITH DIFFERENT Sr/Ti RATIOS

RAZVOJ MIKROSTRUKTURE V SrTiO$_3$ OB RAZLI^NEM RAZMERJU Sr/Ti

Sa{o [turm, Aleksander Re~nik, Miran ^eh

Jo`ef Stefan Institute, Jamova 39, 1000 Ljubljana, Slovenia

The microstructure evo lu tion of SrTiO$_3$ strongly depends on de vi a tions from stoichiometry. In the case of SrO ex cess, anisotropic growth of polytype phases with the ge neric com po si tion Sr$_{n+1}$Ti$_n$O$_{3n+1}$ is pro moted. High tem per a ture XRD data re veal only the first three homo logues; Sr$_2$TiO$_4$, Sr$_3$Ti$_2$O$_7$ and Sr$_4$Ti$_3$O$_{10}$, where Sr$_2$TiO$_4$ is the first sta ble phase at low fir ing tem per a tures (T<1200°C). Microstructural stud ies of SrO doped SrTiO$_3$ show intergrown anisotropic grains with a high as pect ra tio. These grains have a "sand wich-like" struc ture, where a lamella of the polytype is im bed ded in the perovskite ma trix. The mor phol ogy of sand wich-like grains in di cates that the polytype lamellae con trol the growth of the perovskite grains. Be sides anisotropic perovskite grains which in clude polytypoidic lamellae we ob served other microstructur al fea tures, such as square shape neg a tive forms with a spe cial ori en ta tion within the perovskite grains, twin-like polyt ype in cluded in perovskite grains and spec tac u lar morphologies of the ma trix grains which ap pear as closed rod-like rect an gu l ar loops. TEM ob ser va tions show that sin gle and or dered polytypic faults can form square like fault struc tures which can be trans posed to any plane of the {100} fam ily. In ad di tion, TEM stud ies re veal a strong re la tion ship be tween the trans posed or dered pla nar faults and the ap pear ance of the etched square bod ies. Many sim i lar closed rect an gu lar loops made of or dered pla nar faul ts were ob served in side the perovskite ma trix. The lengths mea sured be tween or dered polytypic faults are con sis tent with the XRD data.

Key words: SrTiO$_3$, nonstoichiometry, grain growth, polytypes, pla nar faults

Mikrostruktura SrTiO$_3$ je v veliki meri odvisna od razmerja Sr/Ti. V primeru sintranja SrTiO$_3$ s prebitnim SrO opazujemo napredujo~o anizotropno rast zrn s politipnimi fazami s formulo: Sr$_{n+1}$Ti$_n$O$_{3n+1}$. Na visoko temperaturnem rentgenskem spektru smo dolo~ili samo prve tri homologne faze: Sr$_2$TiO$_4$, Sr$_3$Ti$_2$O$_7$ and Sr$_4$Ti$_3$O$_{10}$, pri ~emer je prva stabilna faza pri nizkih temperaturah Sr$_2$TiO$_4$ (T<1200°C). Mikrostruktura SrTiO$_3$ s prebitnim SrO poka`e zna~ilno prera{~ena anizotropna zrna z velikim med osnim razmerjem, kjer so lamele politipov vklju~ene v matrico perovskita. Visoka anizot ropija in "sendvi~" struktura zrn s politipnimi lamelami ka`e, da je rast teh zrn kontrolirana z rastjo vra{~enih polit ipnih lamel. Poleg politipnih lamel na polirani in jedkani povr{ini perovskitnih zrnih opazimo tudi kvadratne izjedkanine z definirano orientacijo v odnosu na perovskitno matrico, dvoj~kom podobna zrna s vra{~enimi politipnimi lamelami in nenavadne oblike pe rovskitnih matri~nih zrn pali~nih ob li k pravokotnega preseka. TEM raziskave poka`ejo, da lah ko tako izolirane kot urejene ploskovne napake tvorijo pravokotne vzorce, ki se razra{~ajo po katerikoli ravnini dru`ine {100}. Urejene ploskovne napake tu in tam spremenijo smer znotraj {100} dru`ine ravnin. Poleg posameznih ploskovnih napak in politipnih lamel opazimo znotraj perovskitne matrice tudi za klju~ena pravokotna telesa, ki jih gradijo ve~krat transponirane dru`ine politipnih lamel oko li iste osi tako, da vogali telesa ustrezajo {110} ravninam perovskita. Izmerjena razdalja med planarnimi napakami znotraj urejenih politpnih ravnin je v skladu z rezultati dobljenimi iz rentgenskih spektrov.

Klju~ne besede: SrTiO$_3$, nestehiometrija, rast zrn, politipi, ploskovne napake

1 INTRODUCTION

SrTiO$_3$ is a member of the alkaline earth titanates, and shows weak electrical permittivity at room temperature and is therefore considered as an insulator. Small additions of donor or acceptor dopants make SrTiO$_3$ based materials semiconducting with useful dielectric properties. SrTiO$_3$ based materials are applicable as perovskite substrates, internal boundary layer capacitors, varistors, electrode materials for water photolysis and as oxygen sensors[1].

SrTiO$_3$ is a unique ceramic material of technological importance, which at room temperature possesses an ideal perovskite structure with a cubic unit cell of length ~0.39 nm. With excess SrO, SrTiO$_3$ is able to compensate structurally for the nonstoichiometry with the formation of Ruddlesden-Popper phases[2]. The excess SrO in the SrTiO$_3$ is accommodated by the formation of various homologous oxides with the general formula Sr$_{n+1}$Ti$_n$O$_{3n+1}$, where n represents the number of

perovskite blocks between single SrO layers. Tilley[3] reported three polytypic phases, Sr$_2$TiO$_4$, Sr$_3$Ti$_2$O$_7$ and Sr$_4$Ti$_3$O$_{10}$, which differ in their stacking sequence of SrO layers. Calculated enthalpies of formation for these members of the Ruddlesden-Popper homologous series, according to the reaction:

$$SrO + nSrTiO_3 \rightarrow Sr_{n+1}Ti_nO_{3n+1},$$
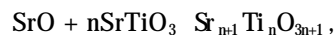
show that the formation enthalpy is different only for the first homologue Sr$_2$TiO$_4$ (E°$_{n=1}$ = -0,11 eV), while for the compounds with n higher than 2 the formation enthalpies remain fairly constant (E°$_{n=2,3,...}$ = -0,14 eV)[4].

The structural compensation of AO rich (where A = Ca, Sr, Ba) planar faults at different sintering temperatures was studied in a more detailed manner in the system CaTiO$_3$-SrO[5]. Planar faults, which are observed at low temperature (1350°C) form random networks parallel to the {110} lattice planes of the orthorhombic perovskite CaTiO$_3$. When SrO doped CaTiO$_3$ is sintered at higher temperatures (1550°C)

single faults are organised into parallel polytypic lamellae forming "sandwich" structures within the host perovskite matrix.

Due to an ideal perovskite structure, $SrTiO_3$ offers a unique possibility to study the extension and ordering of polytypic layers inside the perovskite matrix. In this study, we report on the formation of stable homologues between $SrTiO_3$ and SrO and their crystallographic relations with the perovskite matrix. The formation of polytypic phases was examined using a high temperature powder X-ray diffractometer. The microstructural relationship between the polytypic lamellae and the perovskite grains was investigated in a scanning electron microscope (SEM). To reveal the stacking sequence and ordering of different polytypes and to determine the crystallographic relationships between the polytypic layers and the perovskite matrix we employed conventional transmission electron microscopy (TEM).

2 EXPERIMENTAL PROCEDURE

$SrTiO_3$ (Kyorix ST - HP1) with different additions of SrO up to 5 mol.% was prepared by conventional ceramic procedures. SrO was added to $SrTiO_3$ in the form of $SrCO_3$ (>99% Alfa). The appropriate mixture of $SrCO_3$ and $SrTiO_3$ was homogenised in a planetary mill with the addition of up to 20 vol.% of absolute ethanol, then air-dried at a temperature of 110°C. The powder mixture was then pressed into pellets and sintered at different temperatures in the range from 800°C to 1450°C for 10 hours to achieve compact ceramic bodies. The heating and cooling rates were 10°C/min. Phase composition data for sintered materials was collected by X-ray powder diffractometry employing a Philips PW 1710 diffractometer.

The fired samples were metallographically polished and chemically etched to obtain a better contrast for the microscopic observation. Etched samples were covered with a thin carbon film to produce a conductive surface layer for SEM observations. For the sample

characterization a Jeol JSM 5800 scanning electron microscope equipped with Link ISIS 300 energy dispersive X-ray analyser was used.

For the TEM observations the material was cut into 3 mm discs, mechanically ground and dimpled down to 20 μm in the disc centre. Transmissive regions in the specimen's centre were finally achieved by ion milling using 4 kV Ar$^+$ at an incidence angle of 12°. Specimens were examined in a Jeol 2000 FX transmission electron microscope operated at 200 kV.

3 RESULTS

Figure 1 shows DTA/TG results for $SrCO_3$ at temperatures between 100°C and 1450°C. According to the literature data (M. D. Judd et al.[6]) the first exothermic peak on the DTA trace at 944°C occurs due to the reversible transformation of $SrCO_3$ from rhombohedral to hexagonal. A second, wider, exothermic peak is related to the thermal decomposition of $SrCO_3$ to SrO, which is also indicated on the TG trace by a dramatic weight loss. Decarbonation according to the reaction:

$$SrCo_3 \xrightarrow{T\uparrow} SrO + CO_2$$
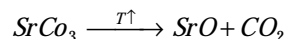
starts as low as approximately 800°C and finishes below 1200°C. Another prominent feature in the TG diagram is a 1.5 wt.% loss above the thermal decomposition (T>1200°C) of $SrCO_3$, most probably a consequence of SrO evaporation. Evaporation of SrO above the temperature of thermal decomposition was confirmed on polished cross-sections of the sintered samples using an optical microscope **(Fig. 2)**. Grains including polytype lamellae were found only in the cores of the sintered pellets while the rims of the samples are free of
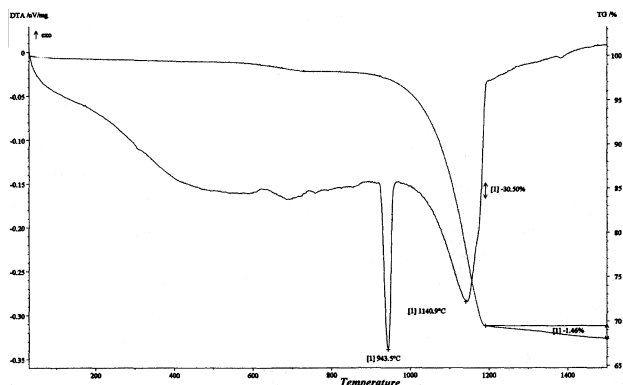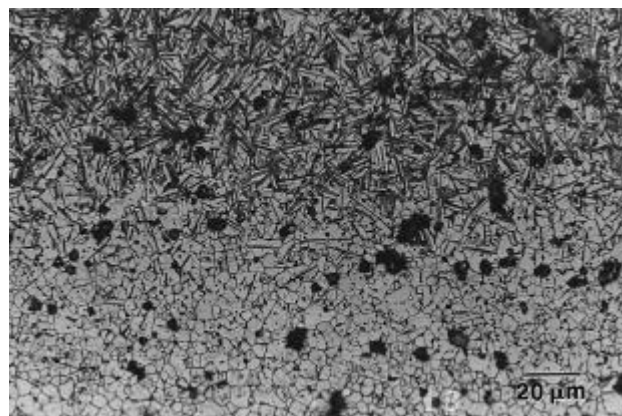

Figure 2: Difference between inner and outer part of the specimen as a consequence of SrO evaporation. SrO rich phases (polytypic lamellae) are situated only in the inner part of the specimen. The microstructure was recorded on the SrO doped $SrTiO_3$ (Sr/Ti=1.05) specimen, sintered in air at 1450°C for 10 hours
Slika 2: Razlika med notranjim in zunanjim delom vzorca kot posledica odparevanja SrO. S SrO bogate faze (politipi) se nahajajo samo v notranjih delih tablete. Posnetek mikrostrukture pripada vzorcu $SrTiO_3$ s prebitnim SrO (Sr/Ti=1.05), sintran na zraku pri temperaturi 1450°C, 10 ur
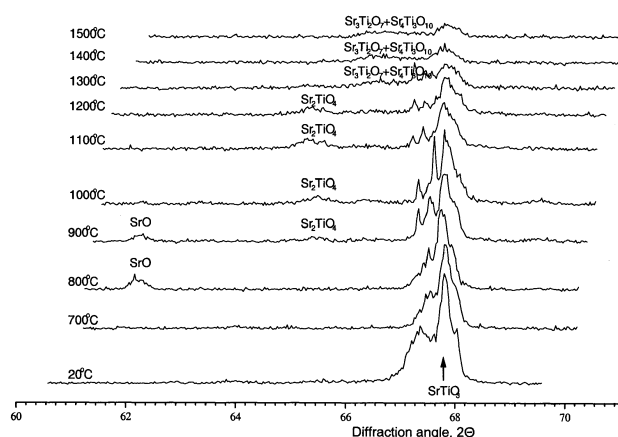

Figure 1: DTA/TG pattern of $SrCO_3$. (range: 20°C/10 K/min/1530°C, atmosphere: air, crucible: Pt-Ir)
Slika 1: DTA/TG spekter za $SrCO_3$ (eksperimentalni parametri: 20°C - 10 K/min - 1530°C, atmosfera: zrak, lon~ek: Pt-Ir)

Figure 3: High tem per a ture XRD pat tern for the com po si tion of pow ders, which cor re spond to the homologue phase $Sr_4Ti_3O_{10}$

Slika 3: Visoko temperaturni rentgenski spekter me{anice prahov, katere sestava ustreza homologni fazi s kemijsko formulo $Sr_4Ti_3O_{10}$

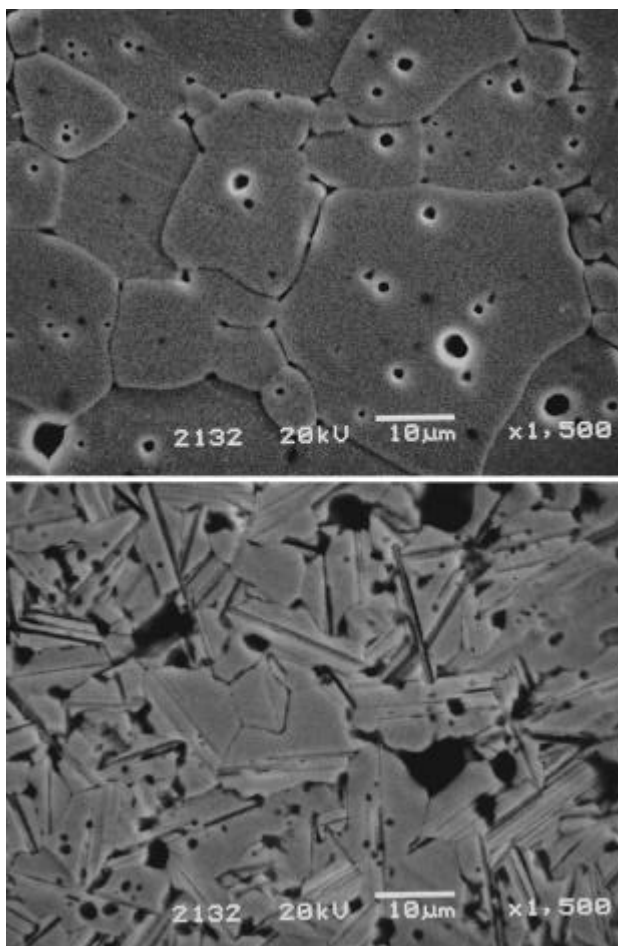**Figure 4:** Microstructure of acid etched stoichiometric polycrystalline $SrTiO_3$ and SrO doped $SrTiO_3$ (Sr/Ti $\approx$ 1.05) sintered in air at 1450°C for 10 hours

Slika 4: Mikrostrukturi kemijsko jedkanega stehiometri~nega polikristalnega $SrTiO_3$ in $SrTiO_3$ s prebitnim SrO (Sr/Ti $\approx$ 1.05); vzorca sta sintrana na zraku pri temperaturi 1450°C, 10 ur

SrO-rich phases and are composed only of polytype-free $SrTiO_3$ grains, indicating a local deficiency in the SrO excess.

High temperature XRD data were collected at different temperatures. The mixture of $SrCO_3$ and $SrTiO_3$ powders was prepared to obtain the lowest Sr/Ti ratio for the polytype phases corresponding to the $Sr_4Ti_3O_{10}$ homologue. **Figure 3** shows high temperature XRD data of the consecutive phase transformations for a given composition, starting from 700°C up to 1500°C, with a heating step of 100°C.

At 700°C the only stable perovskite phase is $SrTiO_3$. As a consequence of the thermal decomposition of $SrCO_3$ a relatively strong peak of SrO is observed in the temperature range between 800°C and 900°C. The SrO peak disappears at temperatures higher than 900°C. The first homologue Sr_2TiO_4 appears above 900°C, while the thermal decomposition of the $SrCO_3$ is still in progress. High-temperature X-ray data indicate that the thermal decomposition of $SrCO_3$ to SrO, and the polytype formation occurs almost simultaneously with Sr_2TiO_4 as the first stable polytype. According to the XRD data the homologue Sr_2TiO_4 is stable in the temperature interval from 1000°C to 1200°C. At higher firing temperatures (1300°C to 1500°C) Sr_2TiO_4 becomes unstable and higher homologues are formed instead, these are observed as increasingly intense peaks of $Sr_3Ti_2O_7$ and $Sr_4Ti_3O_{10}$. The appearance of the first three Ruddleseden-Popper members, with increasing firing temperatures, is in agreement with calculated formation enthalpies where it is energetically favourable for the homologous
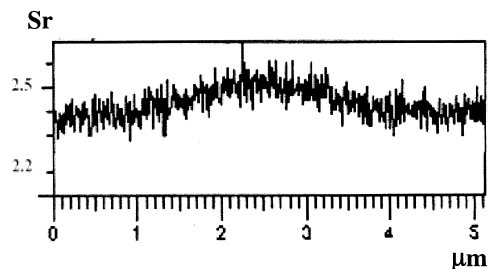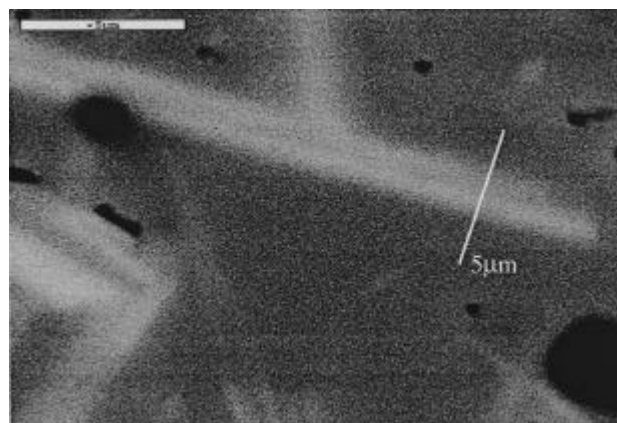

Figure 5: El e men tal pro file for Sr across polytypoidic lamella

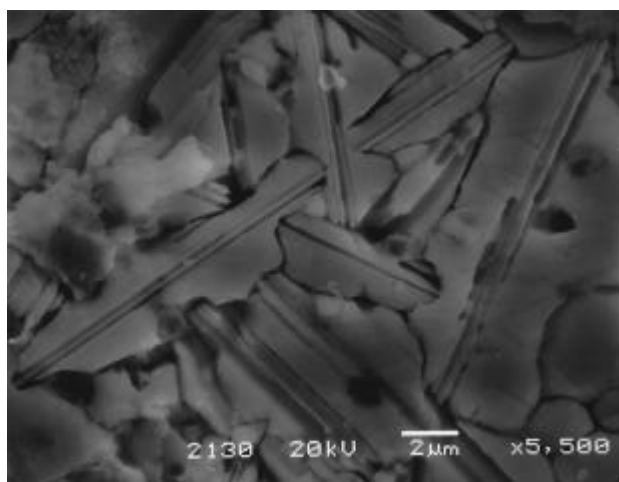**Slika 5:** Elementarni profil stroncija ~ez politipno lamelo

Figure 6: Microstructure of chem i cally etched SrO doped SrTiO$_3$ (Sr/Ti$\approx$1,05) sintered in air at 1450°C for 10 hours
Slika 6: Mikrostruktura kemijsko jedkanega SrTiO$_3$ s prebitnim SrO (Sr/Ti$\approx$1,05), sintranega na zraku pri temperaturi 1450°C, 10 ur

Figure 7: Etched SrO doped SrTiO$_3$ grain (Sr/Ti$\approx$1.05) showing a typical "sandwich" structure
Slika 7: Jedkano zrno SrTiO$_3$ s prebitnim SrO (Sr/Ti$\approx$1.05), ki ka`e zna~ilno "sendvi~" strukturo

perovskite phases Sr$_2$TiO$_4$, Sr$_3$Ti$_2$O$_7$ and Sr$_4$Ti$_3$O$_{10}$ to form (Udayakumar *et al.*)[4].

4 SEM AND EDS STUDY

A comparison between the microstructures of stoichiometric SrTiO$_3$ and SrO doped SrTiO$_3$ with a Sr/Ti ratio of about 1.05 is shown in **figure 4**. Both samples were sintered in air at 1450°C for 10 hours. Microstructural observations of stoichiometric SrTiO$_3$ reveal a typical single-phase system consisting of only isotropic SrTiO$_3$ grains. With an excess of SrO, anisotropic growth of the perovskite grains is observed. Every anisotropic grain contains a "sandwich-like" polytypoidic lamella consisting of polytype phases having the composition Sr$_{n+1}$Ti$_n$O$_{3n+1}$.

Because of the presence of SrO rich Ruddlesden-Popper phases, the local chemistry of the perovskite grains should differ significantly from the polytypoidic lamella. An elemental line scan across the perovskite grain, which includes such a polytypoidic lamella **(Fig. 5),** indeed indicates an enrichment in SrO in the region of the polytypoidic lamella. Polytype phases crystallise with tetragonal symmetry. Due to the observed exaggerated growth in specific crystallographic directions the growth of the polytype lamellae appears to control the growth of the perovskite grains along these directions.

Polished and etched samples of SrTiO$_3$ with SrO excess reveal polytype lamellae as thin platelets inside perovskite grains that grow faster than the matrix grain and are also able to penetrate into the surrounding perovskite grains encountered in the direction of their growth **(Fig. 6)** . If such a polytype lamella impinges upon another, the growth of both grains is usually inhibited at the point of intersection. The microstructure
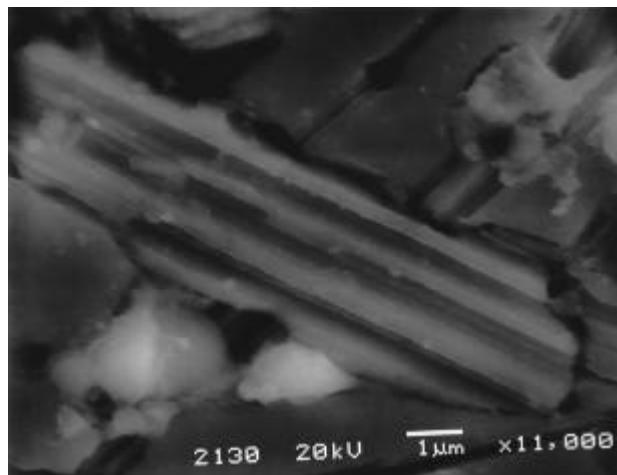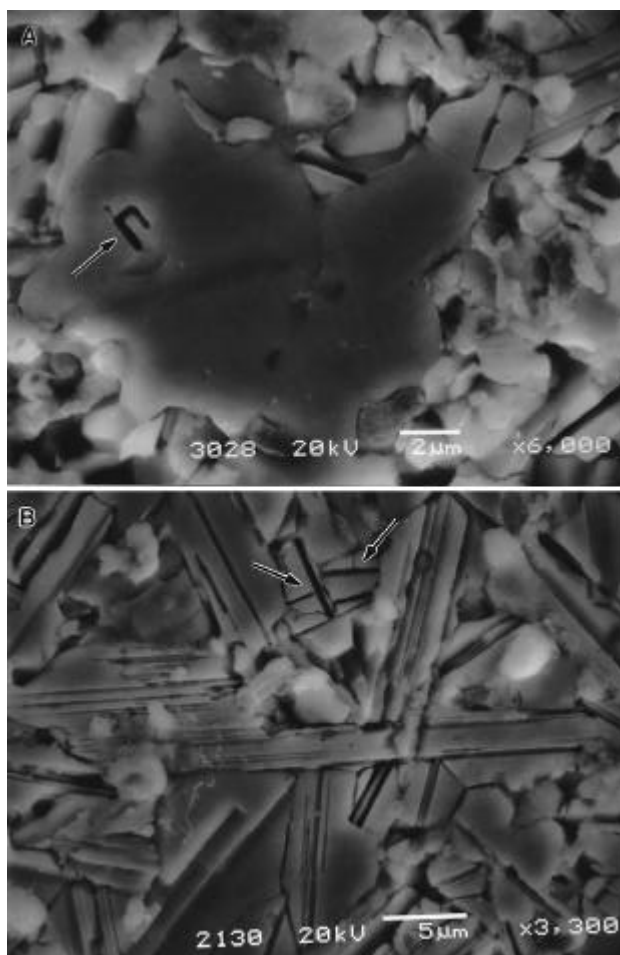

Figure 8: a) Perovskite grain with square like morphology of polytypic lamellae and **b)** Polytype lamella with de fined ori en ta tion in {100} perovskite planes
Slika 8: a) Perovskitno zrno s politipno lamelo, ki se razteza v pravokotnih smereh **b)** Politipna lemela z definirano orientacijo v {100} ravninah perovskita

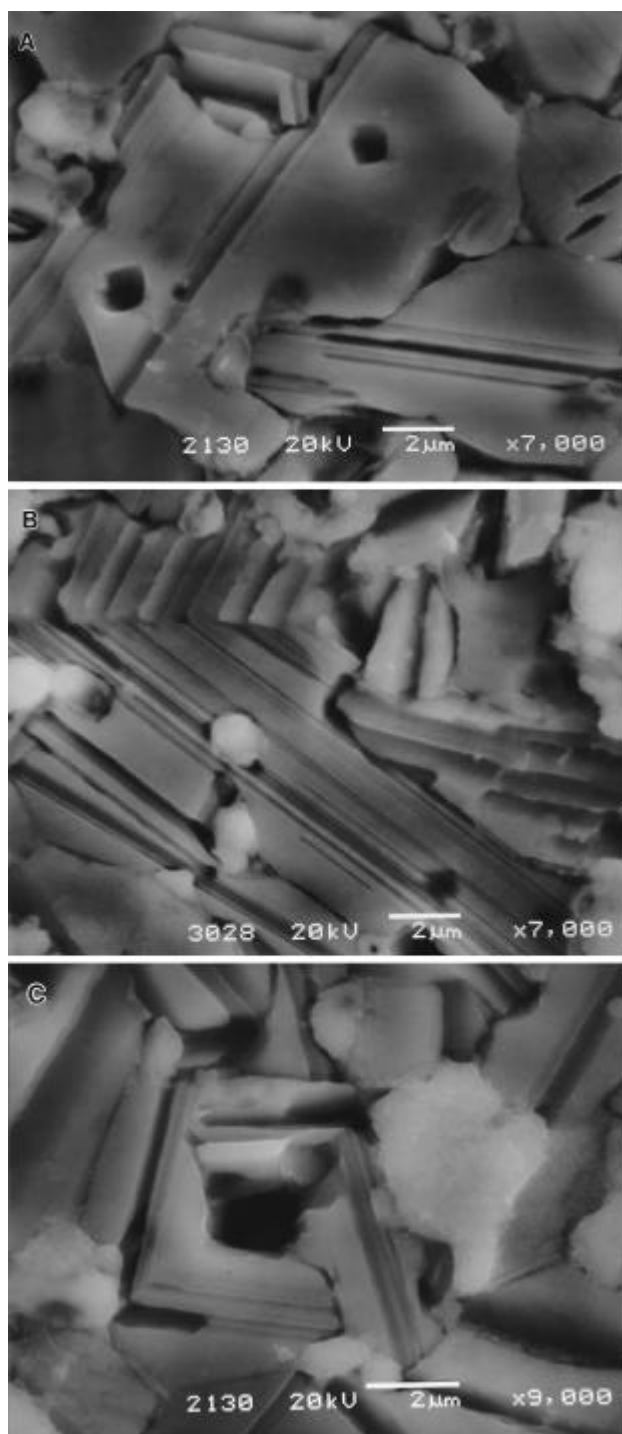evolution of SrO doped SrTiO$_3$ seems to be controlled solely by the growth kinetics of the polytype lamella,

while the growth kinetics of the perovskite matrix are lower compared to that of the hosted polytype. The resulting microstructure is composed of intergrown anisotropic grains with a "sandwich" structure where lamellae of the polytypic phases are imbedded at the core of the perovskite matrix **(Fig. 7)** .

In addition to larger polytypic lamellae in the centre of the perovskite grains many smaller lamellae, which grow in square like morphology are also observed **(Fig. 8a)** . Assuming the c-axis of a polytype lamella is in the plane of the paper, smaller lamellae found in the perovskite matrix may extend along any of the {100} perovskite planes **(Fig. 8b)** . The assumption is made on the basis of the orientation of polytype layers, due to faster growth of polytype lamella in the a-b direction.

Chemically etched polished samples reveal square shape negative forms, with their edges rotated by an angle of 45° against the polytype lamella **(Fig. 9a)** . Another feature often observed in the microstructure is the transposition of some perovskite grains rich in polytype lamellae by an angle of 90°. The resulting grains obtain a twin-like appearance **(Fig. 9b)** . If the perovskite grain including a polytype phase, is transposed at least 3 times by 90° about the same axis the resulting morphology is a closed rod-like rectangular loop. This phenomenon is frequently observed in perovskite grains with larger portions of polytype lamellae, *id est* higher SrO additions **(Fig 9c)** .

5 TEM STUDY

In order to study the crystallographic relationships between the polytypes and the hosting perovskite matrix we used conventional TEM techniques, such as selected area diffraction and phase contrast TEM. The observations of the same samples, as used for the SEM
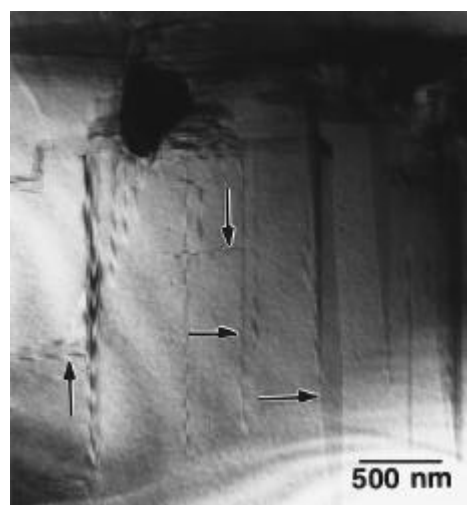
Figure 9: a) Square shape bodies appeared during etching with [110] lattice planes toward polytype lamella. **b)** Twin like perovskite grains rich with polytypic lamella **c)** Closed square loop of perovskite grain with greater portions of polytypic lamella

Slika 9: a) Liki kvadratnih oblik se poka`ejo med jedkanjem. [100] ravnine likov so z robom usmerjene proti politipni lameli. **b)** Dvoj~kom podobna perovskitna zrna bogata s politipnimi lamelami **c)** Zrno v obliki zaprte pravokotne zanke, ki vsebuje ve~ji dele` politipnih lamel

Figure 10: TEM bright field image of single planar faults alternating along the {100} directions in the perovskite matrix
Slika 10: TEM slika v svetlem polju posameznih planarnih napak, ki se znotraj perovskitne matrice raztezajo v smeri {100}
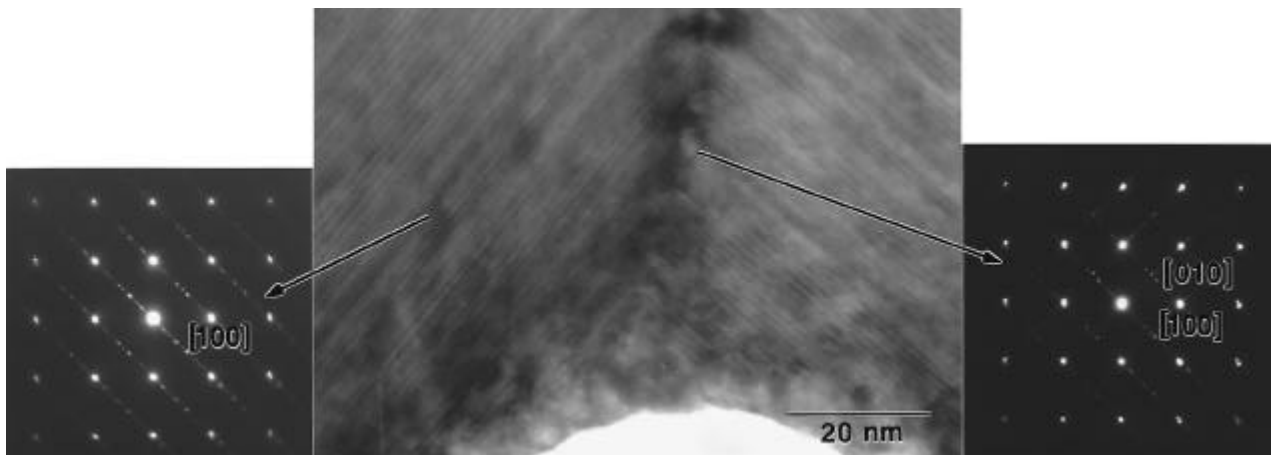
Figure 11: SAD pat terns of a su per struc ture or der ing of polytypic pla nar faults (lamella and the spot of trans po si tion) with a cor re spond ing TEM bright field im age of a trasposition of polytypic pla nar faults, both in [100] view

Slika 11: Uklon na izbranem podro~ju, ki potrjuje nadstrukturno urejanje politipnih planarnih napak (uklon na lameli in na ravnini transpozicije) z ustreznim TEM posnetkom transpozicije politipnih planarnih napak. Uklon in slika sta posneta v [001] smeri
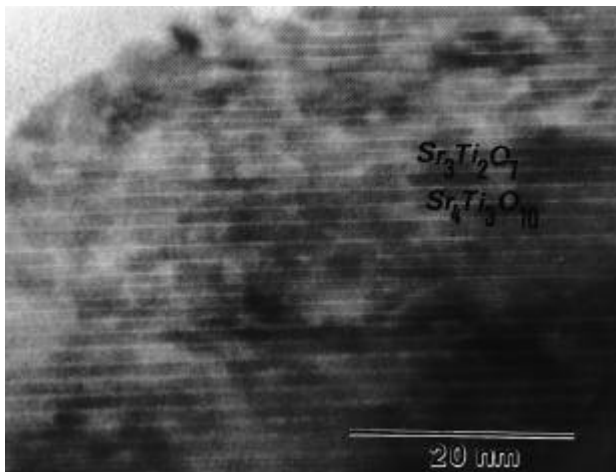

Figure 12: Two types of or dered polytypic se quences as found in polytypic lamelae

Slika 12: V politipnih lamelah opazimo dve urejeni politipni sekvenci

planar faults in almost every perovskite grain. Both single and ordered planar faults show a square-like morphology. SAD patterns reveal that single and ordered faults typically occupy (100) perovskite planes and can be intermittently transposed to any plane of the $\{100\}$ family. Weak reflections which appear in the corresponding SAD pattern in addition to the basic perovskite reflections, indicate a superstructure ordering. **Figure 11** demonstrates a transposition of planar faults that extend in two sets of $\{100\}$ lattice planes.

The smallest measured lengths between ordered polytypic faults in **figure 12** show that the periodicity found over a wide range of polytype lamella correspond to $Sr_3Ti_2O_7$ (n=2). The homologue $Sr_4Ti_3O_{10}$ (n=3) was found in a narrow range, while Sr_2TiO_4 was never observed. The polytypic sequences found in our TEM study are in agreement with the XRD data, which indicate that only the homologues with n ≥ 2 are stable at higher temperatures (T>1300°C).

study, reveal the presence of single **(Fig. 10)** and ordered
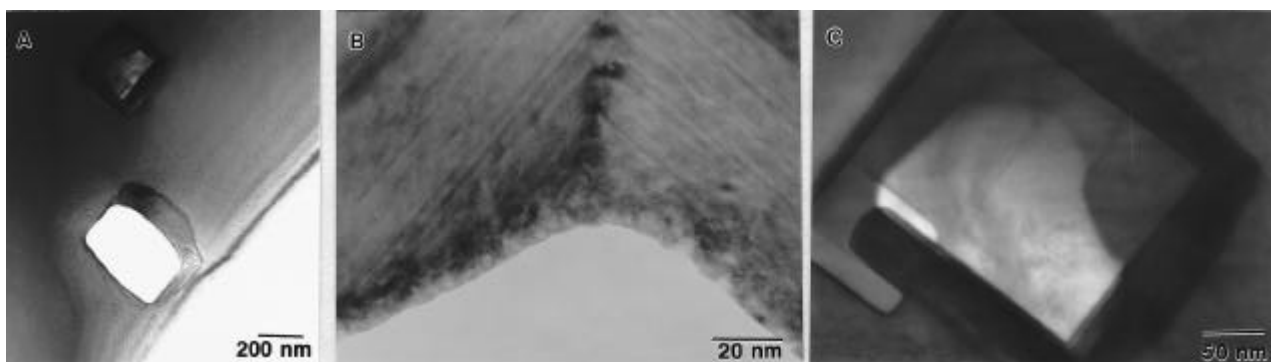

Fig ure 13: a) Square like polytype loops and rect an gu lar etched holes sur rounded with polytype lamellae, **b)** Polytype lamellae on the edges of square shaped hole **c)** Closed square loop of the polytype lamella in the perovskite ma trix

Slika 13: a) Za klju~ene politipne zanke in jedkane luknje pravokotnih presekov obdane s politipno lamelo, **b)** Politipna lamela ob robovih pravokotne luknje **c)** Zaprta pravokotna zanka politipne lamele v perovskitni matrici

Figure 13a shows square-like polytype loops in the thin foil of the specimen. Many similar rectangular etched holes are observed in the same specimen. A TEM bright field image reveals a polytype formation near the corner of the eroded rectangular hole. The polytype layers extend along the edges of the rectangular hole while the corners match with the plane of the transposed polytypic lamellae **(Fig 13b)**. When ordered planar faults are transposed to another set of {100} planes the periodicity normal to the fault plane is usually destroyed, and thus the interface is not bound to any specific plane forming a zig-zag extended boundary. **Figure 13c** shows a polytypic lamella transposed 3 times by 90° about the same axis forming a closed rectangular loop. An SAD pattern of the inner part of a closed loop made of polytype faults reveals only the perovskite structure. The presence of the rectangular holes in etched samples seem to be related to the growth and transposition of the polytype lamella and are not likely to be the remains of precipitates formed in the classical manner.

6 DISCUSSION

During sintering the SrO doped $SrTiO_3$ forms an ordered structure with the generic formula $Sr_{n+1}Ti_nO_{3n+1}$. The nonstoichiometry caused by SrO additions is therefore structurally compensated through the formation of Ruddlesden-Popper phases rather than forming solid solutions with the hosting perovskite phase, as already pointed out by some authors[25].

From XRD data we may conclude that the polytypes form depending on firing temperature according to the following solid-state reactions:

Thermal decomposition of $SrCO_3$:

$$SrCO_3 \xrightarrow{\text{firing}} SrO + CO_2 \uparrow$$
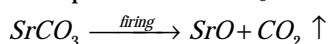
Formation of low temperature polytypes:

$$SrO + nSrTiO_3 \xrightarrow{n=1} Sr_2TiO_4$$
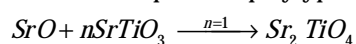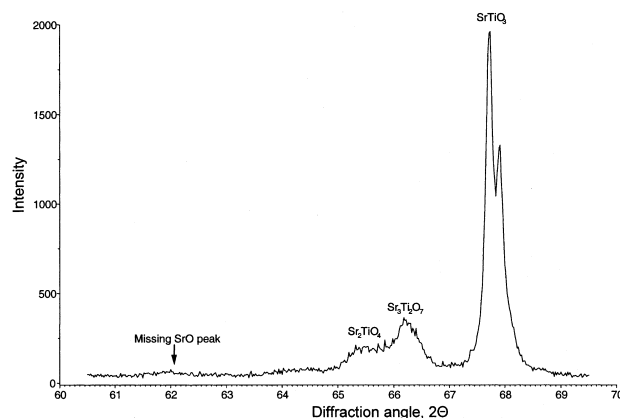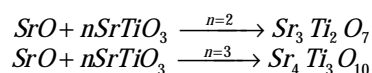
Formation of high temperature polytypes:

Figure 14: XRD pattern of SrO doped $SrTiO_3$ fired at 900°C for 10 hours

Slika 14: XRD spekter s SrO dopiranega $SrTiO_3$ žganega pri temperaturi 900°C, 10 ur

$$SrO + nSrTiO_3 \xrightarrow{n=2} Sr_3Ti_2O_7$$
$$SrO + nSrTiO_3 \xrightarrow{n=3} Sr_4Ti_3O_{10}$$

The polytype Sr_2TiO_4 is stable at low temperatures (T<1200°C), whereas the polytype phases with n higher than 1, such as $Sr_3Ti_2O_7$ and $Sr_4Ti_3O_{10}$ form in the higher temperature range. Because of similar values for the formation enthalpy for Sr_2TiO_4 ($E°_{form.}$ = -0.11), $Sr_3Ti_2O_7$ ($E°_{form.}$ = -0.14) and $Sr_4Ti_3O_{10}$ ($E°_{form.}$ = -0.14) there is no strong energetic predisposition for the formation of any particular homologue member. In spite of this, XRD measurements show certain affinity of different homologue phase formation at different firing temperatures. Accompanying studies made during this work show that even at low temperatures (T=900°C) Sr_2TiO_4 is formed while no residual SrO could be detected **(figure 14)**. This indicates that during the high temperature XRD experiment the mixture of SrO and $SrTiO_3$ did not reach an equilibrium state. The transformation between the constituent powders and the polytypes takes place within a narrow temperature range of 100°C.
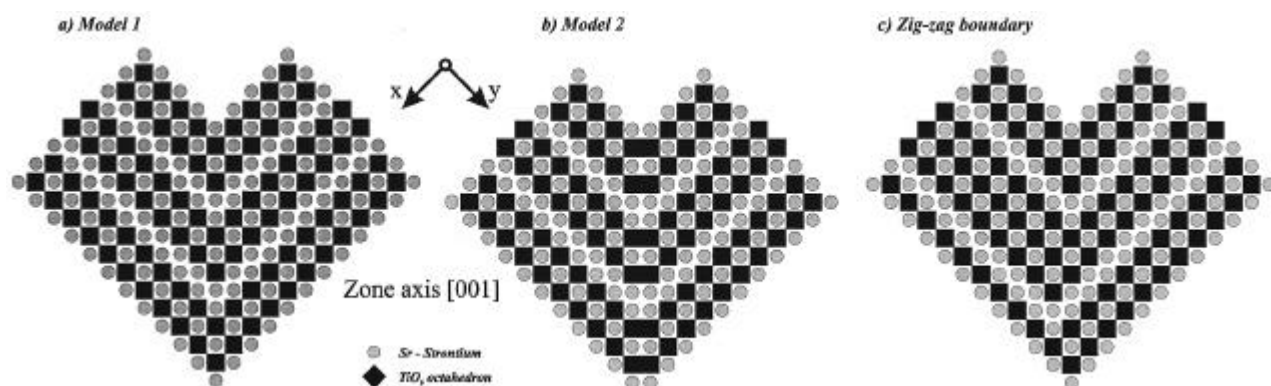

Figure 15: Two possible models for the transposition of the polytypic layers; **a)** with unchanged stacking sequence across the [100] plane of transposed planar faults; **b)** and edge-sharing of TiO_6 octahedra across the interface plane; **c)** Motive for the zig-zag boundary and destroyed periodicity

Slika 15: Hipotetična modela transpozicije politpnih plasti; **a)** z ohranjenim zlogom preko [100] ravnine transpozicije; **b)** TiO_6 oktaedri se stikajo z robovi na ravnini transpozicije; **c)** Motiv za na sta nek cika-cak meje in porušene periodičnosti

The results of our XRD data agree with those of Tilley[3] that stable polytypes can be observed at temperatures between 1100°C and 1400°C. The absence of polytypes with n higher than 3 is again in agreement with the calculated formation enthalpies of Udayakumar et al.[4] which show no energetic preference for the formation of any particular higher member of the Ruddlesden-Popper homologous series.

A correlation between SEM and TEM microstructural and morphological studies reveal interesting features similar to those found in SrO doped $CaTiO_3$. ^eh et. al.[5] have reported the existence of the square like morphology of single polytypic faults within the perovskite matrix and observed ordering of parallel planar faults ordered into polytypic lamellae at higher formation temperatures. Planar faults in their system run parallel to {110} lattice planes of orthorhombic $CaTiO_3$, that correspond to {100} lattice planes of cubic $SrTiO_3$. The same features were observed in our system, only that the square like morphology following the {100} perovskite planes is also obeyed in the case of ordered polytypic faults. The latter phenomenon causes a condition where the whole polytype lamella is transposed to another set of {100} lattice planes forming a twin-like interface between the transposed polytypes. Grains, which are observed in SEM and show "twin-like" and "closed-loop" morphology are very likely caused by the multiple transposition of the polytype lamella. Observed anisotropic growth of sandwich-like grains clearly indicates that the growth of the whole grain is in fact controlled by the growth direction of the polytypic lamella within. In addition, we found that polytypes can be transposed to any of the {100} planes, implying diverse grain morphologies starting from simple plate-like anisotropic grains toward rod-like grains containing closed loops of multiply transposed polytypic layers.

Idealised models for the transposition of the polytypic layers propose two possible different stacking sequences across the [110] plane of transposed planar faults **(Fig. 15)** .

The first model assumes similar stacking across the transposition interface as found in the perovskite structure, while the second model introduces an edge-sharing of TiO_6 octahedra across the interface plane. Both proposed models assume that the polytype periodicity is retained across the (110) plane of transposition. In the real situation we observe the appearance of the zig-zag boundary at the interface between two perpendicular polytypic lamellae, which forms if a planar fault extends beyond the ideal plane of transposition. The consequence of these features is also destroyed periodicity **(Fig. 15c)** . TEM bright field images of transposed planar faults reveal the interface as a series of (hk0) planes. The periodicity of transposed planar faults is therefore closely correlated to a fraction of different (hk0) planes on the interface.

7 CONCLUSIONS

The prevailing defects in SrO doped $SrTiO_3$ are SrO-rich planar faults. The appearance of polytypes depends on the firing temperatures, implying that higher polytypes are stable at higher sintering temperatures. Rectangular networks can be formed either with single planar faults or even with polytypic lamellae. Special morphological features observed by SEM and TEM such as "twin-like" and "closed square loop" grains result from the transposition of the polytype lamellae along any of the perovskite {100} lattice planes. The existence of negative rectangular forms after etching of the samples is related to the presence of multiply transposed rod-like ordered polytype planar faults. Inside these closed loops only the perovskite structure is observed, which greatly reduces the likelyhood that precipitates are the origin of the etched square holes.

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