

Initial transient structure and chemistry of intergranular glassy films in ferric-oxide doped strontium titanate ceramics

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Received: 30 August 2010 / Accepted: 11 January 2011 / Published online: 26 January 2011
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Abstract Intergranular glassy films (IGFs) often play a key role in the formation of microstructure and the resultant properties in titanate-based materials. In this article, a systematic study of IGF structure and chemistry is reported in Fe₂O₃-doped SrTiO₃ ceramics sintered under different temperatures and dwelling times. IGFs exhibit a large variation in their thicknesses, although majority of them are still formed by the lower energy {100}, {110}, and {111} planes from one side, which is also true for those grain boundaries (GBs) without IGF and reveals no particular effect of crystallography on IGF width. Furthermore, two trends of IGF chemical composition were found coexisting in each sample, one rich in Ti and the other in Sr, and both containing Fe segregants. The change of sintering temperature did not show significant effect on the distributions for both trends. However, increase of the dwelling time is effective to turn some Sr-rich IGFs to Ti-rich IGF, indicating that the former is in a transient state and the equilibrium IGF has most likely a TiO₂-based composition.

Introduction

In polycrystalline titanate-based ceramics (e.g., SrTiO₃ and BaTiO₃), grain boundaries (GBs) often play a key role not only in the development of microstructure but also in the materials' properties [1–3]. As well known, internal interfaces (including GB) can reduce the ionic conductivity especially in doped material systems. This is often attributed to the formation of space-charge layer that compensates the extra charges from dopants or impurities segregating to GB, which may lead to the formation of double Schottky barriers [4–7].

In fact, the formation of GB structure is sensitive to several factors, such as the crystallography or energy of GB plane as well as the interfacial chemical, especially during the microstructure development process. Ernst et al. [8] have analyzed the orientation relationships between neighboring grains in SrTiO₃, BaTiO₃, and Pb(Zr_xTi_{1-x})O₃ ceramics, and revealed a significant preference for Σ3 relation. Saylor et al. [9] have reported that more boundaries were terminated by low-energy {100} planes than other planes in polycrystalline SrTiO₃ materials. In Bi₂O₃-doped (Sr,Ba)TiO₃ ceramics, two types of GB structures, TiO₂-rich intergranular glassy films (IGFs) and nano-Bi precipitates were observed in the same materials due to the local amount of Ti at GB during the cooling [10].

Although considerable researchers devoted their efforts to the study of GB in Fe-doped SrTiO₃ as a model system for the acceptor-doped perovskite, most of them focused on GBs in bicrystals which might not represent GBs in polycrystalline materials [11–13]. Indeed, IGFs were often observed in various ceramics samples which exhibited also quite different dopant segregation behaviors as compared to these coherently structured GBs [14–16], and there is no exception for SrTiO₃ [17, 18]. In this regard, we present

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here a systematic study of IGF structures and chemistries in a series of Fe_2O_3 -doped SrTiO_3 ceramics by utilizing principally the analytical electron microscopy. Strong variations of IGF structure and chemistry were found and their orientation relationships were examined.

Experimental

The ceramic materials studied here were fabricated from high-purity SrTiO_3 and Fe_2O_3 (AR: analytical reagent; Sinopharm Chemical Reagent Co. Ltd, China) powders by conventional synthesis method. The powders of SrTiO_3 with 0.8 mol% of Fe_2O_3 additives were milled in ethanol for 24 h in a planetary ball-mill machine and were dried afterward. 5 wt% of PVB (polyvinyl butyral) was added as the binder before the powders were pressed into disks with

a diameter of 15 mm and thickness of ~ 3 mm. These disks were sintered in air for 4 h at 1350, 1410, and 1450 °C, respectively. Accordingly, the sintered ceramic samples were named after SF-1, SF-2, and SF-3. For the sake of comparing the effect of sintering time, a sample was sintered at 1410 °C but held for 10 h, which was given the name of SF-2*.

Transmission electron microscopy (TEM) specimens were prepared by conventional specimen preparation techniques, including mechanical cutting, grinding, polishing, dimple-grinding, and ion-beam milling. TEM imaging was carried out with JEM-2010 and JEM-3000F electron microscopes (JEOL Co., Japan). The cation concentrations were measured quantitatively by energy dispersive X-ray spectroscopy (EDXS) system (Link/ISIS, Oxford Instruments, UK), which was attached to JEM2010. The actual probe for EDXS analysis was

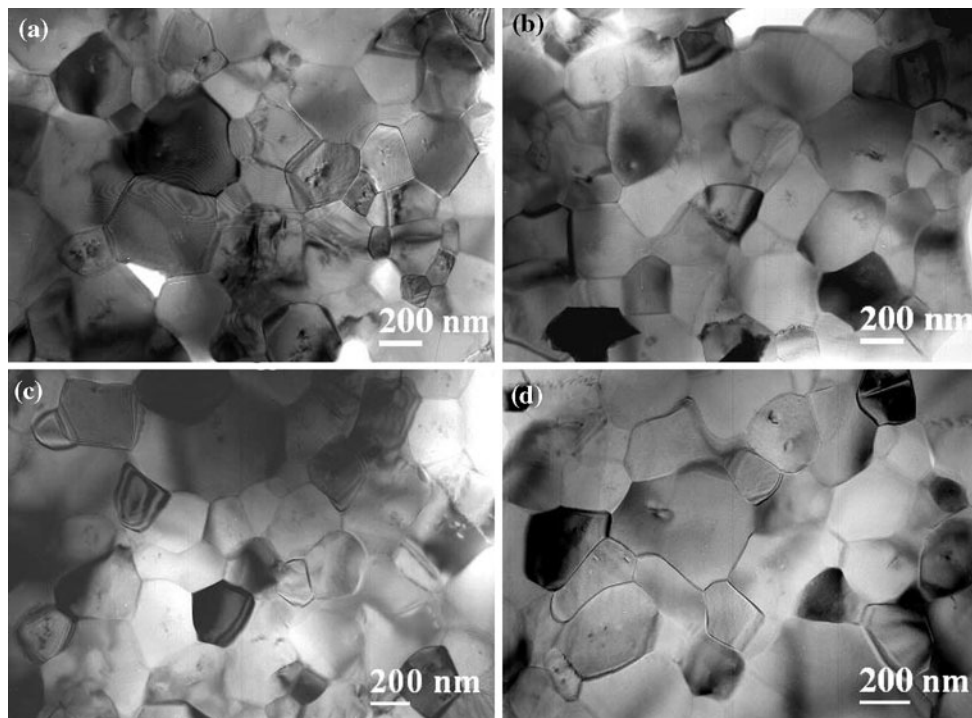


Fig. 1 TEM images of microstructures in Fe_2O_3 -doped SrTiO_3 ceramics: **a** SF-1, **b** SF-2, **c** SF-2*, **d** SF-3

Table 1 Summary of sintering conditions, microstructural, and micro-chemical parameters in Fe_2O_3 -doped SrTiO_3 ceramics

Sample	Temp. (°C)	Time (h)	Grain size (nm)	Fe:Sr ratio	Ti:Sr ratio	Γ_{Fe}	Γ_{Ti}
SF-1	1350	4	260 ± 130	0.003 ± 0.002	0.979 ± 0.054	8.11 ± 3.34	-8.61 ± 16.11
SF-2	1410	4	285 ± 110	0.003 ± 0.003	0.984 ± 0.063	7.17 ± 3.54	-9.45 ± 14.57
SF-2*	1410	10	275 ± 110	0.003 ± 0.002	1.006 ± 0.078	7.72 ± 3.11	1.08 ± 15.99
SF-3	1450	4	280 ± 110	0.006 ± 0.005	1.004 ± 0.089	9.04 ± 3.77	-6.41 ± 15.59

measured to be 35 nm, which gave sufficient current to acquire spectra. The elemental quantification was based on the Cliff–Lorimer equation with the standard-less routine and using ZAF corrections. Measurement of

dopant segregation to GB was performed by spot mode with positioning the probe on and off GBs [15, 19]. Excesses of segregants were quantified according to [10, 15].

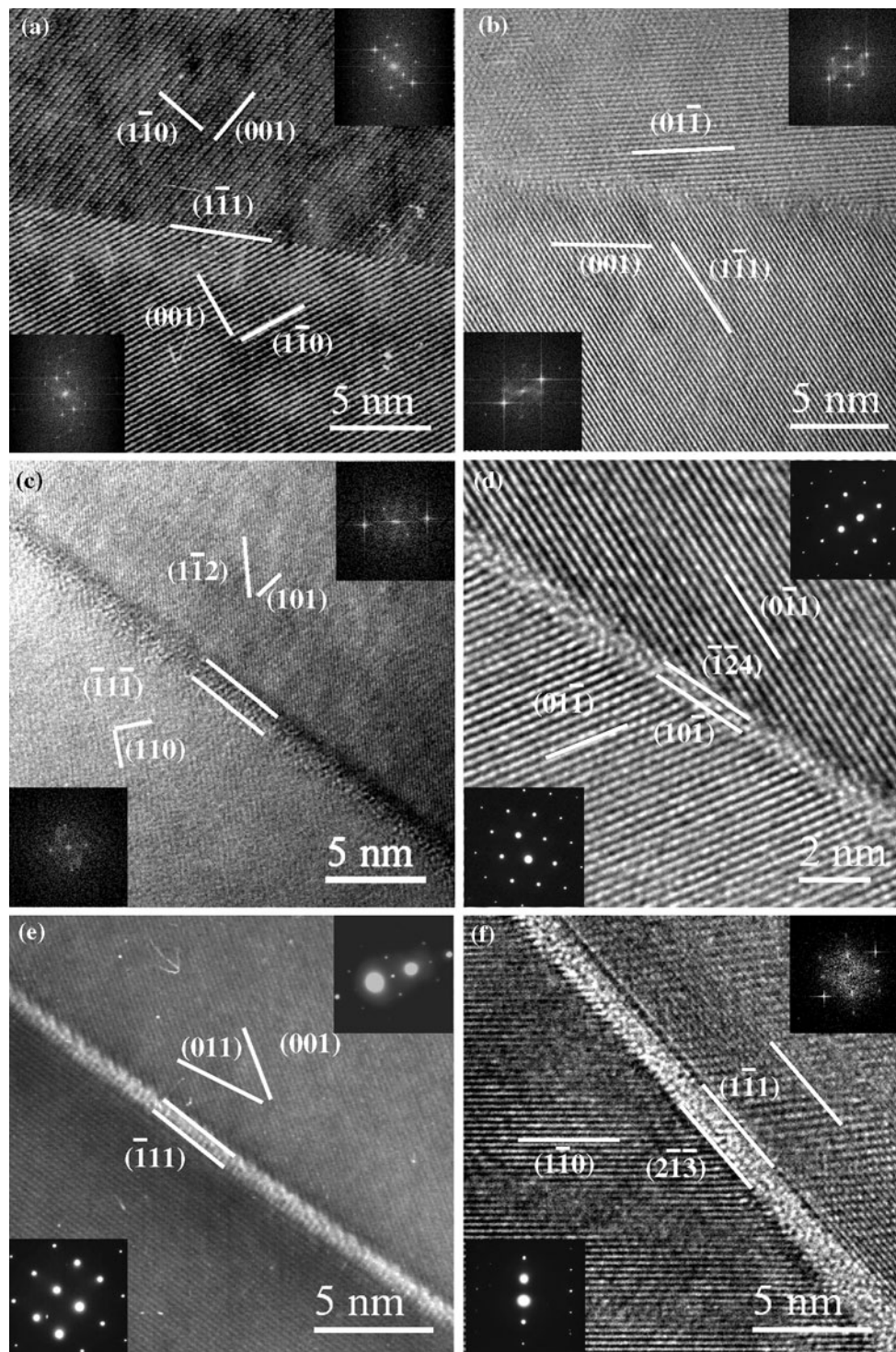


Fig. 2 HRTEM images of **a–b** GB without IGF, and **c–f** GB with IGF, all sampled in the sample SF-3. *Insets* are the corresponding fast Fourier transform (FFT) or selected area diffraction (SAD) patterns of

neighboring grains, which were utilized to identify the interface planes of each IGF in addition to HRTEM

Results and discussion

Common microstructure and different GB structures

Typical TEM images from the Fe₂O₃-doped SrTiO₃ samples are shown in Fig. 1. All the samples exhibit the uniform microstructures by equiaxed grains with similar average grain sizes all close to 300 nm, as given in Table 1. The common microstructure characters indicate that neither sintering temperature nor sintering time has significant effect on the grain growth, which provide a simple system to study the behaviors of GB structures during sintering, without involving any effect from grain growth.

GB structures were characterized by high-resolution transmission electron microscopy (HRTEM), and strong variation in GB structures was found in each sample. Taking the sample SF-3, for example, some GBs have no IGF to form either coherent or incoherent interfaces (Fig. 2a, b); most GBs are covered with IGFs, but in different thicknesses (Fig. 2c–f). Such a variety of GB structures and variation in IGF width are common for all these samples. The grain surface planes of IGF could also be determined either from HRTEM directly (with the help of fast Fourier transformed diffractogram) or from electron diffraction [15]. {100}, {110}, and {111} planes are rather common as the interfacial planes for IGFs. Therefore, we attempted a systematic correlation of IGF thickness with the grain surface structures in SF-3 sample. By removing the lattice fringes from the HRTEM image via Fourier filtering to highlight the amorphous structure [14], the thickness of each IGF was measured. The interfacial planes of these GBs are summarized in Table 2 and arranged in the order of IGF thickness that varying from 0.5 to 2.6 nm. It is worthy of mentioning that the measured width of IGF using a non-corrected microscope could be slightly larger due to the delocalization effect at interfaces. This may make the uncertainty in IGF thickness exceeding the widely believed 0.1 nm, but on the other hand, this should still be less than 0.2–0.3 nm [20, 21], which validates the analysis in this study. Among 15 GBs with IGF investigated in SF-3, there are five cases that one interfacial plane to be {100} plane, six cases to be {110} plane, three cases to be {111} plane. It seems that, comparing with the other planes with higher indexes, the {100}, {110}, and {111} planes were preferred as the habit interfacial planes between the amorphous and the crystalline structures, at least from one side of the IGF. Moreover, these low-index interfacial planes generally appear as atomically flat, as shown in Fig. 2e, f, while the high-index interfacial planes do not, as shown in Fig. 2c, which is consistent with the observations from Chung et al. [22]. These results may also be due to the fact that these low-index planes are much

easier to be targeted using HRTEM technique that prefers flat interfaces.

The formation of IGFs with varying thicknesses could be rationalized as a behavior due to the change of GB energy with different interfacial crystallographies. Saylor et al. proposed that the GB energy was correlated to the surface energies of the planes on either side of the boundary and that the binding energy between the two surfaces was approximately constant. Consequently, the GB population in SrTiO₃ was correlated to the sum of the energies of the surfaces comprising the boundary, and the most frequently observed boundaries should have the lowest energies [9]. Holm et al. [23] have shown that the population of GBs with relatively a low energy increased, while the population of high energy GBs decreased during the grain growth. Therefore, our results show that {100}, {110}, and {111} planes are common to be the interfacial planes between IGFs and the adjacent grains is consistent with this trend. Luo [24] has demonstrated the anisotropic wetting of Bi₂O₃-enriched surface amorphous films on ZnO. He ascribed the anisotropic effect to the induced order between the ZnO surface structures and the bismuth oxide units constituting the amorphous film. In Table 2, the two GBs with wide IGF over 2 nm both take {111} planes as one of the two interfacial planes. While for IGFs with thickness less than 1 nm, {110} planes prevail as one of the interfacial plane, except GB12 and GB13. In SrTiO₃ lattice, the (100) plane is alternatively made of SrO or TiO₂

Table 2 Characteristics of GBs with IGF in SF-3

Analyzed boundaries	Interfacial plane ^a		IGF width (nm)
	Grain 1	Grain 2	
GB1	($\bar{1}\bar{1}$)	–	2.6
GB2	(111)	(010)	2.5
GB3	–	–	2.0
GB4	($\bar{1}$ 10)	(0 $\bar{1}$ 1)	1.4
GB5	($\bar{1}\bar{1}$)	($\bar{2}\bar{1}\bar{3}$)	1.2
GB6	(001)	(112)	1.1
GB7	(001)	–	1.0
GB8	(02 $\bar{1}$)	($\bar{2}\bar{1}\bar{3}$)	1.0
GB9	–	($\bar{1}\bar{1}$ 0)	0.9
GB10	–	(0 $\bar{1}$ 1)	0.8
GB11	($\bar{1}\bar{1}$ 0)	($\bar{1}\bar{1}$ 0)	0.8
GB12	(001)	–	0.8
GB13	–	–	0.7
GB14	(10 $\bar{1}$)	($\bar{1}\bar{2}$ 4)	0.7
GB15	(100)	($\bar{1}$ 01)	0.5

^a Interfacial planes were determined by the corresponding fast Fourier transform (FFT) or selected area diffraction (SAD) patterns (see text for more details)

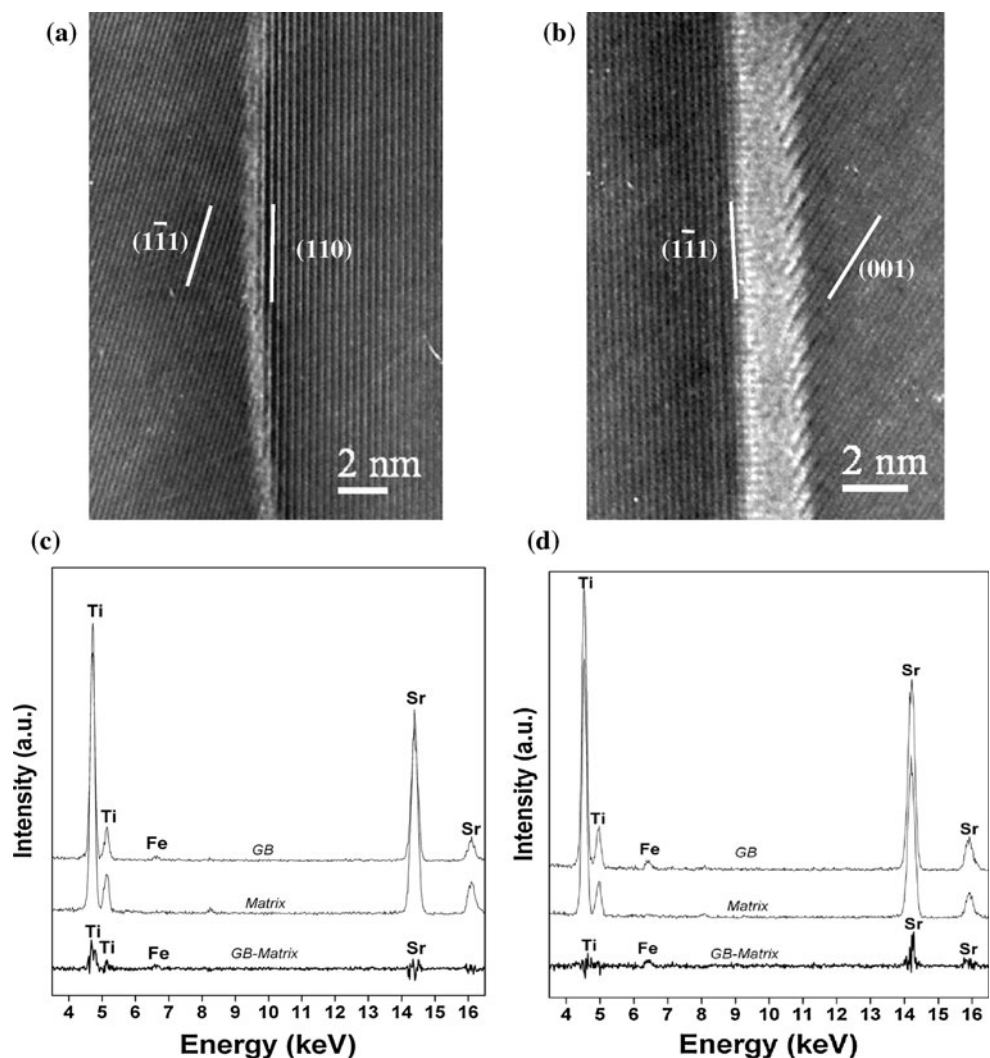
compositions, which is charge-balanced, hence non-polar. The (110) plane is alternatively O_2^{4-} or $(SrTiO)^{4+}$ plane, and the (111) plane is Ti^{4+} or $(SrO_3)^{4-}$ plane, hence both planes are polar, which may initiate permanent dipole moments at the grain surface [25]. In the actual observation of surface structure (111) terminations were found to be Ti or reduced SrO_{3-x} [26]. The stoichiometry of SrTiO is likely to be observed for (110) termination [27]. According to the results of Pojani et al. [27], the averaged surface energies \bar{E}_s is almost independent of the actual surface composition for (111) termination. For (110), the values of \bar{E}_s are more contrasted and depend upon the surface geometry and stoichiometry. \bar{E}_s of the stoichiometric SrTiO–O₂ slab is lower than that of (111) termination, which indicates that (110) is relatively more stable than (111). Thus, supposing a common interfacial plane from one side, the GB with (110) as the other interfacial plane should reach the equilibrium state easier than the GB with (111) plane as the second interface. GB2 and GB15 shown in Table 2 are just like the case, which accommodates with

IGF of 2.6 and 0.5 nm, respectively. Nevertheless, it is difficult to draw a conclusion that the thickness of IGF is clearly depend upon the interfacial plane since the statistic is far from sufficient, and it is very difficult to get the complete crystallographic information from both sides of IGF to proceed such assessment.

Two typical chemistries for IGFs

Segregations of Fe and Ti to GBs were measured by EDXS analysis described in “Experimental.” About 20 GBs were detected in each sample. Since these GBs were selected more or less randomly, GB with or without IGF should all be included and the selection should correspond to a good representation of actual population of GB structures. Solution and segregation data in average are given in the Table 1. It can be seen that Fe solutions in all the samples are very low. Most of Fe^{3+} dopants are segregated to GBs, which were also found by earlier studies [17, 28]. The excess of Fe^{3+} at GB exhibits almost no change with

Fig. 3 Two IGFs with different compositions in SF-3: **a–b** their HRTEM images; **c–d** their EDXS spectra and the processed spatial difference, corresponding to (a) and (b), respectively



sintering temperature or sintering time, although it might vary if we increase the level of Fe_2O_3 doping, similar to the case of Nb_2O_5 doping in SrTiO_3 ceramics [29]. Yan et al. [30] have discussed the main driving forces for solutes segregation at interfaces as the elastic energy, the electrostatic potential and the dipole interactions. Under the same six-coordinated configurations, the size of Fe^{3+} ions (0.065 nm) is quite close to that of Ti^{4+} ions (0.061 nm) [31], the elastic energy due to the size mismatch could be neglected. Therefore, the main driving forces for Fe^{3+} segregation to GB should be either electrostatic potential and/or dipole coupling.

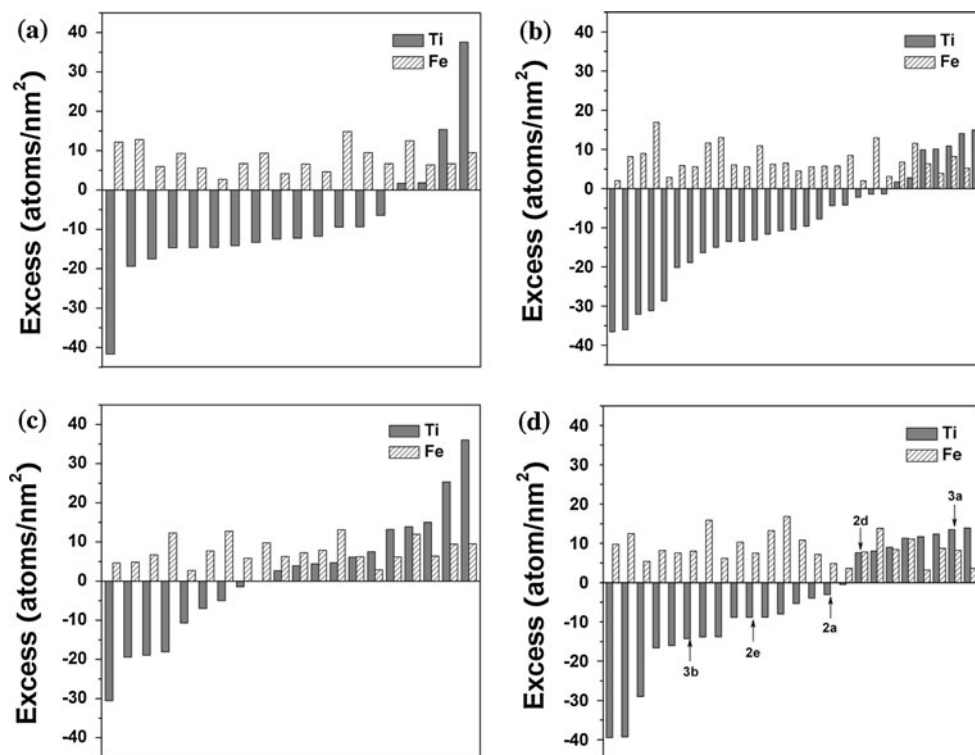
The level of Ti at GB exhibits a quite different behavior from Fe segregation. The excess of Ti varies over a wide range that extends well into negative domains in each sample. The negative excess of Ti corresponds to the lower level of Ti content in GB than in the neighboring grains, indicating a depletion of Ti from GB zone and consequently the enrichment of Sr in GB [10]. Indeed, two kinds of IGF chemistries were detected by utilizing the EDXS spatial difference method [10, 32]. Figure 3a shows the HRTEM image of a thin IGF, from which the spatial difference spectrum (Fig. 3c) reveals that it is abundant in Fe and Ti, which is consistent with the excesses of $\Gamma_{\text{Fe}} = 8.2$ atoms/ nm^2 and $\Gamma_{\text{Ti}} = 13.5$ atoms/ nm^2 . In contrast, the IGF shown in Fig. 3b is composed of excessive Fe and Sr as revealed in Fig. 3d by the same spectral processing, which corresponds to the excesses of $\Gamma_{\text{Fe}} = 8.0$ atoms/ nm^2 and

$\Gamma_{\text{Ti}} = -14.2$ atoms/ nm^2 . Recently, Shih et al. [33] have also reported the Sr-rich GB in SrTiO_3 , which was associated with the abnormally grown grains but in the absence of IGF. Fe segregation in our case might contribute to a solute-drag effect to hinder the grain growth [34]. Nevertheless, the observation of Sr-rich IGF is still a puzzle that is reported for the first time in SrTiO_3 materials to our best knowledge.

Evolution of IGF chemistry

To further understand the distribution of GB chemistries, we plot Ti excess in correlation with Fe excess from the GBs, as shown separately in each sample in Fig. 4; GBs already shown in Figs. 2 and 3 from SF-3 are marked by arrows in Fig. 4d. Insensitive to the sintering temperature, it is common to exhibit a wide range of distribution for GB chemistry from Sr- to Ti-rich: the Sr-rich GBs are majority in numbers, while the number of Ti-rich GBs increases slightly with temperature from $\sim 22\%$ in SF-1 to $\sim 33\%$ in SF-3. In contrast, the effect of dwelling time to change the GB chemistry is more remarkable with the population of Ti-rich GBs increasing more than doubled to overtake the Sr-rich GBs, from $\sim 24\%$ in SF-2 to $\sim 55\%$ in SF-2*. These distributions not only demonstrate a tendency for Sr-rich GB to turn into Ti-rich, they also indicate that, comparing with the sintering temperature, the increase of dwelling time is more effective to facilitate such a trend. Although no IGF

Fig. 4 Correlated distributions of Ti and Fe excesses from GBs in samples: **a** SF-1, **b** SF-2, **c** SF-2*, **d** SF-3. Data are arranged in the order of Ti excess; the corresponding GBs and IGFs from SF-3 are marked in (d)



was observed, recently Bäurer et al. [35] have also reported a similar trend of Sr-rich GB to change into Ti-rich GB with extended annealing time in SrTiO₃ materials with TiO₂-excess, which is consistent with our case.

The eutectic temperature of SrTiO₃–TiO₂ is at 1440 °C [36] and only the sample SF-3 was sintered above this temperature. However, the liquid phase could be formed at about 1200 °C in SrO–Fe₂O₃ system [37], suggesting that all the samples may involve the liquid phase during sintering, at least at the early stage of sintering. Nevertheless, the existence of two typical IGF chemistries and the wide distribution of IGF thickness (0.5–2.6 nm) indicate that the GBs are far from equilibrium, both chemically and structurally, and covered by intergranular liquid to retain even after sintering in all samples. Dillon et al. [38] and Harmer [39] proposed the concept of GB complexion based on their study of alumina, and assumed that abnormal grain growth (AGG) occurs when two or more different GB complexions coexist in the same microstructure. However, no AGG phenomenon occurred although GB with and without IGF coexist in this study. Therefore, an extensive evolution of IGF chemistry occurred before the start of any micro-structural evolution in our case. Indeed, a similar situation was reported in low-TiO₂-doped alumina ceramics with minor-SiO₂ impurities, where the IGF chemistry had also evolved to certain extent to initiate the anisotropic grain growth [40].

Conclusions

In this study, we have presented a systematic investigation of the structures and chemistries of GBs in a series of Fe₂O₃-doped SrTiO₃ ceramics sintered with different temperatures or dwelling times. Irrespective of sintering conditions, all the samples exhibit the equiaxial uniform microstructures. It might be related to the strong Fe segregation to GBs. GBs with or without IGF were observed in each sample. IGFs exhibit a large variation in their thicknesses. Majority of them are formed by the lower energy {100}, {110}, and {111} planes from at least one side, which is also true for those GBs without IGF and reveals no particular effect of crystallography on IGF width. Two trends of IGF chemical composition were found coexisting in each sample, one rich in Ti and the other in Sr, and both containing also Fe segregants. Dwelling time is much more effective to turn Sr-rich IGFs to Ti-rich IGF comparing with the sintering time, indicating that the former is in a transient state.

Acknowledgements This study was financially supported by the National Natural Science Foundation of China via Grants No. 50525205. The authors appreciate beneficial discussions with Dr. M. Čeh of Jožef Stefan Institute of Slovenia.

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