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To cite this article: Hao Yang, Paul G. Kotula, Yukio Sato, Miaofang Chi, Yuichi Ikuhara & Nigel D. Browning (2014) Segregation of Mn^{2+} Dopants as Interstitials in SrTiO_3 Grain Boundaries, Materials Research Letters, 2:1, 16-22, DOI: [10.1080/21663831.2013.856815](https://doi.org/10.1080/21663831.2013.856815)

To link to this article: <https://doi.org/10.1080/21663831.2013.856815>



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Segregation of Mn^{2+} Dopants as Interstitials in SrTiO_3 Grain Boundaries

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(Received 15 September 2013; final form 14 October 2013)

Supplementary Material Available Online

Mn-doped SrTiO_3 shows promising magnetic and electrical properties, but the doping mechanism remains unclear. In this research Mn^{4+} is found to substitute Ti in bulk SrTiO_3 , but Mn^{2+} segregates inside grain boundaries at both Sr and interstitial sites. Mn interstitial doping has never been reported, but is found possible with the formation of Sr vacancies. This finding is significantly different from the amphoteric doping of Mn^{2+} substituting Sr and Mn^{4+} substituting Ti sites, therefore leads to different understanding on the defect mediated electrical and magnetic properties of transition metal-doped perovskites.

Keywords: Z-Contrast Imaging, Atomic EDS, Dopant Segregation, Grain Boundary

Oxide semiconductors doped with magnetic 3d transition metals are promising candidates to implement multiferroic/magnetoelectric properties into device architectures.[1–3] Transition metal doping is believed to induce a long-range magnetic ordering in dielectrics; however, many reported magnetic phenomena in the bulk have so far been attributed to experimental artifacts and extrinsic factors.[4–6] Instead, the origin of the magnetism may come from extrinsic sources including segregation of secondary ferromagnetic phases in non-magnetic semiconductors and insulators such as ZnO or TiO_2 [5] and structure defects in Mn-doped SrTiO_3 . [7] Therefore it is important to understand the Mn-doping behavior in SrTiO_3 , not only in the bulk but also in defect structures of grain boundaries (GBs) and dislocations which are known to dominate the bulk properties in many practically important nanocrystalline devices.

In the bulk SrTiO_3 , Mn impurity centers can be associated with either Sr or Ti sites due to their ionic multivalent state. Reports [8–10] have shown an amphoteric doping of Mn in the SrTiO_3 lattice with Mn^{4+} substituting for Ti sites and Mn^{2+} substituting for mainly Sr

sites, and the dielectric properties were attributed to the off-center relaxation of Mn^{2+} at the Sr site in the highly polarizable SrTiO_3 lattice.[8–10] Inside defect structures of GBs, transmission electron microscope (TEM) results showed that Mn exhibited a reduced oxidation state (less than 4+) without significantly altering the GB atomic structure,[11] and a similar study detected the presence of Mn^{2+} residing on the Ti site inside the GB plane.[12] Although these GB-doping studies were performed before the advent of aberration correction for TEM, they do illustrate that the doping behavior of Mn in defect structures is quite different from the bulk. Therefore, it is advantageous to further investigate the Mn-doping behavior inside bulk and defect structures of the SrTiO_3 lattice.

In the research reported here, we use aberration-corrected (scanning) transmission electron microscopy (STEM) techniques to evaluate the distribution of dopants inside the GB plane. To study the fundamental principles of Mn-doping behavior in SrTiO_3 GBs, bicrystals are used as model structures. A SrTiO_3 bicrystal containing a 22.6° (510)/[100] Σ 13 symmetric boundary was

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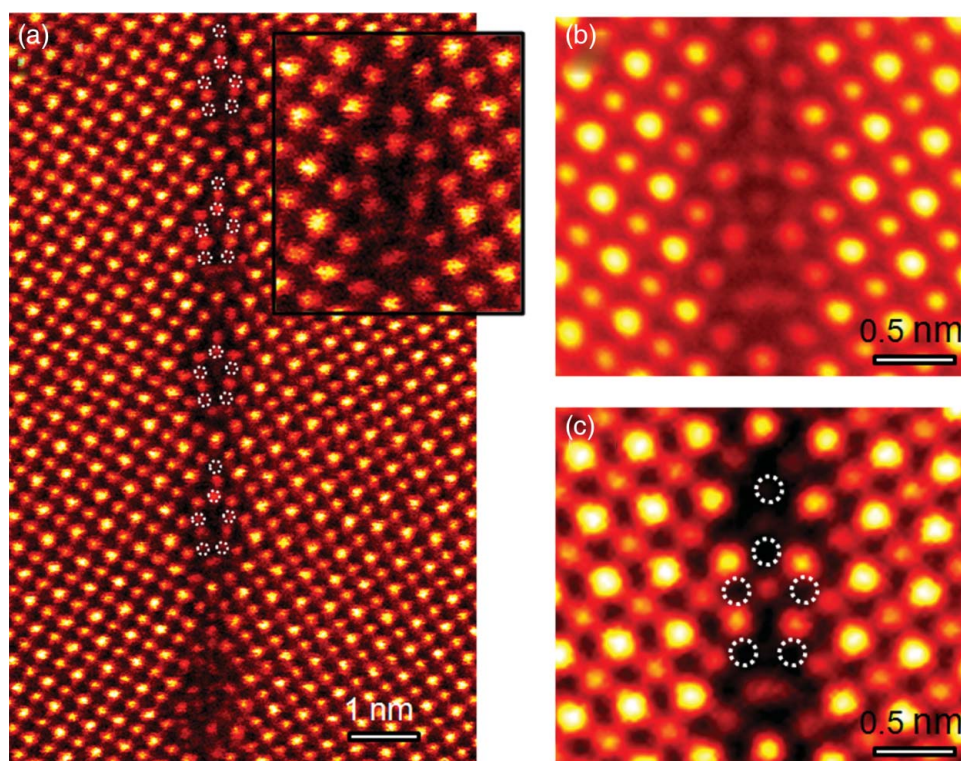


Figure 1. STEM Z-contrast images of (a), (b) the Mn-doped and (c) undoped SrTiO_3 $22.6^\circ \Sigma 13$ (510)/[001] grain boundary. (a) STEM image showing image contrast in several interstitial sites inside the boundary, as indicated by open circles. An inset of a magnified region clearly shows columns in interstitial sites. (b) A statistical averaging of over 80 STEM images shows clearly the presence of atomic columns in several interstitial sites. (c) As a comparison, the undoped grain boundary with the same misorientation angle contains no image intensities in the corresponding interstitial sites as indicated by open circles.

fabricated by joining two single crystals (Furuuchi Chem. Co. Ltd.) using the diffusion bonding technique.[13–15] A thin layer (~ 5 nm thin) of Mn was coated onto the surface of one crystal before the diffusion bonding for the Mn doping. And the diffusion bonding was carried out at the highest temperature of 1,350°C for over 20 h in order to obtain sufficient Mn diffusion. TEM samples were prepared by mechanical polishing and ion-milling. STEM and electron energy loss spectroscopy (EELS) characterizations of the GB atomic structures were performed using an aberration-corrected FEI Titan operated at 300 kV in the EMSL facility in Pacific Northwest National Laboratory (PNNL). STEM Z-contrast images were collected using a high-angle annular dark field detector with a collection angle of 70–190 mrad. For chemical analysis of GBs, atomic resolution energy dispersive X-ray spectrometry (EDS) analysis was performed using a 200 kV FEI ChemiSTEM installed with an aberration corrector and silicon drift detector (SDD) at Sandia National Laboratory.

Figure 1 shows Z-contrast images of the Mn-doped and the undoped GBs. In the Z-contrast image in Figure 1(a) and an enlarged region as an inset, several interstitial sites show distinctive columns which occur periodically along the Mn-doped GB plane, as indicated

by circles in the STEM Z-contrast image in Figure 1(a). The presence of columns at interstitial positions was evaluated from statistical analysis of relative large GB areas, so as to avoid structural determination based on a single image and the errors that can be associated with that. An averaged image (Figure 1(b)) of 86 repeated structural units is obtained by intensity-based cross-correlation template matching of 45 Z-contrast images similar to Figure 1(a), and detailed procedures of image averaging were described in previous studies.[16–18] Consistent with an individual image in Figure 1(a), atomic columns at several interstitial sites are clearly resolved from the averaged Z-contrast image in Figure 1(b), therefore it is statistically confident that these GB interstitial sites are occupied. As a direct comparison, no occupied interstitials can be seen from the undoped GB structure of the same misorientation, with the corresponding interstitial positions being indicated by open circles in Figure 1(c). This direct comparison confirms that the Mn doping creates interstitials inside the GB and implies that the interstitials are Mn atoms.

A direct comparison between the undoped and doped GB indicates that no significant change in the basic structural units is induced by Mn doping. However, previous analysis of the undoped $22.6^\circ \Sigma 13$ GB has highlighted

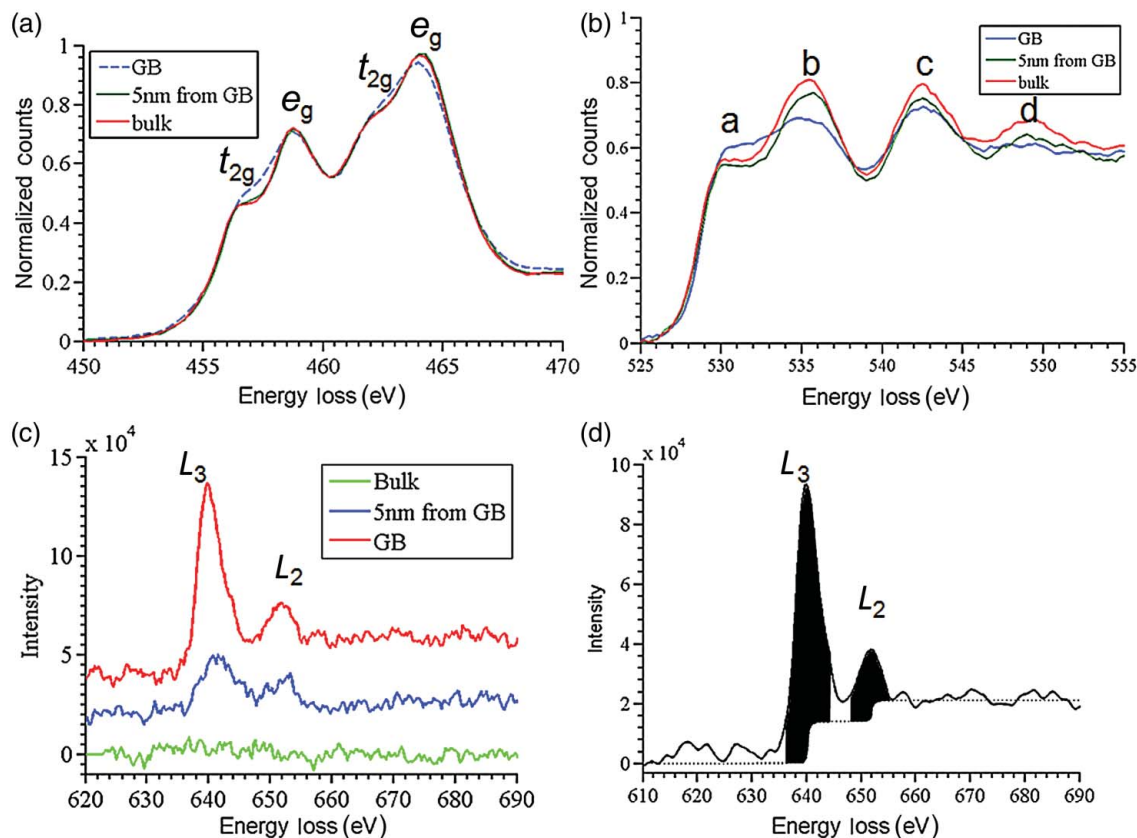


Figure 2. EELS analysis of (a) Ti L, (b) oxygen K and (c) Mn L edge from the grain boundary, 5 nm away from GB and the bulk region. Mn $L_{3,2}$ spectra show detectable signal 5 nm away from GB with a different L_3/L_2 peak ratio than in GB. (d) Quantification of Mn L_3/L_2 intensity ratio was performed by subtracting a continuum background of a 2:1 two-step arctangent function and integrating peak intensities over an 8 eV energy window on each peak.

the presence of two types of atomic structures—the symmetric structure shown in Figure 1(c) and an asymmetric structure containing a rigid-body translation along the GB plane.[16] The asymmetric structure has been shown to contain a Ti-rich nonstoichiometry and a relatively lower GB energy.[16] The asymmetric structure has not been found in the Mn-doped $22.6^\circ \Sigma 13$ GB from micron-scale sample areas, even though both the undoped and Mn-doped grain boundary bicrystals were fabricated under the same experimental conditions. As the statistical prevalence of competing structures in GBs serves as an effective indicator of grain boundary energetics,[16] the fact that only symmetric structure has been observed led us to believe that the symmetric structure observed in Figure 1 is stabilized by the presence of Mn ions.

To investigate the effect of Mn doping on the GB electronic structure, EELS analysis were performed in STEM from three different regions—inside the GB core, 5 nm away from the boundary, and bulk region far from the GB. The oxidation state of Ti inside the GB remains the same as in bulk, as no chemical shift is observed in either the Ti $L_{3,2}$ edge (Figure 2(a)) or the oxygen K edge (Figure 2(b)). Quantification of the Ti $L_{3,2}$ intensity ratio shows almost no difference between the GB core

and the bulk, and the minor difference in Ti $L_{3,2}$ profile is attributed to the weakened crystal field splitting due to TiO_6 octahedral distortion inside the GB. An increase in oxygen vacancy concentration inside the GB is supported from the damping of the oxygen K peak a, b and c because the oxygen K edge fine structure is sensitive to O—O bond ordering.[19] In addition, a decreased intensity in peak b as well as an increased intensity in lower energy side of peak b in the GB oxygen K (Figure 2(b)) also indicates the presence of Sr vacancies inside the GB. This is because the peak b and its peak shoulder in the lower energy side come from the hybridization between oxygen 2p and Sr 4d state in bulk SrTiO_3 , and this observed oxygen K edge fine structure is consistent with the Sr vacancy model based on theoretical simulations.[20] Furthermore, Figure 2(c) shows clearly a different Mn oxidation state in the GB core as compared with in the bulk. The L_3/L_2 peak intensity ratio is 3.8 inside the GB core and 2.1 about 5 nm away from the GB core, and a chemical shift of 1.3 eV is found between the L_3 peaks, therefore Mn is close to 2+ inside the GB but 4+ inside the bulk. The Mn L_3/L_2 intensity ratio is calculated based on the literature [21] by subtracting a continuum background of 2:1 two step arctangent functions and integrating

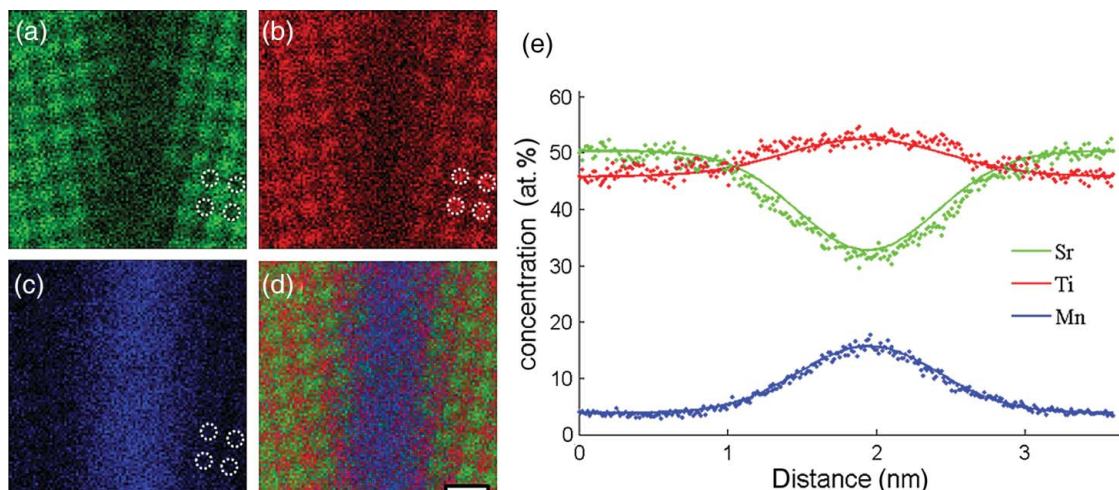


Figure 3. Quantitative Atomic resolution EDS mapping of the Mn-doped grain boundary. Pure compositional maps of (a) Sr, (b) Ti, (c) Mn, and (d) composite map were obtained from the MSA with RGB false colors applied. The scale bar is 0.5 nm. A few nm away from the GB core, Mn has a much lower but detectable concentration, and substitutes the Ti site as indicated by the coincident dashed circles in (b) and (c). The relative concentration profile (at%) across the GB in (e) is obtained by concerting the vertically summed up EDS signal of the two-dimensional map using the Cliff–Lorimer factors of a 200 kV microscope.

the intensity over an 8 eV energy window as shown in Figure 2(d).

A clear understanding of the doping behavior requires an accurate identification of the chemical composition inside the GB. Atomic-resolution EDS mapping is therefore applied using the SDD installed in the aberration-corrected FEI ChemiSTEM with a large collection angle (0.7 sr). To enhance the signal-to-noise ratio, the spectra image was processed using the multivariate statistical analysis (MSA) package [22] developed in Sandia National Laboratories, which is an automated spectra image analysis algorithm that converts abstract principal components into physically interpretable pure components.

Three major component images were identified corresponding to the compositional map of Sr, Ti and Mn, as shown in Figure 3(a)–(c), respectively. As shown from the Mn compositional map, no distinctive Mn columns are clearly resolved within the GB core region of roughly 1 nm wide. Assuming that the Mn map reflects the spatial distribution of Mn ions inside the boundary, this suggests that Mn not only resides in the interstitial sites but also substitutes the GB SrTiO_3 lattice. Dechanneling of the electron beam as it propagates along possibly distorted Mn columns could blur the contrast in the Mn map, which explains why no distinct Mn columns could be resolved in the EDS mapping. Similar Mn distribution was shown in the EELS mapping of Mn $L_{3,2}$ core loss in Supplemental Figure S2, where Mn shows strong signals in interstitial positions but no columns could be resolved. In addition, it is also clear that Mn diffuses into the bulk, and 1 nm away from the GB core the Mn signal is still clearly resolved even though the concentration is much lower. In this bulk region, the Mn signal is coincident with the Ti lattice

rather than the Sr lattice as indicated by dashed circles in Figure 3(a)–(c), therefore Mn substitution on Ti sites instead of Sr sites outside the GB core region is directly visualized from the EDS map.

Inside the GB core region, both the Sr and Ti compositional maps (Figure 3(a) and 3(b)) show clearly decreased concentration as compared with the bulk, therefore suggesting the presence of Sr and Ti deficiency. Further quantification is applied to the EDS spectra image and the relative concentration profiles across the GB are plotted by summing up the EDS signals vertically (shown in Figure 3(e)). The Cliff–Lorimer factors based on the reference data from a 200 kV microscope [23] are used to calculate the relative atomic percentage, and together with a possible systematic source of error from electron channeling are the two major source of errors, therefore a standard deviation of up to about 10% is expected. However, the trend in the concentration profile clearly shows how composition changes in GB as compared with in the bulk. As shown in Figure 3(e), 1 nm away from the GB 50 at% of Sr and Ti/Mn collectively making up another 50% of the cations (46% Ti and 4% Mn) confirms that Mn^{4+} occupies the Ti sites in bulk serving as neither donor nor acceptor. Inside the GB core, the relative concentration of Mn rises to 15%, Sr falls to 32% and Ti rises to 53%. As shown in Supplemental Figure S3, Ti shows an increased atomic fraction even though the signal counts were decreased inside the GB. The reason for the increased Ti atomic fraction is due to a larger decrease in Sr concentration, therefore this concentration profile quantifies the presence of Sr vacancies inside GB core region, which is also consistent with reduced intensities in GB Sr (Figure 1(b)) and the oxygen K fine structure discussed above. The formation

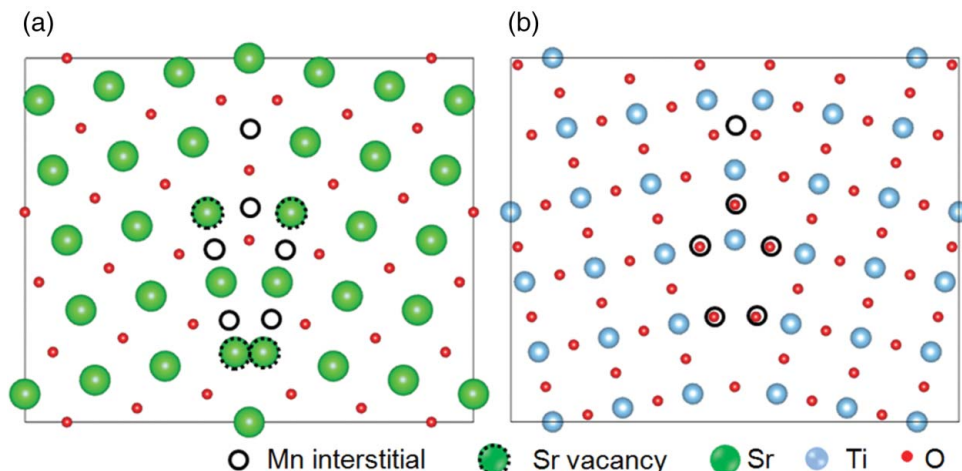


Figure 4. The possibility of Mn doping on (a) the SrO plane and (b) TiO_2 plane of the $\text{SrTiO}_3 \Sigma 13$ grain boundary. (a) On the SrO plane, with the presence of Sr vacancies (dashed circles) Mn ions have enough space to sit on the interstitial sites (solid circles). (b) On the TiO_2 plane, Mn ions need to sit on the oxygen vacancy site.

of Sr vacancies provides enough space for Mn^{2+} ions to reside on both the Sr sites and the nearby interstitial sites, as is supported by the widespread distribution of Mn shown in the EDS map (Figure 3(c)). In addition, the $(\text{Mn}^{2+} + \text{Sr}^{2+})/\text{Ti}^{4+}$ composition ratio is only 89%, which is consistent with the EELS analysis showing the presence of oxygen vacancies. Based on the charge neutral formula of $(\text{Sr,Mn})_{1-x}\text{TiO}_{3-x}$ where x denotes the oxygen vacancy concentration, up to 11% of oxygen vacancies are required to balance the charge. In addition, the Mn substitution on Sr site and Mn interstitials inside the GB core region is further supported from the EELS spectra imaging (Supplemental Figures S1 and S2). As shown from the EELS $\text{L}_{3,2}$ map, Sr map (Figure S2a) shows reduced concentration at several columns, and Mn map (Figure S2c) shows high concentration of Mn at and near Sr columns rather than Ti columns. And in the composite map (Figure S2d) using RGB false colors, the presence of purple color (mix of Sr red color and Mn blue color) at a few columns indicates the substitution of Mn on Sr. Given that the sample under study was sintered in the oxidized atmosphere, it is interesting that Mn ions with a reduced oxidation state tend to segregate inside the GB meanwhile remains 4+ in bulk. The reason why Mn^{2+} preferentially segregates inside the GB is believed to originate from the intrinsic structural difference in local strain and bonding environment between GB and the bulk. As the Z-contrast image in Figure 1(b) is only a two-dimensional projection, the location of interstitial Mn ions has two possible locations along the electron beam direction—either on the SrO plane or on the TiO_2 plane, as indicated by solid circles in Figure 4(a) and 4(b), respectively. Without the presence of Sr vacancies, the space is not large enough for an Mn^{2+} ion ($0.66 \text{ \AA}$) to sit on the SrO plane due to the relatively large ionic radius of Sr^{2+} ($1.18 \text{ \AA}$). With

the formation of Sr vacancies confirmed by both quantitative EDS and EELS, Mn^{2+} has enough space to either sit on either Sr sites as substitution or nearby interstitial sites. Due to the relative big difference in ionic radius between Sr^{2+} and Mn^{2+} , pure substitution or interstitial does not help to relieve the strain or lower the GB energy. As Mn^{2+} on Sr site has been shown to exhibit strong off-center relaxations ($\sim 0.77 \text{ \AA}$) in bulk,[24] it is possible that the anisotropic bonding environment or strain inside the GB leads to a stronger off-center displacement so that the Mn^{2+} appears as both Sr substitution and interstitials, forming a Mn^{2+} rich zone as was seen from the EELS map (Figure S2). A second possibility is for Mn to reside on the TiO_2 plane. In this scenario, the presence of Mn ions has to be facilitated by the formation of oxygen vacancies. As the ionic radius of Mn^{2+} is much smaller than O^{2-} , there is enough space for Mn^{2+} to reside on oxygen vacancy site. However, in this case the Mn ions experience a strong Coulomb repulsion from surrounding cations, thus it is energetically unstable for Mn to sit on the TiO_2 plane. Therefore, the formation of interstitial Mn^{2+} ions is facilitated by the presence of Sr vacancies on the SrO plane.

With the segregation of Mn^{2+} inside the GB, different electrical and magnetic properties are expected inside the GB as compared with in bulk. In this previous study,[12] Mn^{2+} was believed to substitute at Ti^{4+} sites as an acceptor dopant to explain the measured electrostatic potential and space-charge using the electron holography. However, making use of advanced imaging and spectroscopy techniques allowed by the aberration-corrected STEM, we found that Mn^{2+} occupies mostly interstitial sites and Sr sites rather than Ti sites. Mn^{2+} ions do not necessarily act as an acceptor by substituting Ti sites in order to explain the measured electrostatic potential and space-charge, because the presence of Sr

deficiency as observed in this study can also result in the same electrostatic potential. In addition, since Mn ion is in 4+ state in bulk and 2+ state inside the GB, Mn has d3 electronic configuration in bulk and d5 at GB. When both Mn^{4+} and Mn^{2+} are assumed to be in the high-spin state, Mn^{2+} has a higher magnetic moment than Mn^{4+} . The formation of such a Mn^{2+} rich zone inside the grain boundary as discussed above, could potentially dominate the presence of ferromagnetic properties than in the bulk.

In conclusion, Mn is found to have completely different doping behavior inside the GB as compared with the bulk in perovskite SrTiO_3 . Mn^{4+} is found to substitute Ti site as in the bulk, but Mn^{2+} segregates inside the GB and resides on both Sr sites and interstitial sites. This initial finding of Mn^{2+} interstitial doping in SrTiO_3 has never been reported in any 3d transition metal-doped perovskite systems, and is probably only possible in the defect structures of GBs and interfaces inside which the strain and chemical environment greatly deviate from those in the bulk. The possible locations for Mn interstitials are discussed, and the interstitial Mn^{2+} is believed to locate on the SrO plane facilitated by the formation of Sr vacancies. This initial finding of interstitial Mn inside the GBs leads to new understanding how Mn affects the electrical properties of GBs. And as a result of Mn^{2+} segregation, a stronger magnetic moment is therefore expected to appear inside the GB than in bulk, leading to the engineering of GB magnetism in future.

Supplementary online material A more detailed information on experiments is available at <http://dx.doi.org/10.1080/10.1080/21663831.2013.856815>

Acknowledgements This work is supported by the US Department of Energy Grant No. DE-FG02-03ER46057. A part of the work was conducted in the ShaRE user facility at Oak Ridge National Laboratory, and in the Research Hub for Advanced NanoCharacterization, The University of Tokyo, supported by the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan. The research described in this paper is part of the Chemical Imaging Initiative at PNNL under Contract DE-AC05-76RL01830 operated for DOE by Battelle. A portion of the research was performed using EMSL, a national scientific user facility sponsored by the Department of Energy's Office of Biological and Environmental Research and located at PNNL.

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