Study on Ca Segregation toward an Epitaxial Interface between Bismuth Ferrite and Strontium Titanate

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ABSTRACT: Segregation is a crucial phenomenon, which has to be considered in functional material design. Segregation processes in perovskite oxides have been the subject of ongoing scientific interest, since they can lead to a modification of properties and a loss of functionality. Many studies in oxide thin films have focused on segregation toward the surface using a variety of surface-sensitive analysis techniques. In contrast, here we report a Ca segregation toward an in-plane compressively strained heterostructure interface in a Ca- and Mn-codoped bismuth ferrite film. We are using advanced transmission electron microscopy techniques, X-ray photoelectron spectroscopy, and density functional theory (DFT) calculations. Ca segregation is found to trigger atomic and electronic structure changes at the interface. This includes the reduction of the interface strain according to the Ca concentration gradient, interplanar spacing variations, and oxygen vacancies at the interface. The experimental results are supported by DFT calculations, which explore two segregation scenarios, i.e., one without oxygen vacancies and Fe oxidation from 3+ to 4+ and one with vacancies for charge compensation. Comparison with electron energy loss spectroscopy (EELS) measurements confirms the second segregation scenario with vacancy formation. The findings contribute to the understanding of segregation and indicate promising effects of a Ca-rich buffer layer in this heterostructure system.

KEYWORDS: BiFeO₃, oxide heterostructure interface, segregation, atomic-resolution TEM, EELS and EDS, oxygen vacancy, density functional theory (DFT)

1. INTRODUCTION

Perovskite materials have a structure of 2 or more cations and oxygen in the arrangement ABO₃ and provide a huge variety of physical phenomena and functional properties.¹ One of the most promising properties is the coupling between ferroelectricity and the magnetic properties in multiferroic materials, which has attracted significant attention in the past years. Besides the fascinating physics underlying this effect, its potential applications include memory devices with superior speed and storage density,² spin valves, spintronic devices, and sensors.³ BiFeO₃ is among the few single-phase magnetoelectric multiferroics with Néel and Curie temperatures far above room temperature and is therefore a material of strong relevance to practical applications. The successful demonstration of the electrical control of antiferromagnetic domains further increased the interest in BiFeO₃ (BFO).⁵

Doping of BFO with cations such as Ca or Mn offers further possibilities for tuning the magnetic and electric properties. In particular, it has been shown that Ca doping on the A-site leads to an increase in the oxidation state of Fe atoms, which has experimentally been determined to be 4+ at 300 K and a pairing of 3+ and 5+ at 15 K.⁶ Furthermore, Mn doping on the B-site has been shown to restore the weak ferromagnetic behavior received through Ca doping to the antiferromagnetic behavior of pure BiFeO₃.

For such doping-related phenomena, segregation processes of cations are a critical aspect since they can lead to strong agglomeration at surfaces, grain boundaries, or interfaces and a depletion of the bulk. With this, they have a significant influence on the behavior and function.⁷ Therefore, a deeper understanding of the processes underlying the segregation process is required to prevent property degradation.

There are many studies available on segregation toward surfaces, since there is a variety of surface-sensitive but also surface-limited analysis techniques. This includes low-energy ion scattering (LEIS), Auger-electron spectroscopy (AES), X-ray photon spectroscopy (XPS), secondary ion mass spectroscopy (SIMS), atomic force microscopy (AFM), and scanning tunneling microscopy (STM).⁸ Different factors for segrega-

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tion, which have so far been identified,\textsuperscript{9} include non-stoichiometry of the cations,\textsuperscript{10} the charge and the radius of the dopants,\textsuperscript{11–13} the crystallinity of the sample,\textsuperscript{6} lattice strain,\textsuperscript{14} temperature history,\textsuperscript{11,15} external electrical polarization,\textsuperscript{16} and the gas atmosphere, in particular, the oxygen partial pressure.\textsuperscript{11}

Since experimental studies of segregation processes toward nonsurface interfaces require cross-sectional transmission electron microscopy (TEM) analysis, atom probe tomography (APT), or coherent Bragg rod analysis (COBRA),\textsuperscript{17} the segregation toward nonsurface interfaces is not as widely studied for perovskites. In the study of Yoon et al.,\textsuperscript{18} the motivation for the choice of Ta and La as dopants in Ca\textsubscript{1/4}Cu\textsubscript{3/4}Ti\textsubscript{1}O\textsubscript{3} was to minimize the influence of the dopant radius and focus on the space charge effect.\textsuperscript{19} Thereby, it was demonstrated that besides the influence of the electrostatic potential near the interface, the segregation behavior is the same whether the segregation is toward a surface, the interfaces with secondary Cu excess phases, or a grain boundary with or without amorphous materials in between.\textsuperscript{18} Interestingly, for epitaxial Cu\textsubscript{1/4},Ti\textsubscript{3/4}O\textsubscript{3} films on (100) SrTiO\textsubscript{3} (STO) substrates, a Cu enrichment close to the surface could only be observed for very thin films but not for films above 14 nm thickness.\textsuperscript{19}

In studies of heterostructures for solid oxide cells, it was shown that in (LaSr)CoO\textsubscript{3}/LaSrCoO\textsubscript{3} heterostructures, a Sr enrichment in the interfacial region stabilizes it against detrimental Sr segregation receiving a much better surface-enrichment in the interfacial region stabilizes it against observed for very thin Ca\textsubscript{1/4}Cu\textsubscript{3/4}Ti\textsubscript{1}O\textsubscript{3} was to maintain the stoichiometry of the cations,\textsuperscript{10} the charge and the radius of the dopants, 11 for the choice of Ta and La as dopants in Ca\textsubscript{1/4}Cu\textsubscript{3/4}Ti\textsubscript{1}O\textsubscript{3} films on (100) SrTiO\textsubscript{3} (STO) films but not for films above 14 nm thickness.\textsuperscript{19}

Segregation processes in BiFeO\textsubscript{3} have been scarcely studied. For a BiFeO\textsubscript{3} thin film on a (100) LaAlO\textsubscript{3} substrate, chemical interdiffusion of La atoms into the first atomic layers of the film with the suspected reason for stress reduction was found.\textsuperscript{20} For B-site Ti doping in BiFeO\textsubscript{3} nanograins, a segregation toward the grain boundary has been observed.\textsuperscript{21}

Exsolution effects can be seen in a Bi\textsubscript{2}Fe\textsubscript{2}MnO\textsubscript{5} thin film on the STO substrate, which has led to Mn\textsuperscript{4+}-rich antiphase boundary (APB) defects, which nucleate at the substrate where they have Ti at the core and form a stepped structure. Below the APB, the film is highly strained, while above it, it is relaxed and close to the bulk state.\textsuperscript{22} Besides Nd nanorods formed through exsolution,\textsuperscript{20,26} Ti-rich APBs are formed in Nd- and Ti-codoped BFO separating tetragonal distorted regions with strong polar ordering at each side of the defect.\textsuperscript{20,26} Similar structures have been reported in other BFO-based systems.\textsuperscript{26,30}

In this work, we demonstrate the segregation of the Ca dopant in a bismuth ferrite thin film at the interface with a strontium titanate substrate, which was formed via diffusion during and shortly after the thin-film deposition, while still at high deposition temperatures of 700 °C, using various transmission electron microscopy (TEM) techniques as well as density functional theory (DFT) calculations. Atomic-resolution scanning transmission electron microscopy (STEM) with simultaneous recording of high-angle annular dark field (HAADF) images, electron energy loss spectroscopy (EELS), and energy-dispersive X-ray (EDS) spectroscopy reveal that the vast majority of available Ca is agglomerated at the interface. Its concentration at the interface leads to the formation of oxygen vacancies, while the oxidation state of Fe\textsuperscript{3+} of an undoped BiFeO\textsubscript{3} film is maintained. High-resolution transmission electron microscopy (HRTEM) examinations were performed to analyze the local strain states via geometric phase analysis (GPA) at the interface and revealed that, in contrast to a film without Ca, its agglomeration at the interface leads to a reduction of the compressive strain exerted by the substrate. The intensity analysis of large-area HAADF data and GPA analysis showed that the strain reduction is directly linked to the Ca content at the interface. DFT calculations showed that the Ca agglomeration at the interface was energetically more favorable and the interatomic distances from the calculations show good agreement with the measured ones. To our knowledge, this is the first observation of A-site dopant diffusion toward interfaces in BiFeO\textsubscript{3}, and the understanding of this process is crucial to prevent device failure in future applications.

2. EXPERIMENTAL AND CALCULATION DETAILS

2.1. Thin-Film Fabrication. Two bismuth ferrite thin films were fabricated via pulsed laser deposition (PLD): a Ca- and Mn-codoped Bi\textsubscript{0.95}Ca\textsubscript{0.05}Fe\textsubscript{0.95}Mn\textsubscript{0.05}O\textsubscript{3} (BCFMO) film and an only Mn-doped Bi\textsubscript{0.95}Mn\textsubscript{0.05}O\textsubscript{3} (BFMO) film. The thin films were deposited on a single-crystalline (100)-oriented SrTiO\textsubscript{3} substrate (Kejing Materials Technology Co. Ltd., China) by PLD technique using a KrF excimer laser (Lambda Physik COMPEX PRO 205 F; λ = 248 nm) as the ablation source with a pulse repetition rate of 5 Hz. The laser beam energy was fixed at 320 mJ/pulse for the Ca-doped and at 280 mJ/pulse for the non-Ca-doped film. Prior to film deposition, the substrates were ultrasonically cleaned with acetone, alcohol, and pure water and subsequently blown dry with high-purity nitrogen gas. Afterwards, they were immediately loaded into the PLD chamber. The vacuum chamber was evacuated to about 10⁻⁴ Pa. During film deposition, the substrate was kept at a temperature of 700 °C and the oxygen pressure was fixed at 3.0 Pa. The total deposition time for both film samples was 30 min, resulting in a thickness of approximately 50 nm for the Ca-doped film and 20 nm for the non-Ca-doped film. The crystalline structure of the films was investigated using high-resolution X-ray diffraction (HRXRD) with a four-circle single-crystal diffractometer (D8 discover, Bruker, Germany) and a Cu Kα monochromatic radiation source (γ = 1.5406 Å). X-ray photoelectron spectroscopy (XPS) using an ESCALAB 250Xi (Thermo Fisher Scientific) was performed to confirm that there was a constant Ca level in the target during deposition and to investigate the surfaces of the thin films.

2.2. Sample Preparation. Cross-sectional TEM samples were prepared via the sandwich technique using two film pieces glued together side to side to form a Ti holder. Afterward, the holder and samples were ground from both sides to reach a residual thickness of ≈80 μm and then dimpled from one side to a residual thickness of ≈11 μm. For final thinning, conventional Ar⁺ ion beam milling was done using a Gatan precision ion polishing system (PIPS) model 691 at 3 keV acceleration voltage and first 6° for 20 min and subsequent 4° for a short time until the sample showed a thin area.

2.3. Data Acquisition. High-resolution transmission electron microscopy (HRTEM) investigations were performed on a JEOL JEM 2100 F with an image-side Cs corrector operating at 200 keV and using a Gatan Orius SC1000 camera. An indicated magnification of 600 000 resulting in a pixel size of 0.21 Å and an exposure time of 0.7 s was used. The analytical STEM investigations were carried out on a FEI Titan³ operated at 300 keV at a convergence angle of 19.7 mrad. For analytical data collection, a GIF Quantum energy filter (Gatan) and a super-X EDX detector (FEI) were used with simultaneous HAADF image acquisition with 38 mrad inner and 137 mrad outer detection angles on the Gatan 860 HAADF STEM detector. The EELS collection semiangle was 20.5 mrad, the dispersion index was S\textsubscript{g}, and for the spectrometer channel width 0.25 eV was chosen. All EELS spectra were recorded in the dual mode with the energy range of the core loss region from 300 to 812 eV. The
The integrated column intensity is a robust measurement of the atomic column. Columns that lie not entirely in the image are excluded. The position of all other atoms were relaxed until the residual forces were less than $10^{-3}$ eV/A. The segregation energy was calculated as

$$E_{\text{seg}} = \frac{E(n^{+}\text{Ca}@\text{IF}) - E(\text{IF}) - n^{+}E(\text{Ca}@\text{Bulk}) - E(\text{Bulk})}{n}$$

Here, $E(n^{+}\text{Ca}@\text{IF})$, $E(\text{Ca}@\text{Bulk})$, $E(\text{IF})$, and $E(\text{Bulk})$ are the total energies of the supercell containing $n$ Ca atoms at the interface, a $4 \times 4 \times 4$ BFO supercell with one Ca atom, and similar supercells containing no Ca atoms. In the case of $V_o$ charge compensation, oxygen vacancies were introduced in close proximity to the Ca atoms. The structural models were visualized using VESTA software.

3. RESULTS AND DISCUSSION

3.1. Atomic Structure and Chemical Composition at the Interface. The HAADF image in Figure 1a shows that the interface between STO and BFO consisted of the stoichiometric slabs of STO and BFO joined together along [001] to result in a TiO$_2$-BiO stacking at the interface and a vacuum layer (Figure S1). The individual slabs were constructed from fully relaxed BFO (R3c) and STO. Since STO was used as a substrate for BFO, the equilibrium lattice parameter of STO was imposed when constructing the interface model with the exception of the last SrO and TiO$_2$ layers. The thicknesses of the slabs and the vacuum layer were chosen so as to minimize the surface-induced effects, and, in addition, the dipole correction was applied. The G-type antiferromagnetic order was maintained in BFO. The Brillouin zone integration was performed using a $6 \times 6 \times 1$ k-point grid. All atoms in the STO slab were fixed, except for those belonging to the two atomic layers adjacent to BFO. The positions of all other atoms were relaxed until the residual forces were less than $10^{-3}$ eV/A. The segregation energy was calculated as

$$E_{\text{seg}} = \frac{E(n^{+}\text{Ca}@\text{IF}) - E(\text{IF}) - n^{+}E(\text{Ca}@\text{Bulk}) - E(\text{Bulk})}{n}$$

Here, $E(n^{+}\text{Ca}@\text{IF})$, $E(\text{Ca}@\text{Bulk})$, $E(\text{IF})$, and $E(\text{Bulk})$ are the total energies of the supercell containing $n$ Ca atoms at the interface, a $4 \times 4 \times 4$ BFO supercell with one Ca atom, and similar supercells containing no Ca atoms. In the case of $V_o$ charge compensation, oxygen vacancies were introduced in close proximity to the Ca atoms. The structural models were visualized using VESTA software.
without any visible defects. Both the elemental maps for Fe, Ca, and Ti gained from EELS image data (Figure 1b) and the elemental ratio as line profiles from the EDS data for all cationic elements (Figure 1c) reveal that the Ca is concentrated in the film area close to the interface sitting as expected on the A-site (Bi) position in between the B-site positions (Fe). In the first A-site layer of the film, Ca is even the majority atomic species with an approximate ratio of 3:2 with regard to the Bi atoms on these positions. The Ca concentration in the film decreases with increasing distance from the substrate—film interface and is below detectability after an interface distance of approximately 7 nm (Figure 2a,b). Due to the XPS data of the PLD target, we can be sure that the Ca level is constant during the deposition (Figure S2).

To exclude the possibility that deposition kinetic effects are the cause for the Ca agglomeration at the interface, SRIM simulations were conducted and the backscattering ratios and implantation depths of Ca and Bi on STO and BFO targets were compared. However, neither of these two values provided an explanation for the Ca agglomeration.

Therefore, the conclusion is that the Ca gradient toward the interface must have been formed during and shortly after the thin-film deposition, while the high substrate temperature of 700 °C, which corresponds for BiFeO$_3$ to 0.79\*T$_m$ (T$_m$: melting point temperature, 79% of the melting point temperature), significantly facilitated diffusion of the originally homogeneously distributed Ca and enabled its segregation at the interface. To our knowledge, there is no data about Ca diffusion in BiFeO$_3$. The study of Francois-Saint-Cyr et al. investigated the diffusion coefficients for a range of different elements in amorphous SiO$_2$.\cite{Francois-Saint-Cyr2007} Thereby, Ca showed by far the highest diffusion coefficient $D$ in the range of 10$^{-16}$ cm$^2$/s$^2$ at a temperature of $T = 1000$ °C = 0.64\*T$_m$ and is even larger than the one for oxygen diffusion.\cite{Francois-Saint-Cyr2007} In crystalline MgO at $T = 700$ °C = 0.31\*T$_m$ the Ca diffusion coefficient is in the range of 10$^{-15}$ cm$^2$/s$^2$.\cite{Lanckau1993} Lanthanide cobalt oxides (LnCoO$_3$) show tracer diffusion coefficients in the range of 10$^{-14}$ cm$^2$/s$^2$ for $T = 700$ °C = 0.57\*T$_m$.\cite{Hasegawa2011,Kuroyanagi2013} Assuming an average of these values as the Ca diffusion coefficient in BiFeO$_3$, the average diffusion distance during 1 h at 700 °C (30 min deposition time including the time before and during cooling) corresponds to the average diffusion distance of 50 nm (for a value of $D = 10^{-15}$ cm$^2$/s$^2$). Considering that the film thickness is 50 nm, it is reasonable that diffusion and segregation of the Ca from the whole film area toward the interface are reasonable.

In addition, Figure 1 shows a clear indication of intermixing between the film and substrate material, which is typical for this kind of heterostructure.\cite{Shigemoto2016} In the first two layers of the substrate, a clear Ca signal can be detected in the EELS and EDS signals and additionally also a Bi signal in the first layer (EDS). In addition, Sr and Ti can be clearly identified in the first two layers of the thin film. The termination layer of the substrate is identified as TiO$_2$ (Figure 1b), which is the expected one for an untreated STO substrate. Opposite to the Ca, the Mn dopant shows a homogenous distribution within the film.

Note that since no defects at the film interface could be found, a Ca-rich buffer layer at a BFMO/STO interface could manifest as a successful strategy against the unwanted formation of Mn-rich APB at the interface.\cite{Minc2013} However, further studies are necessary, since the effect reported by MacLaren et al.\cite{MacLaren2008} appeared at films with much higher Mn doping ratios of 50% compared to 5% used in this study, which might also critically influence the formation of APBs.

3.2. Influence of Ca on the Interfacial Electronic Structure. Ca is an alkaline earth metal and offers only two electrons in the sp valence complex in contrast to Bi, which has three electrons. Hence, Ca leads to p-type or hole doping. There are two n-type or electron-doping mechanisms, which can occur and counteract the p-type doping through Ca. These mechanisms are either the creation and implementation of oxygen vacancies or the oxidation of a fraction of Fe$^{3+}$ into Fe$^{4+}$.\cite{Wachtman2007,Minc2013,Shigemoto2016} For example, in the CaFeO$_3$ perovskite, where all Bi atoms are replaced with Ca, the Fe atoms are found in the 4+ oxidation state.\cite{Zhang2007,Kuroyanagi2013} Therefore, to understand the interface structure and chemistry better, analyzing the Fe oxidation states is crucial.

Electron energy-loss near-edge structures (ELNES) of Fe-L and O-K edges can be used to determine the oxidation state of the Fe atoms.\cite{Kuroyanagi2013,Li2010} It has been previously shown that the energy onset difference ($\Delta E$) between the O-K and Fe-L$_2$ edges shows a clear correlation with the Fe oxidation state, where an
increase would mean a shift from 3+ to larger oxidation states. However, as can be seen in Figure 3a, there is no change in $\Delta E$ in a Ca-rich interface region compared to a Ca-poor region (3 nm away from the interface). The exact locations where the spectra have been recorded are indicated by the white rectangles in Figure 1b. Furthermore, the measured energy onset difference of $\Delta E = 178.00 \pm 0.25$ eV corresponds within the measurement tolerance to the values in the literature of $178.25 \pm 0.30$ and $178.5 \pm 0.25$ eV. We defined the edge onset as the point where the edge exceeds 15% of the edge maximum, to prevent falsifying influence from prepeaks and noise, as suggested by Tan et al. In Figure 3b, it becomes obvious that while the O-K edge shape changes in the Ca-rich interface region compared to the Ca-poor region, the onset remains unchanged. The change in the edge simply stems from the overlapping of the two different O-K edge shapes in the substrate and the film (Figure S3). Likewise, the onset position of the Fe-L$_2$ edge does not change, as can be seen in Figure 3c. Additionally, the ratio of the Fe-L$_3$ and L$_2$ edges is also an indication of the oxidation state and known to have its maximum for Fe$^{3+}$. The L$_3$/L$_2$ ratio, which does not decrease in the Ca-rich area as becomes obvious in Figure 3c for the normalized Fe-L edges, is a further indication that a shift to higher Fe oxidation states does not take place. Summarizing, we find that Fe atoms in the Ca-rich interface region remain in the 3+ oxidation state, which suggests that oxygen vacancies are present at the interface to counteract the p-type doping of Ca.

3.3. Influence of Ca Segregation on the Strain State of the Film. To see if the Ca agglomeration on the interface has an influence on the strain state of the thin film, HRTEM investigations together with GPA were carried out. Figure 4a demonstrates that, in the Ca-doped thin film, identifying the exact atomic layer where the film starts in the HRTEM image is not a trivial matter. Ca agglomeration at the interface leads to very similar image contrast because of more similar Z per column compared to those of the Sr columns in STO. This leads to a similar contrast between the substrate and the first few layers of the film. To overcome this issue, image simulations were conducted via JEMS. For that, a supercell modeling the interface based on an STO unit cell ($Pm\bar{3}m$ symmetry) was created by 15 times multiplication in the $[001]$ direction. Figure S4a shows the resulting crystallographic atomic model, whereby the Sr and Ti cations were replaced completely or partly on the corresponding positions by Ca, Bi, and Fe to model the heterostructure interface according to the cation concentration displayed in Figure S4b. The simulated HRTEM image for a sample thickness of 10.54

![Figure 3. EELS analysis of the Fe oxidation state at the Ca-rich interface. (a) Energy onset difference ($\Delta E$) between O-K and Fe-L$_3$ edges for the Ca-rich region directly at the interface (red) and for the Ca-poor region at a distance of approximately 3 nm from the interface (black). The position where the spectrum stems from is indicated in Figure 1b by the dashed white rectangles. Compared to the Ca-poor region, the Ca-rich interface shows no change in $\Delta E$. (b) EELS region of the O-K edges enlarged showing that there is no relative shift in the edge onsets. (c) Energy region of the Fe-L$_3$ and L$_2$ edges enlarged showing again no relative shift in the edge onset. The Fe-L edge intensities are normalized by integrating the background-subtracted intensity from 708 to 761 eV showing that the L$_3$/L$_2$ peak ratio does not change as well.

![Figure 4. GPA strain analysis from HRTEM images for the films with and without Ca agglomeration at the interface. (a) HRTEM image, (b) in-plane ($\varepsilon_{xx}$) and (c) out-of-plane ($\varepsilon_{yy}$) strain maps, and (d) line profiles of the strains averaged over the width of the strain maps in the $[001]$ direction of the film with Ca agglomeration at the interface. The green square indicates the region where the out-of-plane strain is reduced compared to the rest of the film. (e) HRTEM image, (f) in-plane ($\varepsilon_{xx}$) and (g) out-of-plane ($\varepsilon_{yy}$) strain maps, and (h) averaged line profiles of the strains for the film without Ca doping.](https://dx.doi.org/10.1021/acsami.9b20505)
Figure 5. Correlation of the Ca content and out-of-plane ($\epsilon_{yy}$) lattice strain. (a) HAADF image of the heterostructure interface, where the primary scanning direction was vertical. The white rectangle indicates the area used for the strain and intensity analysis. The magenta curve indicates the interface (not a straight line due to the small image drift in the right half of the image). (b) Intensity map by integrating over the atomic positions of the HAADF image in (a). (c) Out-of-plane strain ($\epsilon_{yy}$, black curve) received via GPA from (a), which is possible to receive reliably, since the primary scanning direction is oriented parallel, compared with the intensity of the A-site positions (red squares) in (b). Both were averaged horizontally within the white rectangle in (a) and (b). The green overlay indicates the area where the intensity analysis revealed the presence of Ca and the increase of the out-of-plane strain is simultaneously delayed.

nm in Figure S4c displays that the contrast in the first 2–3 A-site rows of the film (with 60, 40, and 20 atom % Ca compared to Bi) is almost identical to the contrast in STO. It is important to note that for these imaging conditions, the bright spots in the cells containing only Bi and Fe on the cation positions (unit cells 10 and 11) indicate the Fe positions and not the Bi ones. The simulated image accurately corresponds to the real HRTEM image in Figure S4d.

The image simulations allow one to determine the location of the interface in the film with the Ca agglomeration in Figure 4a. GPA analysis of the HRTEM image shows no significant in-plane lattice strain $\epsilon_{xx}$ which is the supposed situation for an epitaxial interface, as depicted in Figure 4b,d by the strain distribution and integrated profile. The out-of-plane lattice strain $\epsilon_{yy}$ of the film (cf. Figure 4c,d) is on average around 3%. This elongation along the [001] direction is expected, since the lattice of BFO is simplified to a pseudocubic system, with a lattice constant of 3.965 Å approximately 1.5% larger than the lattice parameter of STO. The novel aspect is that the increase of the out-of-plane strain directly after the heterostructure interface in the first 2 nm of the film is delayed. In Figure 4c,d, the out-of-plane strain value of the film is reached notably later than for the non-Ca-doped film in Figure 4e–h, whose strain increase sets in immediately at the interface. The fact that the area with the delayed out-of-plane strain has a very similar HRTEM image contrast compared to the substrate indicates that it corresponds to the area of Ca agglomeration. This leads to the conclusion that Ca agglomeration at the interface results in a reduction of the out-of-plane strain, which is a probable driving force behind the segregation process of Ca.

Compared to HRTEM, HAADF images have the advantage that the column intensity is directly proportional to $Z^2$ and therefore allows direct conclusions regarding the Ca content at the interface, in comparison to the indirect approach from HRTEM analysis where more detailed knowledge about the chemical composition and simulations is necessary. The atomic-resolution HAADF image of the interface area with Ca agglomeration in Figure 5a has, due to shorter recording times compared to spectral images, less severe distortions stemming from drift while covering simultaneously a larger area. The color-coded intensity map shown in Figure 5b is calculated by integrating the intensities for each atomic position. Knowing from the EDS data that the first film layer contains 60 atom % Ca compared to 40 atom % Bi on the A-site positions, resulting in an average Z number (assuming that the columns have everywhere the same thickness and same number of atoms in the projection direction) of $Z_{\text{m}} \approx 54.7$ (larger than the Z value of 38 for Sr), it can be clearly identified where the film starts.

While in HRTEM images, phase shifts caused by thickness or Z variations might introduce errors into the GPA analysis, the nature of the scanning procedure itself introduces errors into STEM images. However, distortions in the slow-scan direction caused by sample drift and the so-called “fly-back” error are significantly larger than in the fast scanning direction. Without using more elaborate techniques to correct scanning artifacts, like, for example, the method developed by Sang and LeBeau, 61 by aligning the fast scanning direction parallel to the principal axis of the strain, a reliable strain value in the fast scanning direction is received. 62–63 Therefore, the fast scanning direction in Figure 5 was oriented perpendicular to the interface, allowing the analysis of the out-of-plane strain $\epsilon_{yy}$ and linking it to the Ca concentration in the interface area. Figure 5c shows the out-of-plane strain received via GPA analysis (black curve) and the intensity values (red squares), both from the area marked by the white rectangle in Figure 5a,b, which shows the least drift in the image, and averaged along the direction parallel to the interface.

In Figure 5c, the averaged intensity increases in the first six A-site rows ($\approx 2.4$ nm) of the film after the interface, indicating the decreasing Ca content. Starting from the seventh A-site layer, the intensities reach a plateau value and remain there with little changes, indicating that the chemical composition stays largely unchanged. Simultaneously, the out-of-plane strain starts increasing after the interface from the substrate level and reaches its plateau value of $\approx 3.5\%$ in the film, exactly when in the intensity analysis no Ca can be detected anymore. This indicates a direct correlation between the lattice strain and the Ca content. The significantly reduced strain by
integrating Ca in the film structure at the interface is one possible driving force behind the observed Ca segregation. Additionally, it can be seen in Figure 5c that, while the intensity in the substrate side is very uniform, the last A-site layer of the substrate shows a reduced intensity, indicating the interdiffusion of Ca in the top substrate layer, as already observed in Figure 1. The strain data in Figure 4 and especially the direct correlation between Ca content and the strain value in Figure 5c indicate that the strain reduction and thereby minimization of elastic energy are the driving forces for the segregation to the interface. The ionic radii for Ca$^{2+}$ compared to Bi$^{3+}$, which it replaces on the A-sites, are 1.18 Å compared to 1.24 Å (both for coordination number 9). The $\sim$4.8% smaller cation radius for Ca instead of Bi leads to a smaller lattice parameter and subsequent reduction of strain, if it segregates to the STO/BFO interface. The observed segregation process in this study is related to segregation processes toward the surface for larger dopant radii, e.g., described by Lee et al. Therefore, for a deeper understanding, DFT calculations have to be done.

### 3.4. Density Functional Theory (DFT) Calculations

DFT modeling was used to investigate the energetics of Ca segregation to the STO/BFO interface by means of calculating the segregation energies, i.e., the energy change upon relocating Ca from bulk BFO to the interface. When this energy is negative, it indicates the propensity toward Ca segregation. Two segregation scenarios were explored: (1) a Bi atom in the BiFeO$_3$ is replaced with a Ca atom; and (2) a complex of two Bi atoms at the interface is replaced with two Ca atoms and one oxygen vacancy. The first case corresponds to Fe oxidation from 3+ to 4+, while the second case corresponds to charge compensation by the vacancy mechanism. The resulting segregation energies are presented in Figure 6. In the case of the Fe-oxidation mechanism, one observes a slightly negative segregation energy for the 1/2 monolayer (ML) of Ca coverage at the interface, which becomes more prominent for 1 ML and even more so for 2 ML, reaching the value of about $\sim$0.2 eV per Ca atom (crystallographic models are shown in Figure S1). To verify whether the p-doping introduced by Ca was indeed compensated by Fe oxidation, the electronic density of states (DOS) and the volumes of the FeO$_6$ octahedra were analyzed. Ca doping leads to the emergence of the acceptor gap state localized on the FeO$_6$ octahedra next to Ca (Figure S5b). Also, the volumes of these octahedra decreased as compared to the volumes of FeO$_6$ units away from Ca. These two observations confirm the shift of the oxidation state of Fe$^{3+}$ to Fe$^{4+}$, in agreement with the analysis of Gebhardt and Rappe. When considering the second segregation scenario, i.e., involving the oxygen vacancies, the segregation energy was found to be even lower ($\sim$0.3 eV per Ca atom). In this case, no acceptor state occurs (Figure S5c). Though both considered scenarios are found to favor Ca segregation, only the one that assumes formation of the oxygen vacancies is supported by the EELS assessment presented before and is also consistent with the previous reports on the effect of Ca doping in BiFeO$_3$. These findings give strong evidence of charge compensation by O vacancies and, most importantly, confirm the tendency for Ca segregation to the STO/BFO interface.

The analytical STEM data from Figure 1 suggest that the Ca/Bi ratio is approximately 6:4 in the first film layer. The energetically most favorable configurations in the DFT calculations appear to have higher Ca/Bi ratios. This is not a contradiction, since the Ca atoms can cluster in the investigated TEM sample, which was 25 nm thick ($t/\lambda = 0.22$) and corresponds to 60 pseudocubic unit cells. It also needs to be kept in mind that channeling effects influence EELS and EDX results in atomic resolution and, in both techniques, cause signals from neighboring columns.

Figure 6b compares experimental and theoretical results of the out-of-plane cation distances received either from the HAADF image in Figure 5a or from the relaxed unit cells of the DFT simulations. The distances of the DFT calculations start in the last substrate layer because the parameters of the other cells in the substrate are fixed. According to the results from Figure 5c, the first A-site distances in the film are smaller compared to the plateau level reached deeper into the film. The distances received from the DFT simulations show that for 1 ML of Ca in the first layer of the film, the interplanar distances are very similar to the ones from the HAADF data,
showing the absolute minimum of the distances between the first two Bi layers. For 2 ML of Ca in the first and second layers of the film, the minimum is on the same position as for 1 ML but also, compared to the experimental data, much more pronounced, since it concentrates more Ca at the interface than observed in the sample. The spacings received from the DFT simulations from the third film layer onward do not approach the experimental ones further from the interface, mostly, because thermal lattice expansion was not included in the calculations, the finite model size, and also due to limitations of the employed exchange–correlation functional.

In the literature, segregation phenomena have been studied in metals and compounds including oxides.\textsuperscript{11,67–70} There are two primary mechanisms identified that drive segregation: minimizing the Coulomb energy in nonmetals and the strain relief.\textsuperscript{11,67,68} In the case of Ca segregation to the STO/BFMO interface, it seems to be defined in part by the strain relief, as judged from the comparison of the ionic radii of Bi\textsuperscript{3+} and Ca\textsuperscript{2+}, but also by the chemical interactions of the Ca-rich layer with the interface. No significant amount of Ca found on the upper surface of the BFO film requires further investigation, as surface segregation is often observed in perovskite materials.\textsuperscript{11} One of the possible explanations could be that surface Ca has evaporated while the film is at high temperatures, as it is relatively volatile.

4. CONCLUSIONS
In summary, we have fabricated a BFO thin film with a minor initial Ca doping in the target of Bi\textsubscript{0.98}Ca\textsubscript{0.02}Fe\textsubscript{0.95}Mn\textsubscript{0.05}O\textsubscript{3}. The advanced STEM investigations of the film revealed that the Ca had diffused completely to the area of the compressive strain interface. An estimation of the value for the diffusion coefficient demonstrated that diffusion in this scale is reasonable. EELS investigations showed that in the Ca-rich areas no shift in oxidation state took place, indicating the formation of oxygen vacancies at the interface. HRTEM strain analysis of the interface revealed that compared to the Ca free film, the increase of the out-of-plane lattice strain at the interface is delayed due to the Ca at the interface. Analytical HAADF information of the interface region together with strain analysis proves the direct causality of Ca and strain reduction at the interface. Finally, in accordance with the measurement results, DFT calculations confirmed that it is energetically more favorable when Ca is agglomerated at the interface and the received lattice spacings from the calculations fit to the measured ones.

This study is of great importance to accordingly understand the segregation behavior of dopants at oxide heterostructure interfaces and its effects on the atomic and electronic structure. Especially in light of functional devices using these materials, segregation behavior must be considered and addressed with prevention strategies if necessary. Alternatively, the process could be used purposefully to engineer electric and magnetic properties of the two-dimensional system realized at the BFO/STO interface. A Ca-rich buffer layer at a BFMO/STO interface may be a successful prevention strategy against the unwanted formation of antiphase boundaries at the interface, since they could not be observed here.

■ ASSOCIATED CONTENT

* Supporting Information*

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.9b20505.

Calculation of the average Z number for the first film layer, three exemplary examples for the supercells used in the DFT calculations, XPS results showing that Ca distribution in the target was uniform during deposition, superposition of the O-K edge from the substrate and film at the interface, image simulations to confirm the observed HRTEM contrast in the interface region, atom- and position-resolved electronic density of states (DOS) of an undoped STO/BFO interface and 2 ML Ca-doped interfaces compensated either by charge shift from Fe\textsuperscript{3+} to Fe\textsuperscript{4+} or by oxygen vacancies, HAADF overview images of the film–substrate interface for the BCFMO and BFMO films, XRD data and XPS spectra from both films and a low-magnification bright field (BF) TEM image (PDF).

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**Author Contributions**

Z.Z. conceived and supervised the project. U.H. prepared the Ca-doped TEM samples, performed the TEM and HRTEM investigations and data analysis, and wrote the main part of the manuscript with input from all other authors. G.H. and G.K. performed the analytical STEM measurements and supported the interpretation. W.P., J.C., and Y.H. fabricated the thin films and did the XPS and XRD investigations. D.K. wrote the program for the intensity analysis and supported the usage of it. M.N.P. and L.R. did the DFT calculations and the
interpretation of the results for the observed film structure. A.G. contributed to the data evaluation, interpretation, and discussion of the results. Z.Z. contributed to the writing of the manuscript. All authors read through the manuscript and contributed to the discussion of the results.

Notes
The authors declare no competing financial interest.

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