Room temperature deposition of freestanding BaTiO$_3$ films: temperature-induced irreversible structural and chemical relaxation

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Received: 25 March 2022
Accepted: 19 June 2022
Published online: 12 July 2022
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ABSTRACT

The room temperature aerosol deposition method is especially promising for the rapid deposition of ceramic thick films, making it interesting for functional components in energy, mobility, and telecommunications applications. Despite this, a number of challenges remain, such as an enhanced electrical conductivity and internal residual stresses in as-deposited films. In this work, a novel technique that integrates a sacrificial water-soluble buffer layer was used to fabricate freestanding ceramic thick films, which allows for direct observation of the film without influence of the substrate or prior thermal treatment. Here, the temperature-dependent chemical and structural relaxation phenomena in freestanding BaTiO$_3$ films were directly investigated by characterizing the thermal expansion properties and temperature-dependent crystal structure as a function of oxygen partial pressure, where a clear nonlinear, hysteretic contraction was observed during heating, which is understood to be influenced by lattice defects. As such, aliovalent doping and atmosphere-dependent annealing experiments were used to demonstrate the influence of local chemical redistribution and oxygen vacancies on the thermal expansion, leading to insight into the origin of the high room temperature conductivity of as-deposited films as well as greater insight into the influence of the induced chemical, structural, and microstructural changes in room temperature deposited functional ceramic thick films.
Introduction

The aerosol deposition method (AD) is a room temperature deposition process based on accelerating micron-sized particles through a specifically designed nozzle toward a substrate, resulting in particle fracture and subsequent impact consolidation into a nanograined coating [1]. During the deposition process, the kinetic energy of the particles is initially based on the pressure difference between the aerosol generator and the deposition vacuum chamber as well as the nozzle geometry, particle size, and particle morphology. The resulting thick films are nanograined with densities in excess of 97% [2–7]. In addition to being a room temperature process, it also requires no process additives, such as binders or plasticizers, common with traditional high-temperature ceramic processing methods. As such, AD allows for the integration of ceramics, metals, and glass coatings on various substrates, including low cost and low melting temperature metals, [8] in addition to multilayered ceramic and metallic composite structures [9]. For electrical applications, [10, 11] ceramic films can be directly deposited on a metallic or metallized substrate, thus providing an integrated electrode [4, 8, 12]. For these reasons, the AD method is gaining significant interest for the industrial applications, such as in semiconductors, [13] solid-state lithium ion battery [14], dielectric energy storage capacitors [5], and solid-oxide fuel cells [15].

Despite these advantages, however, there are a number of technical challenges that remain unresolved. In particular, previous investigations have demonstrated that the impact consolidation process induces large internal residual stresses of up to approximately 2 GPa dependent on various factors, such as the carrier gas, as reported by Schubert et al., [16] that can significantly influence the functional properties [17]. Similarly, other investigations using focused ion beam digital image correlation as well as micro-synchrotron X-Ray diffraction have also demonstrated internal stresses on the order of 500–800 MPa [8, 18]. In fact, these large stresses can lead to the delamination of films, in particular during thermal treatment, which is a significant issue for successful integration into application [19]. Although the origins of these internal stresses remain under debate, they are understood to be primarily due to particle impact during deposition resulting in the transformation of kinetic energy into plastic deformation and fracture of the particles [20]. In addition, numerous studies have shown that as-deposited ceramic films also display significant electrical conductivity, which leads to lossy polarization–electric field hysteresis behavior and increased dielectric loss.
[8, 21, 22]. Interestingly, however, some investigations have shown that under certain deposition conditions a slim polarization–electric field response without the apparent influence of significant electric conductivity can be observed in as-processed films, although it is important to note that various factors can play an important role, such as measurement frequency as well as maximum applied electric field. Here, for example, Imanaka and Akedo observed a slim P-E loop and relatively low dielectric loss in as-processed BaTiO₃ ceramics films deposited with O₂ as the carrier gas [9]. Interestingly, a response similar to linear dielectrics with comparatively low maximum polarization is observed before thermal treatment [23–25]. The origins of this response, however, remain unclear.

Thermal treatment of as-deposited films has been shown to enhance the functional properties of AD films in part through the reduction of internal residual stresses and electrical conductivity, [26–28] which increases the dielectric permittivity and polarizability [8, 10] in addition to reducing the dielectric loss and providing better aging behavior [29]. Although grain growth has also been suggested as a possible mechanism to enhance the functional response, studies have typically required significantly higher annealing temperatures on the order to 1000 °C to achieve increased grain size [30]. Here, there is extensive work by Exner et al. [26] showing the influence of thermal treatment on the microstructure as well as the electronic and ionic conductivity of AD films. In contrast, thermal post-treatment at significantly lower temperatures has been found to dramatically improve functional properties of ferroelectric films. For example, previous work has shown that annealing BaTiO₃ and Pb(Mg₁/₃Nb₂/₃)O₃–PbTiO₃ films deposited on metallic and glass substrates at 300–500 °C in air is sufficient to significantly decrease internal stress and electrical conductivity [18, 31]. Here, however, the influence of annealing atmosphere and its interplay with thermal effects has not been comprehensively studied.

Although there is an apparent improvement in electrical properties and a reduction in internal stress of ceramic films after annealing, the origins of this behavior remain unclear. Importantly, the interactions between the film and the substrate must be also considered. The thermal treatment of ceramic AD films is typically limited by the temperature stability of the substrate as well as the coefficient of thermal expansion (CTE) mismatch between the ceramic film and the substrate, which can result in delamination due to additional internal stress build up that can fully detach the film [19, 32–34]. Therefore, the film-substrate interactions are understood to be an important factor to improve the functional properties of ceramics films, as shown by Han et al. on Pb(Zr,Ti)O₃ films [35]. Despite this, the presence of a substrate prevents direct observation of the temperature-induced changes of AD film that are important to understand the nature of the change in residual stress and electrical properties, necessitating a freestanding film in the as-deposited state. Previous methods have achieved freestanding AD films through thermal treatment at elevated temperature utilizing the CTE mismatch to induce film delamination [19, 32–34]. These methods, however, expose the film to elevated temperatures that alter the as-processed state, in terms of the crystal and defect structure as well as the internal stress state.

In this work, we demonstrate a simple technique to create freestanding BaTiO₃ thick films without requiring heat-treatment. By depositing a ceramic film on a water-soluble sacrificial buffering layer of sodium chloride (NaCl), freestanding ceramic films can be produced in various geometries and thicknesses without the need for thermal treatment. NaCl is established in thick and thin film technology as a suitable sacrificial material, [36] and it has been reported as a substrate for pulsed-laser-deposition albeit with the limitation of heat treatment, [37] self-supporting Au thin films, [38] a nanogap former, [39] and as a high-temperature sacrificial substrate [40]. In the field of aerosol deposition, NaCl has been used to reveal the film substrate interface [41] and as a sacrificial material for nanostructuring polymer surfaces [42]. Using this method, this investigation provides for the first time a direct observation of the thermal expansion and temperature-dependent crystal structure of an AD film in the as-processed state without the influence of an attached substrate, where possible origins of the thermal processes responsible for the observed electrical and mechanical film response are discussed. Here, a sharp drop in the thermal expansion related to a significant macroscopic contraction in the freestanding film is observed, corresponding to a related change in the crystal structure determined using ex situ and in situ temperature-dependent X-ray diffraction (XRD). Both Raman spectroscopy and transmission electron microscopy (TEM) are
used to help elucidate the role of various possible mechanisms, providing information on the crystallinity and the crystallographic phase transition of the freestanding AD film. In addition, as defects in the parent composition have been found to play a central role, both donor (\(\text{Nb}^{5+}\)) and acceptor (\(\text{Fe}^{3+}\))-doped \(\text{BaTiO}_3\) [43–50] are also deposited and contrasted to stoichiometric \(\text{BaTiO}_3\), revealing oxygen vacancy concentration-dependent variations in the thermal expansion response. In particular, the influence of oxygen partial pressure of the carrier gas during deposition and during annealing was specifically considered to help distinguish between internal defect redistribution and oxygen reincorporation.

**Experimental procedure**

\(\text{BaTiO}_3\) ceramic powders were synthesized using the conventional solid-state reaction method. In addition to undoped \(\text{BaTiO}_3\), 2 mol% \(\text{Nb}\)-doped \(\text{BaTiO}_3\) and 2 mol% \(\text{Fe}\)-doped \(\text{BaTiO}_3\) were also prepared. Raw powders of \(\text{TiO}_2\) (Alfa Aesar, 99.6% purity) and \(\text{BaCO}_3\) (Alfa Aesar, 99.8% purity) with dopants \(\text{Nb}_2\text{O}_5\) (Alfa Aesar, 99.9% purity) or \(\text{Fe}_2\text{O}_3\) (Alfa Aesar, 99.9% purity) were stoichiometrically weighed and mixed, homogenized for 24 h, and subsequently calcined at 1100 °C for 6 h. The calcined powders were milled for 15 h using 5 mm yttria-stabilized zirconia (YSZ) milling balls in a rolling mill at 70 rpm to obtain a particle size \(d_{50}\) of 1.2 \(\mu\)m (\(d_{10} = 0.4 \mu\)m, \(d_{90} = 2.8 \mu\)m) appropriate for our AD setup.

All compositions (\(\text{BaTiO}_3\), \(\text{BaTiO}_3\)-2\(\text{Nb}\), and \(\text{BaTiO}_3\)-2\(\text{Fe}\)) were deposited on mirror polished 10 × 10 mm SUS 304 stainless steel substrates using a deposition scan rate of 5 mm/s and a carrier gas (\(\text{N}_2\), 99.999% purity) flow rate of 4 L/min with a nozzle-to-substrate distance of 7 mm. In this work, a slot nozzle with an orifice size of 1 mm × 10 mm was used for the processing of all AD films using the same parameters mentioned above. Only the number of scans was varied to achieve a targeted film thickness. Films for TEM and scanning electron microscopy (SEM) were fabricated at a thickness of 15 \(\mu\)m using 50 scans, whereas freestanding films for Raman spectroscopy, XRD, and CTE measurements were fabricated with a 45 \(\mu\)m thickness using 250 scans on a pre-treated substrate with a sacrificial NaCl layer described below.

In order to obtain freestanding films, a water-soluble sacrificial layer with an approximate thickness of 2 \(\mu\)m was formed via AD on the SUS 304 stainless steel substrate using commercially available NaCl. This thickness was found to be sufficient to provide a continuous base layer for further deposition of the intended freestanding film material without significantly affecting the particle–substrate interaction during deposition, compared to deposition without a sacrificial layer. Details describing the powder preparation of NaCl can be found in our previous work [41]. Prior to the deposition of \(\text{BaTiO}_3\), the desired film area was masked with adhesive tape to prevent overlap onto the stainless steel substrate. \(\text{BaTiO}_3\) films of ~ 45 \(\mu\)m thickness were deposited on the sacrificial layer and subsequently removed by means of submersion in distilled water in an ultrasonic bath (Fig. 1). The films were left to soak for 30 min, then treated with ultrasound for 1 min and subsequently filtered from the solution. The obtained freestanding films were dried at room temperature and stored in a desiccator.

Structural characterization was performed with ex-situ XRD (Bruker D8 Eco, Bruker AXS GmbH, Germany) and a temperature-dependent in-situ X-ray powder diffractometer (X’Pert PRO with X’Celerator detector, PANalytical B.V., Netherlands) equipped with an HTK-1200 N heating stage (Anton Paar GmbH, Germany). Both setups are equipped with a Cu source and position sensitive line detector. A 2 K/min heating rate was used for the in situ temperature-dependent measurements. The sample was kept at each targeted temperature step for 5 min before starting diffraction data collection. Diffraction data were collected between 20 to 80° 2\(\theta\) with a step size of 0.02° and for 0.2 s at each step.

In order to quantify the influence of annealing temperature and atmosphere on the thermal expansion properties, freestanding films with different defect concentrations were annealed in nitrogen, air, and vacuum atmospheres up to 500 °C. Freestanding \(\text{BaTiO}_3\) films with a sample size of approximately 0.6 × 0.5 mm² were then placed in a temperature and atmosphere-controlled heating stage (HFS 600 E, Linkam Scientific Instruments Ltd., UK). It is important to note that the achievable purity of the measurement atmosphere in the hot-stage setup is crucial considering the sample size. A continuous inflow of \(\text{N}_2\) ensures an overpressure of 20 mbar above the ambient atmosphere to account for leakage and
temperature related gas volume changes. Imaging was provided via a confocal microscope (Keyence VK-X160K, Keyence Deutschland GmbH, Germany) using a 20× magnification objective, where, importantly, the sample size was selected to fit within the objective field of view to avoid the need to stitch individual images together, reducing software-induced error. The thermal expansion was determined by evaluating six distinctive natural markers, resulting in 15 point-to-point connections distributed over the sample surface (see supplement A1). The influence of film bending was taken into account by measuring a set of undoped BaTiO3 films both on the top surface of the film and the former film-substrate interface. No significant deviation could be observed, indicating that the bending of 45 µm films is negligible within the imaged frame at 20× magnification. Therefore, subsequent films were measured with their AD-top surface pointing to the objective with the smoother film–substrate interface providing a better thermal connection to the heating stage below. Temperature profiles for all measurements, including high-temperature XRD (HT-XRD) and Raman spectroscopy, were performed from room temperature to 500 °C with dwelling time of 1 h. The heating and cooling rate were 5 K/min.

In advance of TEM preparation, BaTiO3 was deposited on a glass substrate using identical parameters to those used to generate freestanding BaTiO3. The glass substrate served as a carrier providing mechanical film stability during milling. BaTiO3 slices with a remaining film thickness of approximately 50 nm were prepared via ion milling and subsequently analyzed using transmission electron microscopy (TEM, JEM-ARM200F, JEOL Ltd., Japan). The temperature profile for annealing the slices was identical to that used for CTE measurements.

A wavelength dispersive Raman spectrometer was used based on a setup described by Veber et al. [51] which was comprised of a 488 nm laser source, a spectrometer (iHR 320, HORIBA Jobin Yvon GmbH, Bensheim, Germany), an 1800 g/mm grating, and a 2048 × 70 pixel CCD camera (Sincerity UV–VIS, HORIBA Jobin Yvon GmbH, Germany). Temperature control was provided in situ by a differential scanning calorimeter (DSC 8500, PerkinElmer, Waltham, MA, USA) with the sample located in a gold crucible. Raman spectra were collected in 10 K steps from 30–500 °C using a 10× magnification objective for a spatial resolution of approximately 10 µm. The exposure time for each spectrum was 60 s with a total of three exposures per temperature step. The heating rate between steps was 15 K/min with 2 min holding time before measurement. The specimens were fabricated to a thickness of 45 µm, well above the optical penetration depth indicated for Raman measurements in non-absorbing ceramic samples [52].

Results and discussion

Microstructure and crystal structure of freestanding BT films

As previously observed, AD results in a cratered film surface due to the impact of deposited particles, [2, 5] which can be also seen in the freestanding films in this study (Fig. 2a). Notably, upon removal of the water-soluble base layer, it is possible to directly view the bottom surface of the AD film that was formerly at the film/substrate interface (Fig. 2b), revealing that the surface is not smooth, as expected by using a mirror-polished substrate, but has small indents that protrude into the film. This can be attributed to the nature of the deposition process and the presence of the NaCl sacrificial layer before dissolution in water. It shows a replication of the surface structure previously reported on the deposition and subsequent removal of NaCl in our previous work focused on the investigation of the film-substrate interface, where the AD process-induced plastic deformation on the surface of the metal substrate through a shot-peening-like effect that increased the substrate surface roughness [41].

The crystal structure of AD films differs from bulk ceramics due to the nanograined microstructure and internal residual stress, resulting in peak broadening without any evident change in crystallographic phase [19]. This effect is shown in Fig. 3, where bulk tetragonal BaTiO3 shows characteristic peak splitting in the 200pc reflection not observed in the BaTiO3 films. This is a common feature of AD-films, attributable to the crystallite size of the films being in the range of 30 nm [53]. For BaTiO3 nanopowders in the range of 100 nm crystallite size, splitting of 200pc reflections into 002/200, a signature of tetragonal phase, is reported [54]. However, such a feature is not present in our case, further showing that the crystallite size of the as-processed freestanding BaTiO3...
film is below 100 nm \[54\]. In order to determine the effect of the various processing steps on the crystal structure of the films, XRD spectra were taken on a BaTiO\(_3\) film deposited directly on a SUS 304 substrate, a BaTiO\(_3\) film deposited on the NaCl buffering layer on a SUS 304 substrate, the as-processed freestanding BaTiO\(_3\) film after removal from the substrate, and the freestanding BaTiO\(_3\) film after annealing at 500\(^\circ\)C in vacuum (Fig. 3). Interestingly, all as-processed, unannealed BaTiO\(_3\) films displayed the same peak broadening characteristic of nanograin AD films without an apparent 2\(\theta\) peak shift, indicating that the presence of the 2 \(\mu\)m NaCl sacrificial layer as well as the removal of the BaTiO\(_3\) film did not significantly affect the internal stress state. Changes in microstructure, such as grain growth, are not expected in as-processed samples without thermal treatment. This is particularly significant as it demonstrates that the internal stress is not primarily due to the film/substrate interaction, rather the internal stress is locked into the resulting nanograin microstructure produced during deposition.

Following annealing of AD films at 500 \(^\circ\)C, however, a decrease in peak broadening as well as a significant shift in peak positions is observed (Fig. 3). Assuming a pseudocubic structure before heat treatment, peak splitting of the 200\(pc\) reflection would also be an indication of partial restoration of tetragonal phase or significant increase in crystallite size; however, this is not observed, indicating that sharpened reflections and decrease in peak width in annealed state possibly originate from a change in internal residual stress \[12, 18\]. Similar observations have been made for AD films annealed while still attached to the substrate \[28\]. Thus, the origin and macroscopic consequences for thermal expansion of this thermally activated structural relaxation remain unclear as the substrate presence during annealing seems to be not mandatory to alter the internal stress state of the AD film. It is also noteworthy that annealing of the film was performed in vacuum, ruling out structural changes due to oxygen reincorporation, indicating that internal processes, such as defect reorientation, are also important.

Influence of annealing on dielectric and ferroelectric behavior

As previously noted, as-processed AD films show an enhanced electrical conductivity that can be significantly reduced with thermal treatment. In Fig. 4a, the temperature-dependent dielectric behavior was characterized during a heating/cooling cycle in air from the initial as-processed state for a BaTiO\(_3\) film on a SUS304 substrate without a NaCl sacrificial layer, where a significant increase in the dielectric permittivity and a corresponding decrease in the dielectric loss can be observed after heating to 500 \(^\circ\)C. As the dielectric response has both intrinsic and extrinsic components, it is expected that the apparent reduction in internal residual stress leads to an enhancement in the observed relative permittivity as domain walls become less mechanically clamped and more mobile. Typically, this behavior would be expected to be accompanied by an increase in the dielectric loss, as extrinsic contributions, such as domain wall motion, are hysteretic in nature. However, a decrease in the loss tangent is observed here, which is understood to be due to a change in the defect structure and concentration. Analogous to the
dielectric response, large field ferroelectric measurements on a BaTiO₃ film on a SUS304 substrate without a NaCl sacrificial layer (Fig. 4b) also show a decrease in the observed hysteresis after annealing in air. It is important to note that these measurements were performed on the same sample, where a clear slimming of the polarization–electric field behavior and an increase in the maximum polarization are found after annealing. In combination with the temperature-dependent dielectric behavior and the XRD data, this response is consistent with a reduction in the electrical conductivity of the film. As such, to get better insight of the temperature-dependent changes, the macroscopic thermal expansion of AD processed freestanding films was investigated.

Thermal expansion of freestanding BaTiO₃ films

During annealing, temperature-dependent processes are induced that lead to significant changes in the macroscopic dielectric and ferroelectric response of the AD-BaTiO₃ film (Fig. 4) as well as the observed crystal structure (Fig. 3). Importantly, these effects are not observed in bulk BaTiO₃ made from the same starting powder, demonstrating that this is related to the aerosol deposition process. During film deposition, the impact consolidation process results in the fracturing of accelerated particles, which bond together. The mechanical and chemical nature of the bonding, however, remains unclear [41]. Although this dynamic process results in large internal stresses [16, 55] as well as elevated temperatures, [56] it is not expected that the starting deposited material changes composition during AD, e.g., through volatilization of particular elements at elevated local temperatures. For this reason, the observed macroscopic properties are likely related to the defect rich grain boundaries that are created from fracture surfaces during the deposition process. At elevated temperatures, it is expected that both defect reorganization and oxygen reincorporation at the grain boundaries are possible, in addition to the formation of a grain boundary space-charge layer, [57] although the relative contributions remain unclear.

Importantly, however, phenomena related to the creation or filling of vacancies, such as oxygen vacancies, can lead to observable changes in the material volume [58]. As such, the temperature-dependent thermal expansion of a freestanding AD film was characterized in air by confocal microscopy. In Fig. 5a, the thermal expansion of an as-processed freestanding film is shown during the first heating/cooling cycle in air, revealing an initial increase and subsequent sharp drop in thermal expansion starting at approximately 200 °C with a remanent thermal expansion change of approximately −1.1%. Interestingly, the second heating/cooling cycle (Fig. 5b) displayed a thermal expansion behavior similar to the bulk material response (blue line, Fig. 5b), with an observed CTE of approximately $11 \times 10^{-6} \text{K}^{-1}$. These data reveal that the AD-process-induced change in negative thermal expansion of the ceramic film is an irreversible effect and is not related to the interaction with the substrate.

Figure 2 SEM-surface image of a top and b bottom (film–substrate interface) surfaces after detachment of 15 µm BaTiO₃ film.
The densification of the nanosized grain structure of the films does not explain this observed effect, as sintering shrinkage of nanocrystalline BaTiO$_3$ with comparable grain sizes in the range of 30–40 nm was observed at approximately 800 °C, considerably below the 200 °C found here \cite{59}. In addition, thermal expansion effects may coincide with a change in unit cell volume at structural phase boundaries \cite{60}. In the case of polycrystalline BaTiO$_3$, the Curie point ($T_c$) at approximately 120 °C separates the lower temperature ferroelectric tetragonal phase and the high temperature paraelectric cubic phase, where the smaller unit cell of the cubic phase results in a sharp drop in thermal expansion at $T_c$, \cite{60–62} which is observable in the bulk BT data shown in Fig. 5b. The volume change associated with the ferroelectric-paraelectric phase transformation, however, is significantly smaller than that observed here and is also reversible, meaning that it does not explain the irreversible drop in thermal expansion observed in the as-processed BaTiO$_3$ freestanding film. Previous investigations on nanograined BaTiO$_3$ structures show positive CTE values for both tetragonal and cubic phases that can be present simultaneously even below $T_C$ \cite{63}. In addition, chemical modification and composite structures can lead to nonlinear or negative thermal expansion, which have been, for example, observed in layered perovskite structures of the same chemical composition or in chemically modified functional perovskite materials such as PZT \cite{64, 65}. Although negative CTE behavior has been observed in doped perovskite structure PbTiO$_3$ between room temperature and $T_C$ \cite{66–69} as well as composite structures of BaTiO$_3$ and Ag, \cite{70} none of the aforementioned mechanisms (doping or composite structure) apply to the BaTiO$_3$ film in Fig. 5.

There are a number of potential mechanisms responsible for the observed nonlinear irreversible thermal expansion, including: (i) recrystallization of amorphous grain boundary phase, (ii) change in grain orientation (grain rotation), (iii) sintering-like densification, (iv) reincorporation of oxygen at grain boundaries, (v) reorganization of grain boundary defects, and (vi) the space charge effect. Due to the nanograined nature of AD films, they contain a high fraction of grain boundaries per volume, which can be non-crystalline, \cite{56, 71} in addition to highly deformed grains \cite{71}. As such, a volume change \cite{72} due to the recrystallization of an amorphous grain boundary phase or defect mediated grain reorientation is possible, both of which can induce a significant shrinkage. On the other hand, due to the AD process itself, where fractured particle surfaces are randomly recombined and consolidated in a rapid, dynamic process, cationic and anionic vacancies along the grain boundary are expected \cite{73}. Here, a redistribution of defects at the grain boundary or a reincorporation of oxygen from the surrounding atmosphere.
can also result in a significant decrease in the apparent unit cell volume [57, 74]. Such significant chemical strains are well-known in oxides. For example, Swallow et al. demonstrated a high-temperature actuator through the electric field controlled electrochemical oxygen exchange and resulting volume change in Pr$_x$Ce$_{1-x}$O$_{2-δ}$ [75]. These two contributions are expected to be closely interrelated, as reincorporation of oxygen can limit the available defects for internal distribution. In addition, the concentration of defects in the starting material also plays an important role, which can be adjusted through aliovalent doping of the deposited BaTiO$_3$ powder, in addition to variations in oxygen partial pressure during annealing and measurement to control possible oxygen reincorporation. Finally, dopant-induced oxygen vacancies may be present in the grains segregating electrons to the grain boundaries, [74] resulting in increased electrical resistivity [76]. It is also possible that the temperature-induced defect recombination during the first heating cycle is responsible for decreased electrical conductivity in the annealed film. Importantly, however, the temperature region of defect recombination is of particular interest as diffusion of oxygen along grain boundaries is kinetically more favorable than through the lattice [77].

In order to address these mechanisms, local structural investigations were performed and will be presented in the subsequent sections. Specifically, in situ temperature-dependent XRD and Raman spectroscopy were used to characterize the change in the internal stress state and local structure of the freestanding films, in addition to TEM, which was performed to directly observe the grain orientation before and after annealing. Importantly, the oxygen vacancy content of the AD films was adjusted by aliovalent doping the deposited starting material, in addition to controlling the oxygen partial pressure at elevated temperatures.

**In situ temperature-dependent structural investigations**

In order to better understand the structural origins of the observed thermal expansion, in situ temperature-dependent XRD was performed on an undoped BaTiO$_3$ film utilizing the identical heating and cooling profile as in thermal expansion measurements. Due to high-temperature XRD heating stage limitations, the measurement atmosphere was restricted to ambient air. Provided that the origin of the thermal expansion anomaly is due to a change in lattice structure, temperature-dependent XRD data is expected to exhibit a change in peak width and peak positions with potential of quantifying the temperature-dependent changes in lattice parameters.

Figure 6a shows the temperature-dependent evolution of the diffraction patterns for a BaTiO$_3$ film during heating from 23 to 500 °C and subsequent cooling back to 23 °C following a dwell at 500 °C for 1 h. In Fig. 6b, c, the intensities of the 111$_{pc}$ and 200$_{pc}$
reflections are highlighted. By utilizing the selected peak fitting scheme, the variation in 200_play, lattice strain and the peak width (FWHM) was characterized as a function of annealing temperature (Fig. 6d, e, respectively), where a remanent change in both was found. This data indicates that the decrease in 200_play lattice strain and FWHM is significant above 150 °C (Fig. 6d, e), matching the onset temperature of the sharp drop observed in thermal expansion measurements (Fig. 5). In addition, a remanent unit cell volume reduction of 2.3% has been calculated (see supplementary section A2).

Changes in peak width and position are attributable to a change in the crystallite size and strain. Similarly, a variation in lattice spacing is indicated by the temperature-dependent shift of the 200_play reflection, hence suggesting a change in lattice strain. It should be noted here that in the case of AD films attached to substrate, temperature-induced change in lattice spacings (stress-relaxation) of the films could be influenced by the substrate. For example, BaTiO_3 films deposited on SUS 304 substrate, given that the CTE of the substrate (23.1 × 10^{-6}K^{-1}) is significantly larger than that observed in either an annealed freestanding BT film (11.1 × 10^{-6}K^{-1}) or bulk BT (9.8 × 10^{-6}K^{-1}), would lead to an increase in the tensile stress in the film during heating. This mismatch is expected to influence the stress relaxation process. Nevertheless, it is evident that, without a substrate present, the hysteretic behavior in lattice parameters and thermal expansion is an intrinsic feature in freestanding AD films (Fig. 5a) and is not entirely related to mechanical interaction from a CTE mismatch with the substrate material. Although, the data presented here clearly indicates the change in crystal structure parameters with increasing temperature, it is not possible to separate the possible contributions, such as change in internal stress, crystallite size (crystallinity) and/or oxygen incorporation to the structural change.

There is no clear evidence of a tetragonal-to-cubic phase transition during annealing within the resolution limitation of the XRD instrument used in this work, likely due to the presence of nanograin. Importantly, Raman spectroscopy has been successfully utilized to investigate the phase transition in nanograin BaTiO_3 as this technique probes the chemical bonds, which is advantageous for the investigation of the local structure [78]. The presence of a tetragonal phase from Raman spectrum is indicated by the sharp E(LO + TO), B_1 band occurring around 305 cm^{-1} and disappearing with transition to cubic state, though the band around 515 cm^{-1} is simultaneously attributed to the tetragonal and cubic phase [79–82]. The sharpness of the 305 cm^{-1} band is influenced by size effects of the grain structure as elaborated by Hoshina et al. [83], finding an increase in linewidth for decreasing particle size. A decrease in intensity with increasing temperature is also observed [84].

The Raman spectra of as-processed and 500 °C annealed freestanding BaTiO_3 films as well as bulk BaTiO_3 are shown in Fig. 7. It is evident that the Raman bands of the as-processed film do not match
with those of the bulk state, which, considering that the grain size of the freestanding film is below 100 nm, suggests a size effect that can be correlated to the aforementioned studies on nanocrystalline BaTiO$_3$. However, the band around the 305 cm$^{-1}$ of the as-processed film does not correspond to that of the tetragonal phase, nor that of cubic phase BaTiO$_3$ of comparable grain size [85]. Interestingly, the room temperature spectrum of the freestanding film after annealing clearly represents the tetragonal spectrum obtained with nanograin BaTiO$_3$. In addition, the 515 cm$^{-1}$ band is shifted to lower wavenumbers with annealing from 522 cm$^{-1}$ in the as-processed state to 510 cm$^{-1}$ after annealing. Sakashita et al. [86] investigated the influence of internal stress on the Raman spectrum of BaTiO$_3$, demonstrating that a shift of 515 cm$^{-1}$ band to higher wavenumbers is related to increasing internal stress. The reported variation in Raman band was limited up to 60 MPa, however, by a linear extrapolation, an approximate decrease of 150 MPa can be expected in our freestanding film due to annealing. As such, our data indicates a thermally induced relaxation of internal stress in freestanding film even without the presence of substrate.

Due to the nanograin nature of the films and the resolution limits of XRD, the structural phase transition could not be directly observed. As such, in situ temperature-dependent Raman spectra were measured during the annealing process to resolve the temperature-dependent structural phase transition behavior and evolution of the internal stress change. The heating (Fig. 8a) and cooling cycles (Fig. 8b) show significantly different responses, where the observed Raman spectra displayed irreversible temperature-dependent changes. Specifically, the slope of the room temperature spectrum between approximately 200 and 300 cm$^{-1}$ varies significantly during annealing, indicating that the as-processed state might not be solely comprised of the tetragonal phase but also include a significant influence of AD process-induced lattice distortion. As reported by Hayashi et al., the tetragonal-to-cubic transition in BaTiO$_3$ is marked by a loss in the sharp 305 cm$^{-1}$ band and a broadening and splitting of the 515 cm$^{-1}$ band [85]. Therefore, a structural phase transformation between the cubic and tetragonal states can be established during heating between 100 °C and 150 °C, although it is important to note that the presence of compressive internal stresses can shift the phase transition temperature in BaTiO$_3$. Under uniaxial and biaxial compressive stress, $T_C$ would be shifted to higher temperatures, [87, 88] whereas a hydrostatic stress would shift $T_C$ to lower temperatures [89]. Conversely, the formation of a 305 cm$^{-1}$ peak can be observed in Fig. 8b during cooling between 150 °C and 100 °C, indicating a cubic-to-tetragonal phase transition around bulk $T_C$ in freestanding BaTiO$_3$ for both cycles.

The shift of the 515 cm$^{-1}$ peak during the initial heating/cooling cycle, identified by its centroid position in Fig. 9, provides information on the temperature-dependent change in internal residual stress during annealing [86]. In particular, the initial as-processed 515 cm$^{-1}$ peak value is significantly higher than both the bulk BaTiO$_3$ and annealed film values at room temperature, demonstrating a significant internal residual stress. In fact, the stress calibration data provided by Sakshita et al. [86] applies a maximum stress of 60 MPa to BaTiO$_3$ corresponding to a shift to 519 cm$^{-1}$, well exceeded by the as-processed film, i.e., 522 cm$^{-1}$. This is a strong indication that the as-processed film is deformed by the impact loading during the AD-process resulting in a lattice distortion [20, 56, 71, 90]. During thermal treatment, as can be seen in Fig. 9, the heating and cooling curves converge at approximately 150 °C, which is consistent with the observed sharp decrease in thermal strain (Fig. 5). At temperatures above 200 °C, a difference between heating and cooling cycle cannot be established by Raman spectroscopy, although it is also important to note that the temperature-dependent shift of the 515 cm$^{-1}$ peak with increasing temperature is of higher magnitude than reported for non-AD processed barium titanate, [84, 85] suggesting that at a given temperature, AD-processed BT films feature a higher increase in thermal stress compared to bulk. Importantly, during cooling the position of the 515 cm$^{-1}$ peak displays a remanent value, where the annealed, room temperature value is similar to bulk BT. This indicates that heat treatment allows the deposition-induced residual internal stress of the AD film to relax [86] and that the irreversible effect responsible for the thermal expansion macroscopically observed in as-processed films is linked to the internal stress state at the microscale.
Temperature-dependent TEM investigation of BT films

Simulation of particle impact during the aerosol deposition process [91] and related cold spraying processes [92] indicate that AD films feature a disordered and plastically deformed microstructure. Sarobol et al. provide evidence that the fractured particles are plastically deformed by dislocation sliding and feature significant microstrain [71]. Importantly, although room temperature dislocation motion along certain preferred slip planes in perovskite oxides, such as SrTiO₃, [93] have been experimentally observed, analogous dislocation motion in BaTiO₃ was found to be only possible at elevated temperatures around 1150 °C due to significant brittleness [94]. As such, although dislocations in the resulting BaTiO₃ films are expected, it suggested that their influence, both due to the brittleness of BaTiO₃ and the limited slip systems required for plastic deformation in polycrystalline ceramics, is likely less critical than other factors in the

Figure 6 In situ XRD of BaTiO₃-AD film as a function of temperature: a overview with highlighted reflections, b, c intensities of the 111̅pc and 200̅pc reflections at discrete temperatures. Temperature-dependent evolution of the lattice strain d and, peak width e based on the 200̅pc peak position. The dashed lines in d and e are added to guide the eye.

Figure 7 Raman spectra of freestanding BaTiO₃ AD film before and after annealing as well as of the bulk ceramic sample. Peaks of interest regarding the cubic-to-tetragonal phase transition of BaTiO₃ are highlighted. The Raman spectrum of bulk BaTiO₃ collected at 500 °C, i.e., at cubic phase is shown for reference.
temperature range investigated here. However, additional studies are required to determine the potential influence of plastic flow-related densification mechanisms in AD ceramic films.

In addition to dislocation motion, grain rotation and grain boundary sliding can serve as a mechanism for plasticity and were found to occur at room temperature in nanocrystalline materials as demonstrated by Wang et al. [95] during uniaxial mechanical loading of Pt thin films. The possibility of grain reorientation has been theoretically discussed by Ask et al. [72]. In addition to this, recrystallization of amorphous phases at grain boundaries could also serve as a mechanism for change in volume. Akedo et al. [96] for example, observed recrystallization in AD-deposited PZT starting at 500 °C, which is, however, much higher than the temperature required to induce the observed relaxation observed here in as-processed freestanding films. Similar studies on nanocrystalline SrTiO₃ support the theory of recrystallization and grain growth being kinetically unfavorable below 900 °C [97]. In this study, the onset temperature for changes in lattice parameters, i.e., stress relaxation observed with Raman and XRD, is approximately 150 °C, making recrystallization an unlikely contributing factor.

In order to directly investigate these effects, scanning transmission electron microscopy (STEM) with nanodiffraction of an as-processed and 500 °C annealed BaTiO₃ AD film was performed, as shown in Fig. 10. Here, both grain (Spot B) and grain boundaries (Spot A and C) were observed (Fig. 10a), as indicated by uniform white contrast and dark lines, respectively. Importantly, the nanobeam electron diffraction patterns show significant variation depending on the area of investigation, i.e., grain (Spot B) or grain boundary (Spot A and C), where the existence of non-crystalline regions at around grain boundaries was found at Spots A and C. Considering the existence of nanograins and large fraction of grain boundary volume in the AD-processed films, it is expected that the structure and chemistry of grain boundary will play crucial role in the observed macroscopic responses. Critically, the observation of crystallite size before and after ex situ 500 °C annealing (Fig. 10b, c) highlights that there is no evident change in crystallite size within this temperature range, suggesting that grain growth is not an important factor in BaTiO₃ AD films for annealing temperatures up to 500 °C. Although this thermal treatment did not result in an observable change in the crystallite size, previous observations of the process-induced plastic deformations in PZT AD films [56] suggest that overall volume changes may be accomplished by grain reorientation or grain boundary sliding during thermal treatment.

Although, ex situ TEM data (Fig. 10b, c) indicates that annealing up to 500 °C does not significantly influence crystallite size, the distinction of individual grains is difficult due to the disordered nanograins at the given resolution. Moreover, a seemingly amorphous structure identified at a grain boundary might be comprised of smaller crystallites. It also provides no information about the influence of defects on mobility of the hypothesized grain rotation mechanism. Therefore, it remains unclear if room

**Figure 8** Raman spectra of freestanding BaTiO₃-AD film: a first heating cycle to 500 °C, b cooling to room temperature. Inset figure shows the representative curves for 30, 100, 150 and 500 °C for the 305 cm⁻¹ band, illustrating a tetragonal-to-cubic phase transition of bulk BaTiO₃.
temperature-induced plastic deformation, [34] grain rotation, [95] or grain sliding can induce the observed thermal expansion at annealing temperatures below 500 °C. In order to address this, additional in situ high temperature HRTEM investigations are required to quantify the total fraction of the crystalline phase or relaxation in the crystal lattice on an atomic scale as a function of temperature.

Influence of aliovalent doping on the CTE of AD-processed freestanding BT films

As previously noted, the AD process induces residual stresses that can be reduced through thermal treatment, which corresponds to a significant irreversible shrinkage. Importantly, however, our work has clearly demonstrated that the relaxation of internal stress and structural change in AD films are not solely dependent on the film/substrate interaction, i.e., CTE mismatch between the substrate and film, as they also occur in as-processed freestanding films. In oxide-based materials, oxygen vacancies, apart from their intrinsic or dopant-induced occurrence, are suggested to be generated at the surface of fractured particles during the AD deposition process [73]. Through the deposition process, it is understood that both cationic and anionic defects are formed at the grain boundaries due to dynamic fracture and random reorganization of newly created nanoparticles. This is expected to lead to three primary types of changes in the defect concentration during annealing:

(i) Local reorganization of defects at the grain boundary through diffusion processes, (ii) Reincorporation of oxygen to fill oxygen vacancies, and (iii) Electron transfer creating a space charge layer [57]. Other mechanisms, such as recrystallization, grain boundary rotation, and densification/grain growth, are also expected to influence the defect concentrations, although their individual contributions remain unclear and require additional more detailed local microscopy investigations.

Oxygen vacancies increase the observed unit cell volume above that of stoichiometric BaTiO3 through cationic repulsion [98, 99]. Therefore, reincorporating oxygen onto an oxygen site through thermal treatment will reduce the unit cell volume, leading to shrinkage in BaTiO3 films. This, as previously noted, can occur through internal redistribution of A, B, and O defects as well as externally through reincorporation of atmospheric oxygen. Conversely, the formation of a space charge layer through electron transfer is thought to reduce the driving force for local reorganization and oxygen reincorporation [100]. The formation of an acceptor-type defect altering the oxidation state from Ti4+ to Ti3+ might lead to a positive lattice strain due to the difference in ionic radii, although the extent of such local strain remains unclear [101]. Importantly, however, although the local redistribution of ions and the formation of a space charge layer can occur in a low oxygen partial pressure environment, the reincorporation of oxygen at the grain boundaries requires the presence of oxygen in the surrounding environment. In addition, the oxygen vacancy concentration and the presence of aliovalent dopants in the starting composition are also critical to controlling this process.

It is well-known that aliovalent B-site doping can be used to alter the oxygen vacancy concentration as well as potentially induce cation vacancies, where donor and acceptor doping decrease and increase the oxygen vacancy concentration, respectively [43–50]. This, for example, has significant effects on the macroscopic ferroelectric and piezoelectric properties of ferroelectrics [102, 103]. As such, B-site donor- and acceptor-doped BaTiO3 were used to directly investigate the observed thermal expansion effects. Figure 11 shows the thermal expansion of Fe-doped, undoped, and Nb-doped freestanding BaTiO3 films during the heating and cooling from the as-processed state to 500 °C in both air and N2. Importantly, all thermal expansion curves show an initial increase
during heating, followed by a subsequent decrease above approximately 150-200 °C, and a remanent shrinkage, in agreement with previous Raman and XRD data. Interestingly, the temperature-dependent thermal expansion behavior was found to be independent of doping when measured in N₂ within the measurement resolution, yielding negative thermal expansion values of approximately −0.6, −0.7 and −0.7% for BaTiO₃–2Nb, BaTiO₃, and BaTiO₃–2Fe, respectively. With an increase in oxygen partial pressure in samples characterized in air, however, a significant increase in magnitude of the irreversible contribution were observed, where remanent thermal expansion values of −0.8, −1.1 and −1.3% were found for BaTiO₃–2Nb, BaTiO₃, and BaTiO₃–2Fe, respectively.

The observed remanent change in the thermal expansion in N₂, which was found for all compositions, clearly indicates that oxygen exchange with the surrounding atmosphere is not the only factor contributing to volumetric change. In addition, this effect is apparently independent of the dopant concentration in N₂ within the resolution of these measurements, strongly suggesting the important role of a local redistribution of elements and defects. However, with the increase in the oxygen partial pressure, all compositions display an increase in the remanent thermal expansion value, demonstrating that oxygen reincorporation is also a contribution to the observed thermal shrinkage in AD films. Here, deviations between air and N₂ annealed samples began at approximately 200–250 °C, in agreement with both XRD and Raman spectroscopy data, considerably lower than previous molecular dynamics models by Dawson [104] and experiments on single crystal BaTiO₃ by Kessel et al. [105], that showed significant oxygen exchange is not expected below 650 °C. Importantly, this increase in remanent thermal expansion was found to become larger with an increase in oxygen vacancy concentration through doping. Considering the potential occurrence of a space charge effect, creating an electron-rich barrier layer at the grain boundaries, [57] it was shown by Watanabe et al. [100] that the presence of space charges along the grain boundary effectively blocks oxygen diffusion into the grains. Therefore, the space charge effect must be either negligible, which may be attributable to the grain size of AD films reducing the space charge effect in comparable size regions, [57] or there is a different conduction path, such as low-density amorphous regions as reported by Cao et al. [106] on aerosol-deposited TiN layers investigated with high resolution TEM. It is important to note here that these various effects do not operate independently of one another, such that local redistribution can reduce the driving force for reincorporation and vice versa. These data, however, do show that an increase in the oxygen vacancy concentration of the starting material does play an important role in controlling the shrinkage response.

In order to separate structural and chemical effects on the thermal expansion, an ex situ annealing to 500 °C was performed in vacuum prior to thermal

Figure 10 a Annular dark-field (ADF) STEM image and nanobeam electron diffraction patterns of BaTiO₃ film highlighting the variations in crystallinity between grain boundaries (spot A and C) and grains (spot B). Variation in bright-field (BF) TEM images before b and after c thermal treatment at 500 °C for 1 h.
expansion measurement in air for BaTiO$_3$, BaTiO$_3$–2Nb, and BaTiO$_3$–2Fe (Fig. 12). The aim of this measurement was to allow for local, internal processes, e.g., redistribution, to occur, but to eliminate the possibility of oxygen reincorporation from the surrounding environment. Following this, the thermal expansion response was characterized in air, which should provide a direct measurement of the contribution of oxygen reincorporation. For reference, the data for a film annealed in the air is also provided (Fig. 12a), which did not display any remanent shrinkage.

In good agreement with the previous results, the highest remanent shrinkage (−0.5%) can be observed for the Fe-doped films (Fig. 12d), which has the highest oxygen vacancy concentration. The BaTiO$_3$–2Nb film (Fig. 12b) shows the least amount of atmosphere dependent remanent shrinkage (−0.1%), consistent with the reduced oxygen vacancy concentration, with undoped BaTiO$_3$ (Fig. 12c) between these values (−0.2%). For an undoped BaTiO$_3$ film annealed in air instead of vacuum, the oxygen exchange process can be assumed to be complete as no deviation in thermal expansion can be observed in the subsequent heating/cooling cycle (Fig. 12a). As all internal redistribution processes are expected to have been completed during the first heating cycle in vacuum, the values observed in Fig. 12 represent a residual, chemical contribution from the reincorporation of oxygen. It is important to note that the residual shrinkage values observed during this ex situ measurement were approximately 0.1% smaller than those found during the in situ measurement, i.e., −0.4, −0.2, and −0.6% for BaTiO$_3$, BaTiO$_3$–2Nb, and BaTiO$_3$–2Fe (Fig. 11). This indicates that the order in which the mechanisms occur, e.g., simultaneously or in series, has an effect on the macroscopic response. It is likely that local chemical redistribution at the grain boundary or the formation of a space charge can reduce oxygen exchange as well as grain boundary diffusion of oxygen, limiting the influence of the atmospheric partial pressure.

The atmosphere dependent thermal expansion data of doped BaTiO$_3$ demonstrates that as-processed AD-films inherit a significant concentration of AD-process-induced defects, including oxygen vacancies, which supported by XRD, Raman spectroscopy, and TEM data revealing corresponding changes in the crystal structure and internal stress state. Accumulated point defects at the grain boundaries are suggested to be a major contributing factor to an increased electronic conductivity in as-processed AD-films, and reducing their concentration is expected to be the primary contribution to the observed increase in electrical resistivity. These observations coincide with a structural relaxation based on a reduction in unit cell volume that is clearly visible by both direct

![Figure 11](image-url) Variation in thermal expansion of 45 μm thick freestanding a BaTiO$_3$–2Nb, b BaTiO$_3$, c BaTiO$_3$–2Fe films annealed in air and $N_2$. 

optical observation and indirect methods such as in-situ temperature XRD and Raman spectroscopy. Separating chemical and structural relaxation, however, is left with a degree of uncertainty as both mechanisms may occur simultaneously by self-diffusion of oxygen defects [100] at elevated temperatures without extrinsic atmosphere contribution.

**Conclusion**

In this work, we successfully demonstrated the room temperature fabrication of freestanding AD films that preserves the as-processed state of the film. With the role of the CTE mismatch between film and substrate being crucial to understand internal stress relaxation in AD films, we were able to determine the thermal expansion response of AD thick films of BaTiO$_3$. A negative thermal expansion was observed during the first annealing cycle, which was dependent on the oxygen partial pressure of the annealing atmosphere and the oxygen vacancy concentration in the film. This data clearly demonstrated that both internal redistribution effects as well as oxygen reincorporation play an important role. Importantly, oxygen exchange was found to start at approximately 200–250 °C, far below observations in bulk BaTiO$_3$, implying that significant oxygen mobility exists in AD films. These macroscopic measurements were supported by both in situ Raman spectroscopy and XRD investigations that revealed irreversible temperature-dependent structural changes during the heating, concurrent with the ordering and tilting of the crystallites. Ex situ TEM, however, did not reveal a change in crystallite size. This work provides important information on influence of low temperature annealing of room temperature deposited ferroelectric films but also highlights the necessity to study structural relaxation mechanisms in AD films at grain boundary level.

**Acknowledgements**

U.E., N.H.K., and K.G.W. gratefully acknowledge financial support for this work from the Deutsche Forschungsgemeinschaft (DFG) under WE4972/2 and GRK2495F. H.U., M.Š. and M.D. acknowledge the Slovenian Research Agency (project J2-3058, SLO-DE bilateral project BI-DE/20-21-012, young researcher project, research core funding P2-0105). M.D. acknowledges the research core funding P2-0105 and European Union’s Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No. 101031415. This work was also partially supported by JSPS KAKENHI Grant Number JP19KK0124.

**Funding**

Open Access funding enabled and organized by Projekt DEAL.
Supplementary Information: The online version contains supplementary material available at http://doi.org/10.1007/s10853-022-07467-3.

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