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In the present work the longstanding issue of the structure and dynamics of smaller ions in oxides and its impact on the properties was investigated on 7% Li-doped BaTiO_3 . The investigation combined several techniques, notably neutron powder diffraction (NPD), nuclear magnetic resonance (^7Li -NMR), electron paramagnetic resonance (EPR), electron microprobe, electric polarization (EP) measurement, and electronic structure calculations based on density-functional theory (DFT). Electron microprobe confirmed multiple phases, one containing incorporated Li in the BaTiO_3 host lattice and another glassy phase which breaks the host lattice due to excessive Li accumulation. While the average structure of Li in BaTiO_3 could not be determined by NPD, ^7Li -NMR revealed one broad “disordered” and multiple “ordered” peaks. Local structure models with different defect types involving Li^+ were modeled and the corresponding chemical shifts (δ) were compared with experimental values. It is found that the closest defect model describing the ordered peaks, is with Ti^{4+} being replaced by four Li^+ ions. The biexponential behavior of the spin-lattice relaxation of the ordered peaks each with a short and a long relaxation discloses the existence of paramagnetic ions. Finally, EPR revealed the existence of the paramagnetic ion Ti^{3+} as a charge-transfer defect. DFT calculations disclosed local antipolar displacements of Ti ions around both types of defect sites upon insertion of Li^+ . This is in accordance with the experimental observation of pinching effects of the EP in Li-doped BaTiO_3 . These studies demonstrate the huge impact of the local structure of the doped smaller/lighter ions on the functional properties of oxides.

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I. INTRODUCTION

Lithium is an indispensable ingredient in novel energy-storage technologies like solid-state Li-metal barriers [1] and traditional Li-ion batteries. It also plays a critical role in various polar functional materials which exhibit excellent dielectric, piezoelectric, ferroelectric (FE), and multiferroic behaviors [2–6], even in metallic ferroelectrics [7]. Due to its small size, the doped Li ion can affect the structural stability, homogeneity, local environment, and even dynamic behavior of the host materials for achieving optimal performance and properties. However, the Li-ion dynamics, which determine the desired functional properties in applications, are not completely understood and are the subject of ongoing research [8–10]. The probable position of Li ion in a compound is often diverse and thus remains controversial in many cases [11–13]. This is more apparent in low-level Li-doped systems, where limitations of Li^+ detection through

analytical methods prevail, and sample inhomogeneity due to possible Li migration to the grain boundary, development of multiple and/or impurity phases, consequently lead to a deviation from the nominal composition [14]. Thus the resultant functional properties of materials are often poorly understood and incorrectly attributed to the underlying local environment and the topology of the defect structure [11]. In the present paper we elucidate the critical issues such as the position and dynamics of Li ions in a simple but technically important metal oxide perovskite system and demonstrate the influence of the resultant defect topology and degree of homogeneity on the functional properties.

For this purpose, BaTiO_3 is chosen as the host lattice for Li doping. Due to environmental concerns, BaTiO_3 -based solid solution [15–17] is considered as the alternative to the commonly used piezoelectric lead zirconate titanate [18]. Furthermore, it has been demonstrated that Li ions can be effectively doped into BaTiO_3 and related titanates at lower doping levels to improve their piezoelectric properties and sintering ability [19–21]. Recent field-dependent electric polarization (EP) measurements on the Li-doped BaTiO_3 exhibit a constricted, or double polarization–electric field ($P-E$) hysteresis loop [11], which raises a question of the Li-induced defect model.

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Though it has been demonstrated that Li^+ is doped into the lattice of titanate perovskite materials, its site occupancy is still a subject of speculation [11,13,14,22]. According to the previous studies [13,20–22], Li^+ has the possibility to occupy the *A* site, *B* site, as well as the interstitial sites, in either an ordered or disordered manner. Furthermore, the Li^+ could also form the glassy phases locating at the grain boundary [14]. Ions such as Na^+ or K^+ with similar valence as Li^+ were also reported to induce charge-transfer-type defects in doped BaTiO_3 , which is associated with Ti^{3+} [23].

To tackle further the local structure and dynamics of Li-doped BaTiO_3 , we synthesized a 7 mol % Li-doped BaTiO_3 in the nominal form of $\text{BaTi}_{0.93}\text{Li}_{0.07}\text{O}_{2.895}$ as the model system. Considering the features of Li^+ such as light weight and electron density, we combined several techniques, such as electron microprobe associated with the wavelength-dispersive spectroscopy (WDS), neutron powder diffraction (NPD), ^7Li solid-state nuclear magnetic resonance spectroscopy (NMR), electron paramagnetic resonance (EPR), EP measurement, and theoretical calculations to gain the insight of the distribution of Li^+ and associated local structures.

II. SYNTHESIS, EXPERIMENTS, AND CALCULATION DETAILS

The sample $\text{BaTi}_{0.93}\text{Li}_{0.07}\text{O}_{2.895}$ (i.e., nominal Li doping is 7 mol %) was synthesized by conventional solid-state reaction using BaCO_3 , TiO_2 , and Li_2CO_3 as starting materials in several steps. The detailed method is described elsewhere [11]. For the phase identification, purity, and preliminary real-crystal effects, room-temperature x-ray diffraction was carried out using a $\text{CuK}\alpha$ anode. Microstructure and indirect elemental composition analysis were performed using a JEOL JXA-8530F Plus electron probe microanalyzer at the Center for Advanced Microscopy, the Australian National University. High-resolution secondary electron and backscattering electron (BSE) images were used to identify different phases of the well-polished ceramic samples. The microprobe analysis, with a microprobe diameter of $1\mu\text{m}$, was performed in both WDS and energy-dispersive modes. The amount of Li (wt %) was indirectly determined by determining the amount of Ba and Ti in pure and doped samples. For this purpose, as a reference for the pure sample a high-quality single crystal of BaTiO_3 was used as the standard. NPD was performed at the high-resolution neutron diffractometer Echidna at ACNS, Australia Nuclear Science and Organisation. Diffractograms were recorded for 6 h using a neutron wavelength of $1.622\text{ \AA}$. The one-dimensional (1D) and two-dimensional (2D) magic-angle spinning ^7Li -NMR measurements at room temperature were performed on a Bruker Avance III 700-MHz NMR spectrometer, operating at a frequency of 272.18 MHz for the ^7Li nucleus. The sample was packed in a 4-mm zirconia rotor and spun to 10 kHz at the magic angle in a 4-mm HX double-resonance probe head. The T_1 measurements were carried out by a saturation recovery experiment, where a saturation comb of fifty 90° pulses with a delay of 20 ms between them, was used to suppress the ^7Li magnetization, followed by a recovery period of 0.1 to 100 s, and finally another 90° pulse to detect the recovered magnetization. The T_2 relaxation experiments were measured by a series of Hahn echoes with

a recycle delay of 10 s, where the echo delay was increased in integer multiples of the rotor period from 0.2 to 51.2 ms. The area under the peaks yielded the relative fractions of the different Li environments, and the changes in their intensity were plotted against the saturation recovery times and echo delays for the T_1 and T_2 measurements, respectively. The 2D exchange experiments were also acquired with a recycle delay of 10 s, and the exchange time of 0.1, 10, 100, and 300 ms. The ^7Li NMR signal of LiCl (aq) at 0 ppm was used as a reference for the NMR shifts, and additionally, LiBr was compared to LiCl (aq) to act as a solid reference for modeling purposes. The 1D NMR spectra were fit using the DMFIT software [24]. Continuous Wave-X-Band (CW-X-Band) EPR spectra were measured on a commercial Bruker E500 spectrometer equipped with a Bruker ER4122 SHQ resonator. Samples were loaded into conventional X-Band EPR tubes with an inner diameter of 2.8 mm. Spectra were measured at room temperature using 0.474-mW, 9.4-GHz microwaves, and 4-G modulation amplitude. For the polarization-electric field (*P-E*) hysteresis loop measurement, the sintered BaTiO_3 and $\text{BaTi}_{0.93}\text{Li}_{0.07}\text{O}_{2.895}$ ceramic pellets were coated with the Ag electrodes and cofired at 720°C . The resultant pellets were measured by a modified Sawyer-Tower circuit at 10 Hz, triangular waveform (TF Analyzer 2000, aixACCT Systems GmbH, Aachen, Germany). First-principles density-functional theory (DFT) electronic structure calculations were performed by the WIEN2K code using full-potential linearized augmented plane wave plus local orbital method [25]. The value of $R_{\text{MT}}K_{\text{max}}$, where K_{max} corresponds to the largest plane-wave vector, was set to 6. The mesh of special *k* points is selected to be $4 \times 4 \times 4$ and $3 \times 3 \times 3$ depending on the size of the model for total energy calculations. The number of independent atoms in the unit cell varied depending on the used local structure model. For the exchange-correlation energy functional both nonspin and spin-polarized version of the generalized gradient approximation (GGA) in the PBE version was used [26]. The convergence is reached as the difference in the total energies becomes less than 0.000 001 Ry for all calculations. For all local-defect structures, the structural parameters were optimized with an additional convergence criterion based on the forces $<2\text{ mRy/a.u.}$ The isotropic (magnetic) shielding tensor is calculated from the induced local magnetic field, which itself is calculated from the induced current [27]. The Electric Field Gradients (EFGs) and the hyperfine fields were obtained from DFT total energy calculations in order to determine the quadrupolar frequencies, Fermi contact, and dipolar contributions. In order to compare it with the experimentally determined chemical shift, the total shielding was given relative to a reference substance, which is approximated by LiBr in our case. The LiBr calculation was done on a *k* mesh of $3 \times 3 \times 3$ and its structure was obtained from Ref. [28]. Additionally, we also modeled $\text{LiCl}_{(\text{aq})}$ with the approximation of its hydrates [29,30].

III. RESULTS

In order to determine the possible Li^+ sites, high-resolution NPD was first performed on nominal $\text{BaTi}_{0.93}\text{Li}_{0.07}\text{O}_{2.895}$. The single-phase perovskite structure model can predict the collected patterns quite well, but the Rietveld refinements

for various Li crystallographic sites (Part I in Supplemental Material, also Table S1 [31]) either resulted in underestimated/negative occupation or unphysical bond valence sums (BVS) for Li^+ , which is not surprising at all. However, the NPD results still provide indirect evidence for the possible occupied sites of Li, other atomic positions, and overall lattice parameters for further theoretical modeling.

The NMR technique is sensitive to the local chemical environment, which led us to investigate the short-range structure of Li^+ . We first discuss the NMR experiments. The theoretical quantity related to the NMR is the isotropic shielding σ which describes the response of a local chemical environment within the crystal to an external magnetic field. In an NMR experiment this is given relative to a particular reference and denoted as the chemical shift δ [32]. The 1D ^7Li NMR spectrum is plotted in Fig. 1(a) (color spectra in the online version), showing four distinct lithium environments, labeled A–D. Site A (0 ppm) has a broad NMR line shape, which indicates a highly disordered Li environment, while sites B, C, and D (−2.3, −2.7, and −4.1 ppm, respectively) yield very narrow spectra, corresponding to ordered-crystalline environments. A fit to the ^7Li NMR spectra (Fig. S1 [31]), yielding a relative population of the Li species in the different sites [33], indicates that the disordered site A is dominate, corresponding to 77% of the observable ^7Li signal.

The T_1 and T_2 relaxations of the ^7Li NMR signal describe processes that are governed by spin-lattice and spin-spin interactions, respectively. The T_1 describes the recovery of the magnetization of the nuclear spin of Li in the direction of the external field from an applied excitation pulse perpendicular to it. T_2 on the other hand describes the decay of the same excited magnetization components perpendicular to the direction of the external field. Thus T_1 and T_2 are influenced by the overall (long-range) structure and dynamics of the material and allow elucidation of relaxation processes across a broad range of timescales. As shown with the 1D ^7Li NMR spectra [Fig. 1(a)] corresponding to different recovery times of 0.1 to 100 s, the intensity of the different sites increases towards the equilibration value, with increasing recovery time. Fitting the intensity changes with an exponential function [34], we obtain the values for the T_1 for the different sites (Fig. S2 [31] and Table I).

Site B has the slowest relaxation with a T_1 of ~ 47 s from a fitting of a single exponential function. In comparison, the saturation recovery behavior of all other sites is best described by a biexponential behavior, with short and long T_1 relaxation times of ~ 1 and ~ 25 s, respectively. The ^7Li - T_2 relaxation times were measured by a series of Hahn echoes with echo times increasing from 0.2 to 51.2 ms. The resultant ^7Li spectra are plotted in Fig. 1(b), while Fig. S3 [31] shows the fits to the decrease in signal intensity with increasing echo time. Here, the data were best fit by single exponential decay, with site A yielding the fastest T_2 relaxation (0.6 ms) (Table I). In combination with the line-shape analysis and the T_1 and T_2 relaxation measurement, it is clear that the different Li sites in the material experience very distinct dynamical and structural environments. ^7Li 2D-exchange NMR enables us to identify whether these distinct environments are located within the same macroscopic phase or within distinct phase domains. During the exchange time period, site hopping between

FIG. 1. (a), (b) 1D NMR spectra for different evolution times of the spin-lattice relaxation and spin-spin relaxation. (c), (d) ^7Li 2D Exchange NMR spectrum obtained for mixing times of 0.1 and 300 ms (relaxation $T_1 = 10$ s). (e) Short and long relaxation time T_1 for site C and D (schematic). (f) Short and long relaxation time T_1 for site A (schematic).

TABLE I. The values of the spin-lattice relaxation time T_1 and spin-spin relaxation time T_2 obtained from NMR experiments for different peaks A, B, C, and D.

	T_1 (s) (biexponential fitting)		T_2 (ms)
A	0.7 (70%)	29.0 (30%)	0.6
B		46.6 (100%)	16.4
C	0.2 (70%)	26.9 (30%)	18.2
D	4.2 (57%)	21.7 (43%)	22.4

different Li sites occurs, which shows up as off-diagonal intensities in the 2D exchange spectrum as shown in Figs. 1(c) and 1(d). Here, we observe that for the disordered site A, which has a broad distribution of Li environments, the Li atom rapidly exchanges between the different chemical environments on a timescale <0.1 ms [region I in Fig. 1(c)]. The fast exchange of Li ions in site A can account for its short T_2 , where the rapid motion of the cation resulting in fluctuation on internuclear interactions drives the T_2 relaxation process. In comparison, the exchange between sites C and D takes a much longer time [region II in Fig. 1(d)], only visible after 100 ms (Fig. S5 [31]). Within the longest exchange time measured here (300 ms), the exchange has not equilibrated. This indicates a much slower Li hopping rate between the crystalline sites C and D, and these two sites are part of the same crystalline phase. Finally, the site B does not show any clear evidence of exchange with any of the other sites, i.e., it is a well-defined independent crystallographic site. This makes us believe that the signal of site B might arise from the unreacted Li raw materials. The absence of exchange between the disordered site A and the ordered sites C and D may imply that the Li disorder at site A results from a breakdown of the host lattice due to its over-accumulation, leading to a distinct glassy phase (variable bonding environment comparable with Li-containing glasses [35]). Bearing this in mind, we conducted the electron microprobe as well as the WDS measurements on the Li-doped BaTiO₃ sample (Part III in Supplemental Material [31]). The BSE images (Fig. S5 [31]) identify successfully some Li-rich regions with an irregular morphology at the junction of several well-shaped BaTiO₃ grains. Therefore, it is reasonable to assign these regions to the highly disordered site A, i.e., Li-BaTiO₃ glassy phase. Furthermore, the short relaxation time T_1 in the biexponential fitting for sites A, C, and D provides indirect evidence for the presence of paramagnetic ions such as Ti³⁺ [Figs. 1(e) and 1(f)]. The ⁷Li nuclear spin relaxes faster at Li sites in the nanoscale vicinity of (the d -electron cloud of) the Ti³⁺ site, whereas the long relaxing fraction of ⁷Li nuclear spins is due to multiple effects like lattice vibrations, quadrupolar relaxation, and dipolar coupling. Thus, the long relaxation fraction of T_1 reflects that during the saturation recovery timescale not all the Li nuclear C and D (and A) sites are in the vicinity of Ti³⁺ [Figs. 1(e) and 1(f)] [36,37]. Finally, a very low exchange between C and D from the ⁷Li- 2D exchange NMR spectrum reflects the higher activation energy for this exchange.

The diffraction, electron microprobe, and NMR results indicate that the Li mainly interacts with the host BaTiO₃ in two forms. First, a large amount of Li destroys the crystallographic structure of BaTiO₃, forming the glassy phase, which is amorphous with plenty disordered Li sites. Second, some Li atoms occupy or replace the crystallographic sites of BaTiO₃. In the following section, we will turn our attention towards local defect structure models based on Li⁺ which is the key to elucidate our experimental findings and structure-property relationship. We concentrate only on ordered sites C and D, as site B was attributed to the unreacted material. In the first step, supercells were constructed with different types of defects upon partial replacement of the constituents by Li. It was ensured that all ionic constituents have a reasonable BVS in the initial defect structure model. The required lattice

parameters and atomic positions were taken from the NPD refinement. The following defect model types were constructed: BL: Ba²⁺ is replaced by two Li⁺ ions (Fig. S6); BOL: Two Ba²⁺ ions and one O²⁻ ion are replaced by two Li⁺ ion (Fig. S8); TOL: One Ti⁴⁺ and one O²⁻ ion are replaced by two Li⁺ ions (Fig. S9); and TL: One Ti⁴⁺ is replaced by four Li⁺ ions (Fig. S10) [31]. Within each defect model several variants were considered. For a detailed description of the nomenclature see Part IV in Supplemental Material [31]. For all the models, DFT total-energy calculations with force minimization were performed. Specifically, for the defect type TL, due to the much smaller vacant space created by a Ti⁴⁺ vacancy than a Ba²⁺, DFT calculations with volume expansion were performed, resulting in a flat energy minimum for 9–12% of volume change (Fig. S11 [31]). Five variants are considered for type BL (Fig. S6 and Table S2 in Part IV of Supplemental Material [31]). Only two of them are energetically favorable: Li replacing Ba²⁺ along the diagonal BL(d) and on the ab plane BL(ab). For TL, four options are considered. TL3 and TL4 have the lowest total energies, corresponding to the local structure with two Li⁺ ions around the Ti⁴⁺ defect site and two Li⁺ ions on the Ba cuboid. The difference between TL3 and TL4 is attributed to the initial Li configuration (Fig. S10 and Table S5 in Part IV of Supplemental Material [31]). We denote the above models as defects “without charge transfer” due to the conservation of the oxidation states of the constituents (no Ti³⁺). In the next step we calculated the isotropic shielding σ for the above models and then obtained the chemical shift δ to compare with experimental values (Part V in Supplemental Material [31]). Corrections from quadrupolar or hyperfine interactions have been taken into account (Tables S8 and S10 [31]).

Figure S12(c) shows the calculated σ for the energetically favorable variants within each defect type. The calculated δ were given at the top part and serve as comparison [31]. The δ values of Li⁺ for type BOL and TOL and BL(ab) are much larger than the experimental data, and thus these models can be directly ruled out. For TL3 and TL4, the δ values are very close to experimental results, especially after volume expansion, and therefore they are most likely candidates for the defect structure. In fact, a comparison of the volume (from diffraction, see Table S1) of our 7% Li doped with a 5% (not considered further in this work) Li-doped BaTiO₃ revealed an increase of 0.02 Å³ with increasing Li doping which may reflect the volume expansion related to the insertion of 4 Li ions (TL3 and TL4) [31]. Now the question arises how the individual Li positions within these models contribute to the sites.

Looking at the δ values of the individual Li⁺ ions of TL3 (and TL4), it is evident that the Li⁺ ions at the Ti defect site (Li1 and Li2) have lower δ values than the Li⁺ ions at the vertices of the Ba cuboid (Li3 and Li4), owing to different environments [Fig. 2(a)]. This is also obvious from the calculated BVS difference map (BVS-DM) with a contour value of 0.075 above the valence of Li⁺ for TL3 [Figs. 2(b) and 2(c)]. BVS-DM exhibits two parts, a rather localized region around the Ti⁴⁺ defect with Li1 and Li2 and an extended region connecting the vertices of the Ba cuboid which contains Li3 and Li4. Therefore, we identify Li1 and Li2 with site D and Li3 and Li4 with site C. However, the

FIG. 2. (a) TL3 with 4 Li⁺ ions. (b), (c) BVS-DM of 0.075 above BVS (Li⁺) = 1 in different perspectives. The extended part along the Ba cuboid and localized part around the Ti⁴⁺ defect are clearly visible.

sites C and D cannot be further resolved between the Li ions at the same environment (Li1, Li2 and Li3, Li4). The deviation from the theoretically predicted 50% occupation of localized Li (0 K) in the NMR experiment probably comes from entropy effects at room temperature. This identification is also in agreement with a larger value of T_1 (short) relaxation on Ti³⁺ for site D than for site C, as C is closer to the Ti³⁺ site and partially screens Li1 and Li2 of site D.

In the above model discussion, the Ti⁴⁺ oxidation states are assumed to be preserved while Ti³⁺ is indirectly involved in the relaxation process. In the following another type of local defect structure model with changed oxidation state is described. This type of defect was already found in Na⁺/K⁺-BaTiO₃ induced by the higher synthesis temperatures [23,38]. A Ba-O vacancy is created and substituted by a Li⁺ ion in the Ba²⁺ position [Fig. 3(a)]. For overall charge neutrality Ti changes its oxidation state +4 to +3 obtaining an unpaired electron. We call this the charge-transfer-type defect. Due to the d electron at Ti³⁺, a hyperfine interaction between the nuclear spin of Li and spin density may show up, as observed in Li-containing insulators [39,40]. EPR was hence utilized to investigate this type of defect involving charge transfer [41].

Figure 3(b) shows the EPR spectra of Li-doped BaTiO₃. Several signals can be seen at different g values. The g value is a proportionality factor which relates the magnetic moment to its angular momentum. The free electron has a g value of 2.0023. The signal below $g = 2$ results from the Ti³⁺ d electron due to the natural occurrence of the O vacancy. The signal in this range has been seen for Ti³⁺ in many doped anatase and rutile compounds [42–44]. On the contrary, the signal above $g = 2$ comes from the spin density between the adjacent Ti ions mostly from the O vacancy [23,45,46] due to the Li incorporation.

In order to elucidate the EPR results, theoretical modeling was performed. The calculations revealed that the substitution of Li⁺ is energetically favorable for the Ba-O vacancy along c (TLC2; for further details see Table S9 in Part V of Supplemental Material [31]). The calculated total spin and the Ti spins are around $0.3\mu_B$ and 0.12 – $0.16\mu_B$, respectively. This indicates a delocalization of a single electron between the two adjacent Ti ions and significant contribution from the interstitial area. The natural choice would be filling a t_{2g} orbital. The calculated total and partial density of states (PDOS) of $3d$ of the adjacent Ti ions are shown in Fig. 3(c). The

FIG. 3. (a) Schematic view of the replacement of Ba-O by Li⁺ with a residual electron going to the Ti site. (b) EPR spectra of Li-doped BaTiO₃. (c) PDOS of the d states at the Ti sites. (d) Interstitial DOS for GGA + $U = 5$ eV. (e), (f) Spin density in the energy interval -0.65 eV $- E_F$ shown for 0.02 and $0.08 \mu_B/\text{\AA}^3$, respectively.

states due to the formation of the defect manifest themselves around 0.1 eV below the conduction-band edge. It is evident that both Ti ions contribute to the defect states. Figure 3(d) shows the interstitial DOS which also exhibit defect states in the same energy range. The spin density integrated in the energy window above -0.65 eV is shown in Figs. 3(e) and 3(f). The interstitial contribution to the defect states manifests itself as spin density between the Ti ions in the O vacancy area. Furthermore, the localized moment at Ti ions are more of the e_g type (more dz^2) with some admixture. Previous EPR measurements disclosed two types of oxygen vacancies (natural and Na⁺/K⁺-associated O vacancies) in BaTiO₃ leading to spin density at the Ti site [23]. However, in both cases the $3d$ electron occupies the t_{2g} orbital which is confined to one of the Ti ions. This is in contrast to our calculation, where the $3d$ electron is spread between the adjacent Ti ions occupying the e_g -type orbital. The majority of the spin density between the Ti ions is in the O vacancy region via a strong e_g -O vacancy orbital hybridization. Such a ground

FIG. 4. (a) Electric field dependence of EP of BaTiO_3 and $\text{BaTi}_{0.93}\text{Li}_{0.07}\text{O}_{2.895}$, (b), (c), and (d) Local Ti distortions along c in pure BaTiO_3 , TL3, and TLC2, respectively, indicated by vectors.

state was predicted in previous calculations on BaTiO_3 [47] but confirmed experimentally by the current investigation. Therefore, the two distinct EPR signals can be attributed to different d -orbital occupations of Ti^{3+} .

Finally, we investigated the correlation of the local structure models TL3 (TL4) and TLC2 with material properties revealed by the EP measurements. Figure 4(a) shows the emergence of the EP pinching effect through double-hysteresis-like loops upon Li doping in BaTiO_3 . The hysteresis loop of pure BaTiO_3 is shown as a comparison. The calculation shows that the relaxed structures TL3 and TL4 revealed a partial antiparallel local distortion of the Ti ion along c in the vicinity of the Li defect compared to pure BaTiO_3 [Figs. 4(b) and 4(c)]. In case of TLC2 with Ti^{3+} , half of the Ti ions around the defect show antiparallel distortions, thus suppressing FE along c [Fig. 4(d)]. The partial antipolar distortions are not limited to the $2 \times 2 \times 2$ supercells, rather also retained for larger supercells (see Part VI in Supplemental Material [31]). The insertion of Li could result in the antipolar distortion at the local scale, which breaks the long-range ferroelectric order and acts as the pinning center for the domain orientation [48]. It is evident from Figs. 4(c) and 4(d) that each Li^+ ion locally creates more than one antiparallely oriented dipole pairs

influencing the environment of the defect, which explains the massive change to the properties such as the shape of the hysteresis by a low-level Li doping. Therefore, we can partially attribute the constricted P - E hysteresis loop to the local defect structure. Furthermore, the Li- BaTiO_3 glassy phase at the grain boundary is also possible to restrict the domain-wall motion in the surrounded grains, which is another factor for the pinching effect [49].

IV. SUMMARY

In summary, by combining several experimental techniques and theoretical modeling, we have investigated the possible Li occupation sites, the associated local structures, and the correlations between structure and properties of Li-doped BaTiO_3 . ^7Li -NMR revealed one broad disordered peak associated with a glassy phase and three narrow ordered peaks. Two of the ordered peaks can be associated with local structures with two Li ions sitting around Ti^{4+} defect sites and associated with two disordered Li^+ ions on the Ba cuboid, respectively. The diffusion dynamics of the Li among these sites have also been revealed by the NMR measurements. EPR revealed the charge-transfer type of defect structure involving Li^+ and Ti^{3+} , with spin density showing e_g character. The experimental observation of electric polarization pinning effects in Li-doped BaTiO_3 can thus be understood in terms of the local structure and dynamics associated with Li. Future work will investigate the NMR relaxation effects at variable temperature to provide greater details of the Li interactions and dynamics in the material.

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