Dielectric capacitors are particularly suitable to store the electrical energy of a fast-changing nature. Here, we present a review of recent applications of first principles and first-principles-based effective Hamiltonian approaches to the study of energy storage in ferroelectrics, lead-free antiferroelectrics, relaxor ferroelectrics, and nitride semiconductors. Specifically, these approaches are used to investigate the energy density and efficiency in perovskite BaTiO$_3$, PbTiO$_3$, and KNbO$_3$ ferroelectrics; Bi$_{1-x}$R$_x$FeO$_3$ antiferroelectric solid solutions (where R is a rare-earth ion); Ba(Zr,Ti)O$_3$ relaxor ferroelectrics; and epitaxial AlN/ScN superlattices. Ultrahigh energy densities and efficiencies are predicted in some of these compounds. In addition, phenomenological models are used to analyze and understand these energy storage results. Consequently, the numerical methods and simple models detailed here can be easily employed to design novel nonlinear dielectrics with further enhanced energy storage performance.

Keywords: energy storage, ferroelectrics, antiferroelectrics, relaxor ferroelectrics, superlattices

1 INTRODUCTION

Dielectric capacitors with ultrahigh energy density and efficiency are promising for energy storage applications in various electronic applications due to their fast charging/discharging speeds and high stability (Chu et al., 2006; Hao, 2013; Chauhan et al., 2015; Li et al., 2015; Prateek Thakur and Gupta, 2016; Yao et al., 2017; Yang et al., 2019), and intensive efforts have been devoted to improve their relatively low energy densities. For example, dielectric polymers with high dipole density have the potential to achieve ultrahigh energy density with fast discharge and low hysteresis loss (Chu et al., 2006; Li et al., 2015). Recently, antiferroelectrics, relaxor ferroelectrics, and initially nonpolar-based capacitors have been intensively studied because of their low dielectric loss, high polarization, and high breakdown electric field (Peng et al., 2015; Hou et al., 2017; Instan et al., 2017; Pan et al., 2019; Kim et al., 2020; Pan et al., 2021; Wei et al., 2021). For instance, a giant energy density of 154 J/cm$^3$ with a high efficiency of 97% has been observed in epitaxial lead-free relaxor thin films exhibiting a coexistence of ferroelectric (FE) and anti-FE phases (Peng et al., 2015). A high energy density of 112 J/cm$^3$ with a high energy efficiency of 80% has also been achieved in lead-free BiFeO$_3$-BaTiO$_3$-SrTiO$_3$ solid solution films (Pan et al., 2019). Ultrahigh energy densities and efficiencies have also been reported in 0.68Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$-0.32PbTiO$_3$ (133 J/cm$^3$ and 75%) and Sm-doped yBFO-
Finally, effective Hamiltonian schemes used for investigating the ferroelectrics (Luo et al., 2016), lead-free antiferroelectrics (Xu et al., 2017), relaxor ferroelectrics (Jiang et al., 2022), and some La0.67Sr0.33MnO3 electrode (Hou et al., 2017). The stored energy density (which exist between the temperature T_m at which the dielectric response exhibits a peak and the Burns temperature T_b) have been demonstrated to possess ultrahigh energy density and efficiency (Pan et al., 2021), which is promising to optimize properties in other relaxor-FE-based systems and nonlinear dielectrics. Other examples include the ultrahigh recoverable energy density in Ba(Zr,Ti)1-xO3 relaxor ferroelectric thin films that has been experimentally observed to be 156 J/cm3 at a high electric field around 3 MV/cm with an efficiency of 72.8% (Instan et al., 2017); and the highest record of energy density up to 307 J/cm3 with a high efficiency of 89% at 6.6 MV/cm measured in SrTiO3 films grown on an La0.67Sr0.33MnO3 electrode (Hou et al., 2017).

Note that, for nonlinear dielectrics (i.e., ferroelectrics, antiferroelectrics, and relaxors), the stored energy density (U_st or W_st) is determined by integrating the area under the polarization and the charging curve of the polarization versus electric field (P-E) loop, \( U_{st} = \int_0^{P_{max}} EdP \), and the recoverable energy density \( U_{rec} \) is determined by the discharging process, \( U_{rec} = \int_{P_r}^{P_{max}} EdP \), where \( P_{max} \) is the polarization obtained at the maximum applied electric field \( E_{max} \) and \( P_r \) is the remnant polarization. The efficiency can be defined as \( \eta = \frac{U_{rec}/U_{st}}{U_{loss}/U_{loss} \times 100\%} \), where \( U_{loss} \) is the energy loss density (Palmecci et al., 2018; Wei et al., 2021). In order to achieve high energy density and efficiency, one can thus imagine a nonlinear type dielectric material to have large polarization \( P_{max} \) under a high applied electric field \( E_{max} \) and small hysteresis (with small remnant polarization and energy loss).

The aim of this review article is to discuss the recent first principles and first-principles-based effective Hamiltonian studies aimed at predicting and understanding energy storage in some ferroelectrics (Luo et al., 2016), lead-free antiferroelectrics (Xu et al., 2017), relaxor ferroelectrics (Jiang et al., 2022), and some specific nitride semiconductors (Jiang et al., 2021a).

This article is organized as follows. Section 2 provides details about the first-principles methods and first-principles-based effective Hamiltonian schemes used for investigating the energy storage properties of these different systems (Luo et al., 2016; Xu et al., 2017; Jiang et al., 2021a; Jiang et al., 2022). Section 3 reports and discusses energy storage results in ferroelectrics, antiferroelectrics, relaxor ferroelectrics, and nitride semiconductors, from the use of these ab initio methods. Finally, Section 4 provides a summary and perspective on future studies.

## 2 MATERIALS AND METHODS

### 2.1 Effective Hamiltonian for BaTiO₃, PbTiO₃, and KNbO₃

The effective Hamiltonian used to study energy storage in some prototypical ferroelectrics (namely, BaTiO₃, PbTiO₃, and KNbO₃) can be expressed as (Nishimatsu et al., 2008; Luo et al., 2016)

\[
H_{eff} = \frac{M_{dipole}^2}{2} \sum_i \vec{u}_i^2 + \frac{M_{acoustic}^2}{2} \sum_i \vec{v}_i^2 + V^{self} (\{u_i\}) + V^{dip} (\{u_i\}) + V^{short} (\{u_i\}) + V^{rel,homo} (\{\eta_i\}) + V^{rel,homo} (\{w_i\})
\]

\[
+ V^{coup,homo} (\{u_i\}, \{\eta_i\}) + V^{coup,homo} (\{u_i\}, \{w_i\}) - Z^* \sum_i E \cdot \vec{u}_i
\]

where \( u_i \) is the local soft-mode amplitude located at the unit cell i, \( u_i \) is the local acoustic displacement vector, \( \eta_i \) and \( \eta_i \) represent the component of the homogeneous strain tensor in Voigt notation (Nye, 1985), and \( M_{dipole} \) and \( M_{acoustic} \) correspond to the effective masses for local soft modes and acoustic displacements, respectively. The different energies appearing in Eq. 1 are the two kinetic energies associated with the local soft modes and acoustic displacements, local mode self-energy, long-range dipole–dipole interaction, short-range interactions associated with the local soft modes, elastic energies stemming from homogeneous and inhomogeneous strains, coupling between local soft modes and both homogeneous in inhomogeneous strains, and effect of an external electric field, \( E \).

The effective Hamiltonian parameters for BaTiO₃, PbTiO₃, and KNbO₃ FE systems were determined from first-principles calculations [see details in References (Waghmare and Rabe, 1997; Waghmare et al., 1998; Nishimatsu et al., 2010)].

### 2.2 Effective Hamiltonian for Bi₁₋ₓNdₓFeO₃ Solid Solutions

An effective Hamiltonian (\( H_{eff} \)) approach was developed in Refs (Xu et al., 2015; Jiang et al., 2021b) for Bi₁₋ₓNdₓFeO₃ (BNFO) solid solutions. The total internal energy \( E_{int} \) of this effective Hamiltonian can be expressed as

\[
E_{int} = E_{BFEO} (\{u_i\}, \{\eta_i\}, \{\eta_i\}, \{\omega_i\}, \{m_i\}) + E_{Alloy} (\{u_i\}, \{\omega_i\}, \{m_i\}, \{\eta_i\})
\]

where \( E_{BFEO} \) is the effective Hamiltonian of pure BiFeO₃ (Korneev et al., 2007), while \( E_{Alloy} \) represents the effect of substituting Bi by Nd ions in the A sublattice of this perovskite compound. Technically, the effective Hamiltonian of BNFO comprises four different types of degrees of freedom: i) the local soft mode \( \{u_i\} \) centered on the A site i (Bi or Nd ion), which is directly related to the local electric dipole moment centered on unit cell i (Zhong et al., 1995); ii) strain tensor that includes the contributions of both homogeneous \( \{\eta_i\} \) and inhomogeneous \( \{\eta_i\} \) strains; iii) \( \{\omega_i\} \) that characterizes the oxygen octahedral tilting about the Fe ion located at the i site of the B sublattice (Korneev et al., 2006); and iv) magnetic moment \( \{m_i\} \) centered on the B site of Fe ions (Korneev et al., 2007). Note that a local quantity \( \eta_{loc}(i) = \frac{\delta R_{soc}}{8} \sum_j \sigma_j \) centered on the B site i of Fe ion, where \( \sigma_j \) represents the A sublattice atomic configuration distribution in the BNFO solid solutions and the sum over j runs over the 8 A nearest neighbors of Fe site i; \( \delta R_{soc} \) represents...
the $A$ sublattice relative difference of the ionic radius between the Nd and Bi ions. Note also that one can add to $E_{\text{int}}$ an energy contribution given by minus the dot product between polarization and applied electric field, in order to simulate the effect of such a field on physical properties (Xu et al., 2017).

BNFO systems are typically modeled by using $12 \times 12 \times 12$ supercells (containing 8,640 atoms) within this $H_{\text{eff}}$ scheme and inside, in which the $A$ site of Bi and Nd ions is randomly distributed. Practically, the total energy of this $H_{\text{eff}}$ approach can be used in Monte Carlo (MC) simulations to compute the static properties of BNFO solid solutions at a finite temperature. A total of 20,000 MC sweeps are typically used for equilibration, and an additional 20,000 MC sweeps are employed to compute statistical thermal averages at a finite temperature and an electric field, to obtain converged results (Xu et al., 2017).

### 2.3 Effective Hamiltonian for Ba(Zr,Ti)O$_3$ Solid Solutions

The first-principles-based effective Hamiltonian approach has also been recently developed and used to simulate the static and dynamical properties of bulks and films made of Ba(Zr,Ti)O$_3$ solid solutions (Akbarzadeh et al., 2012; Prosandeev et al., 2013a; Prosandeev et al., 2013b; Wang et al., 2016; Jiang et al., 2017; Jiang et al., 2022). The total internal energy of the effective Hamiltonian in Ba(Zr,Ti)O$_3$ contains two main terms too:

$$E_{\text{int}}(\{u\}, \{v\}, \eta_{ij}) E_{\text{loc}}(\{u\}, \{v\}, \{\sigma\})$$

where $\{u\}$ is the local soft mode in unit cell $i$ (which is proportional to the electric dipole moment centered on the $B$ site of Zr or Ti ions), $\{v\}$ are the variables related to the inhomogeneous strain inside cell $i$, $\eta_{ij}$ is the homogeneous strain tensor, and $\{\sigma\}$ describes the $B$-sublattice distribution (that is, Zr or Ti ion located at the $j$ site) in the Ba(Zr,Ti)O$_3$ solid solutions. Note that $E_{\text{int}}$ contains five different contributions: i) the local soft mode self-energy; ii) long-range dipole–dipole interaction; iii) energy as a result of short-range interactions between local soft modes; iv) elastic energy; and v) energy due to the interaction between local soft modes and strains (Zhong et al., 1995). The second energy term $E_{\text{loc}}$ describes how the actual distribution of Zr and Ti ions affects the energetics involving the local soft modes $u$, and the local strain variables (which depend on the $\{\sigma\}$ distribution).

This effective Hamiltonian has been implemented within MC simulations on $12 \times 12 \times 12$ supercells (8,640 atoms), in order to determine and understand energy storage in disordered Ba(Zr,Ti)O$_3$ (BZT) relaxor ferroelectrics, for the fixed composition of 50% of both Zr and Ti, in both bulks and epitaxial films (Jiang et al., 2022). Note that this $H_{\text{eff}}$ successfully predicted the existence of three characteristic temperatures in relaxor ferroelectrics. For instance, for BZT bulks with 50% of Zr and Ti ions, 1) the temperature $T_{\text{m}}=130$ K, at which the dielectric constant can exhibit a peak (Cross, 1994; Akbarzadeh et al., 2012); 2) the so-called novel critical temperature ($T^* = 240$ K) at which static polar nanoregions (PNRs) typically occur and that has been recently observed in relaxors (Svitelskiy et al., 2005; Dkhil et al., 2009; Akbarzadeh et al., 2012); and 3) Burns temperature ($T_b = 450$ K) that marks the dynamical PNRs at which the finite lifetime of polar fluctuations becomes prominent (Burns and Dacol, 1983; Akbarzadeh et al., 2012).

### 2.4 First-Principles Calculations for AlN/ScN Superlattices

In Ref. (Jiang et al., 2021a), first-principles calculations were performed on (001) epitaxial $1 \times 1$ AlN/ScN superlattices within the local density approximation to density functional theory (DFT) and using norm-conserving pseudopotentials (Hamann, 2013), as implemented in the ABINIT package (Gonze et al., 2002). The epitaxial strain can be expressed as $\eta_{\text{in}} = (a-a_{\text{eq}})/a_{\text{eq}}$, where $a_{\text{eq}}$ corresponds to the in-plane lattice constant of the equilibrium structure of the nonpolar $P\bar{6}m2$ phase (Jiang et al., 2019a). A $6 \times 6 \times 4$ grid of special $k$-point and plane-wave kinetic energy cutoff of 50 Hartrees were employed. The effects of dc electric fields applied along the pseudocubic [001] direction on structural properties were taken into account by using finite electric-field methods (Nunes and Vanderbilt, 1994; Nunes and Gonze, 2001; Souza et al., 2002; Zwanziger et al., 2012). The electrical polarization $P$ was computed from the Berry phase approach (King-Smith and Vanderbilt, 1993; Resta, 1994). Note that for each considered strain and magnitude of the applied field, the in-plane lattice vectors were kept fixed while the out-of-plane lattice vector and atomic positions were fully relaxed until all the forces acting on the atoms have a value smaller than $10^{-6}$ Hartrees/Bohr, in order to mimic epitaxial films being under electric fields.

### 3 RESULTS AND DISCUSSION

#### 3.1 Energy Storage in Perovskite Ferroelectrics

Let us first present the energy storage results of the prototypical perovskite ferroelectrics BaTiO$_3$, PbTiO$_3$, and KNbO$_3$. A first-principles-based effective Hamiltonian within molecular dynamics simulations was used for these perovskite ferroelectrics and is described in Section 2.1 and Ref. (Luo et al., 2016).

The temperature dependence of the $P-E$ hysteresis and energy density properties for BaTiO$_3$, PbTiO$_3$, and KNbO$_3$ are shown in Figure 1. The energy density of BaTiO$_3$ slowly increases with the temperature below the Curie point at 380 K. In contrast, the energy density rapidly increases with a temperature above the Curie point. Furthermore, the energy density behavior of KNbO$_3$ was numerically found to be very similar to BaTiO$_3$ because of the similarity in the structural phase transition and field-induced phase transition. In the case of PbTiO$_3$, the energy density varies nonmonotonically with the temperature, that is, it first reaches a peak around 820 K and then decreases. This can be explained by the fact that PbTiO$_3$ exhibits a rather weak polarization for temperatures above 820 K.
ideal for energy storage applications due to the square shape of their hysteresis loops—which typically gives rise to low energy density and efficiency.

### 3.2 Energy Storage in Antiferroelectrics

As compared to typical FE systems, antiferroelectric (AFE) materials are very promising for high-power energy storage...
applications because of their characteristic $P$-$E$ double hysteresis loops, which is schematized in Figure 2A (Xu et al., 2017). There, $E_{\text{up}}$ describes the critical field at which the AFE-to-FE transition appears upon charging when increasing field, while $E_{\text{down}}$ denotes the critical field for the FE-to-AFE phase transition upon discharging (decreasing field). The green area in Figure 2A represents the energy density.

As indicated in Section 2.2, a first-principles-based effective Hamiltonian method was employed to investigate the energy storage properties in the rare earth-substituted BiFeO$_3$ multiferroic systems, in general, and disordered BNFO solid solutions, in particular (Xu et al., 2015). This effective Hamiltonian method successfully reproduced the temperature-solutions, in particular (Xu et al., 2017). There, $E_{\text{max}}$ is the maximum applied electric field being 2.6 MV/cm. The energy density for fields applied along the [001] direction gives the largest values in magnitude. In contrast, the smallest energy densities in Figure 4A correspond to fields applied along the [111] direction. Figure 4B further shows that the highest efficiency corresponds to the electric field applied along the [110] direction.

Three compositions ($x = 0.5$, $0.7$, and $1.0$) were considered for the electric field applied along the [001] direction, and one composition of $x = 0.5$ has been selected for the field along the [110] direction in BNFO solid solutions. The energy storage-related results are shown in Figure 5 [note that the intrinsic breakdown field of $E_{\text{max}} = 4.37$ MV/cm was considered, which is estimated based on an empirical relation (Wang, 2006) that takes into account the experimental band gap of BiFeO$_3$ (Ihlefeld et al., 2008)]. More precisely, the related $P$-$E$ hysteresis curves are shown in Figure 5A, while Figure 5B displays the energy density of BNFO obtained from the $P$-$E$ hysteresis curves of Figure 5A. The energy densities of other experimentally reported materials are shown for comparison and are smaller than that of BNFO systems. The predicted large energy densities (efficiencies) are 164, 191, and 213 J/cm$^3$ (76%, 88%, and 91%), respectively for $x = 0.5$, 0.7, and 1, respectively, for the electric field applied along the [001] direction. Similarly, both energy density and efficiency (161 J/cm$^3$ and 91%) of BNFO with $x = 0.5$ are very large for the
Energy Storage from First Principles

\[ E_{\text{down}} = \left( \frac{\delta E_{\text{down}} - \delta^0}{\delta E_C - \delta^0} \right) E_C \]
\[ E_{\text{up}} = \left( \frac{2\delta E_C - \delta E_{\text{down}} - \delta^0}{\delta E_C - \delta^0} \right) E_C \]

where \( \delta^0 \), \( \delta E_{\text{down}} \), and \( \delta E_C \) are the FE-to-AFE barrier at zero field, \( E_{\text{down}} \), and \( E_C \), respectively. Consequently, combining Eqs 4–8 leads to

\[ W = \left( \frac{\delta E_{\text{down}} - \delta^0}{\delta E_C - \delta^0} \right) \left( U^0_{\text{FE}} - U^0_{\text{AFE}} \right) + \frac{1}{2} \epsilon_0 \omega_1 E_{\text{max}}^2 \]
\[ \eta = \frac{\left( \frac{\delta E_{\text{down}} - \delta^0}{\delta E_C - \delta^0} \right) \left( U^0_{\text{FE}} - U^0_{\text{AFE}} \right) + \frac{1}{2} \epsilon_0 \omega_1 E_{\text{max}}^2}{\left( \frac{\delta E_{\text{down}} - \delta^0}{\delta E_C - \delta^0} \right) \left( U^0_{\text{FE}} - U^0_{\text{AFE}} \right) + \frac{1}{2} \epsilon_0 \omega_1 E_{\text{max}}^2} \]

Interestingly, the energy density and efficiency data obtained by the effective Hamiltonian MC simulations and shown in Figures 4A,B can be well fitted by Eq. 9 and Eq. 10, respectively (the related parameters are shown in Figures 4C–E). These good fits of Figures 4A,B testify the validity of the aforementioned simple model, which can thus be used to understand and analyze energy storage properties for other AFE materials.

### 3.3 Energy Storage in Relaxor Ferroelectrics

Relaxor ferroelectrics have also attracted special attention because of their high energy densities and efficiencies, which is highly promising for energy storage applications. Despite the fact that the highest recoverable energy density was achieved in Ba(Zr,Ti)O₃ relaxor FE thin films at a sustained high electric field of 3.0 MV/cm (Instan et al., 2017), many questions remain to be addressed. For instance, can the first-principles-based effective Hamiltonian method reproduce the experimental finding of ultrahigh energy density in the lead-free relaxor Ba(Zr,Ti)O₃ system? What will happen if one considers the epitaxial strain on energy storage properties? In particular, could such ultrahigh energy density be understood by a simple phenomenological model? To the best of our knowledge, the effect of the direction of the applied electric field on energy density and efficiency is also presently unknown in Ba(Zr,Ti)O₃ relaxor ferroelectrics, both in their bulk and epitaxial films.

This section is to answer all these questions by using the first-principles-based effective Hamiltonian approach in Ba(Zr, Ti)O₃ bulk and epitaxial films (Jiang et al., 2022). The effective Hamiltonian is described in Section 2.3.

#### 3.3.1 Energy Storage in BZT Bulk

Let us focus on the \( P-E \) curves in BZT bulk. Note that the simulated electric field is larger than the corresponding experimental one by a factor of 100, which is typical for atomistic effective Hamiltonian simulations (Xu et al., 2017; Jiang et al., 2018) because structural defects are not considered in the theory. A maximum applied field of 3.0 MV/cm was considered, which corresponds to the experimentally applied one in Ba(Zr,Ti)O₃ thin films (Instan et al., 2017). Figures
6A–C display the polarization versus electric field curves at 300 K for three different fields’ directions (namely, electric fields applied along the pseudocubic [001], [110], and [111] directions, respectively) in BZT bulk. An ideal energy efficiency of 100% is predicted due to the complete reversibility of the charging and discharging processes of the P-E curves.

The local dipole configurations of Figures 6A–C show that the dipoles align along the electric field’s applied direction. Figures 6D–F display the electric field versus polarization (E-P) data for fields applied along the pseudocubic [001], [110], and [111] directions at room temperature, and the green areas represent the energy densities.

The energy density can thus be extracted from the P-E or E-P data for different temperatures and applied field directions. Figure 7A shows that the energy densities linearly increase with temperature for electric fields applied along the [001], [110], and [111] pseudocubic directions. Ultrahigh energy densities are predicted (between 147 and 155 J/cm³), which agree well with experimental values in Ba(ZrₓTi₁₋ₓ)O₃ thin films (Instan et al., 2017).

In order to understand the origin of these energy storage results, a simple Landau-type free energy model was used to describe nonlinear behaviors (Jiang et al., 2021a) and for which, the free energy is given by

\[ F = \frac{1}{2}aP^2 + \frac{1}{4}bP^4 - EP \]  \hspace{1cm} (11)

where \( a \) and \( b \) are coefficients of the quadratic and quartic polarization terms, respectively. At equilibrium condition, one must have \( \frac{\partial F}{\partial P} = 0 \), which thus yields

\[ E = aP + bP^3 \]  \hspace{1cm} (12)

The numerical E-P data for all considered temperatures and field directions were found to be well fitted by Eq. 12, which allows to extract the important \( a \) and \( b \) parameters. Figures 8A–C show the related \( a \) and \( b \) parameters as a function of temperature for electric fields applied along the [001], [110], and [111] directions, respectively, at a maximal
applied electric field equal to 3.0 MV/cm. The $a$ parameter linearly increases with temperature, and the $b$ parameter only slightly linearly decreases with temperature for the three different field directions. These $a$ and $b$ coefficients are involved in the expression of the energy density as (Jiang et al., 2021a).
\[ U = \int_0^{P_{\text{max}}} (aP + bP^3) dP = \frac{1}{2} aP_{\text{max}}^2 + \frac{1}{4} bP_{\text{max}}^4 \quad (13) \]

where \( P_{\text{max}} \) is the maximum polarization at the maximal applied electric field of \( E_{\text{max}} \). Note that \( P_{\text{max}} \) can be obtained from the MC simulations or via Eq. 12 taken at \( E_{\text{max}} \). Figure 8D shows that both methods give nearly identical results. Eq. 13 therefore indicates that only \( a, b \), and \( P_{\text{max}} \) completely dominate the behaviors and values of the energy density but also tells us that the energy density can be decomposed into two rather simple terms, namely, \( \frac{1}{2} aP_{\text{max}}^2 \) and \( \frac{1}{4} bP_{\text{max}}^4 \).

Figures 7B–D show the total and decomposed energy densities calculated from Eq. 13, along with the total energy densities obtained from the MC data (with a maximal field of 3.0 MV/cm). One can clearly see that, for any considered temperature, the energy densities obtained from the MC simulations provide nearly identical results than those given by Eq. 13.

### 3.3.2 Energy Storage in (001) BZT Films

Let us now focus on the energy storage performance for (001) BZT films versus different epitaxial strains. Figures 9A–C display the \( P-E \) curves at room temperature and zero strain for fields applied along the pseudocubic [001], [110], and [111] directions, respectively. Three types of \( P-E \) data are shown in Figure 9C, which correspond to the [110] in-plane component of the polarization \( P_{\text{in}} \), [001] out-of-plane component of the polarization \( P_{\text{out}} \), and the total polarization \( P_{\text{tot}} \). Moreover, Figures 9D–F show the \( E-P \) data at zero strain and room temperature for fields applied along three different directions, which can be well fitted by Eq. 12 (solid red lines). Figure 10A reports the energy density as a function of strain at 300 K and \( E_{\text{max}} = 3.0 \text{ MV/cm} \) for electric fields applied along the [001],
and [111] directions, respectively. Note that the [111]in and [111]out notations distinguish between the in-plane and out-of-plane components of the polarization when the field is applied along the [111] direction. Figure 10A shows that the energy densities for all considered strains are still large in BZT films (basically larger than 100 J/cm³).

In order to understand the origin of the energy density results in BZT films, we can also use Eq. 12 and Eq. 13. Figures 10B–E display the fitting parameters a and b, while Figure 10F shows the \( P_{\text{max}} \) obtained from both MC simulations and Eq. 12 at \( E_{\text{max}} \) as a function of strain. The \( a \) parameter linearly increases with strain ranging between \(-3\%\) and \(+3\%\), while \( P_{\text{max}} \) linearly decreases with strain when fields are applied along the [001] direction. In contrast, the \( a \) parameter linearly decreases with strain while \( P_{\text{max}} \) linearly increases with strain when the field is along the [110] direction. The \( a \) parameter and \( P_{\text{max}} \) related to the in-plane and out-of-plane components for electric fields applied along the [111] direction have the same qualitative behavior as for fields along the [110] and [001] directions, respectively. Note that for all three field directions, the \( b \) parameter of Figures 10B–E is basically a constant with strain.

The behaviors of \( a \), \( b \), and \( P_{\text{max}} \) allow us to understand and analyze the results of the energy density in Figure 10A. The total and decomposed energy densities obtained from Eq. 13 are shown in Figure 11, where the stars display the MC data for the total energy densities for comparison. Figure 11A shows that the first term of \( \frac{1}{2} a P_{\text{max}}^2 \) increases with strain, while the second term \( \frac{1}{4} b P_{\text{max}}^4 \) decreases with strain when the field is applied along the [001] direction. The total energy density for this field direction increases with strain because the change in \( \frac{1}{2} a P_{\text{max}}^2 \) is greater than that of \( \frac{1}{4} b P_{\text{max}}^4 \). In contrast, the energy density behaviors of Figure 11B are qualitatively opposite to the [001] case when the field is applied along the [110] direction. Figures 11C,D show that the energy density associated with the in-plane and out-of-plane components of the polarization for fields applied along the [111] direction is very similar to the cases of field applied along [110] and [001], respectively. This is because increasing the strain from compressive to tensile energetically
disfavors a polarized state having an out-of-plane component while favoring the formation of an in-plane polarization along [110].

3.4 Energy Storage in Epitaxial AlN/ScN Superlattices

In order to improve the energy storage performance, it is timely and important to wonder if there are some multifunctional materials awaiting to be discovered/revealed that have 1) ultrahigh energy storage density; 2) optimal 100% energy efficiency; and 3) giant strain levels when under electric fields. Note that a 100% energy efficiency automatically implies that the transition from the paraelectric/AFE to FE states is fully continuous and reversible. To maximize both energy density and efficiency, one can, for example, imagine a nonlinear dielectric material that exhibits large polarization under feasible high electric fields while being initially in a nonpolar phase at a zero field, and with the charging and discharging processes being completely reversible. The III–V semiconductor-based systems made by mixing AlN and ScN to form Al$_{1-x}$Sc$_x$N solid solutions or AlN/ScN superlattices are attractive as these systems can have very large polarization (on the order of 1.0 C/m$^2$) (Jiang et al., 2019b; Fichtner et al., 2019; Noor-A-Alam et al., 2019; Yasuoka et al., 2020; Yazawa et al., 2021), and an FE phase is energetically close to a nonpolar phase (such that the ground state may be tuned by a physical handle) (Jiang et al., 2019b), which is highly promising for the energy storage performance. The aim of Ref (Jiang et al., 2021a) was to demonstrate that ultrahigh energy storage performance can be achieved in 1 × 1 AlN/ScN superlattices, by using first-principles calculations (the method is described in Section 2.4).

Let us now focus on some physical properties of 1 × 1 AlN/ScN superlattices under different epitaxial strains. Previous studies have predicted the existence of different strain-induced regions in 1 × 1 AlN/ScN superlattices (Jiang et al., 2019b), including a wurtzite-derived structure (polar $P\bar{3}m$$_1$ space group with a polarization along the $c$-axis) and a hexagonal-derived phase (paraelectric $P\bar{6}m$$_2$ space group). They are related to each other by a continuous change in the internal parameter ($u$) and the axial ratio ($c/a$) (Levin et al., 2010). Figure 12 shows the $P$-$E$ curves for different compressive strains smaller than −1%, all having the wurtzite-derived structure for ground state (see Figure 13C for such structure). A similar information is displayed in Figure 13A but for compressive strains and tensile strains larger than −0.5%, which result in a hexagonal-derived ground state (see Figure 13B for such phase). The values of the electric fields considered here are the theoretical ones divided by three, in order that the $P$-$E$ loop of the 1 × 1 AlN/ScN system under a −3% strain becomes very similar to the experimental one corresponding to the Al$_{0.57}$Sc$_{0.43}$N film (Fichtner et al., 2019)—as demonstrated in Figure 12B. Note that ab-initio electric fields are known to be typically larger than their experimental counterparts (Lu et al., 2019; Chen et al., 2019; Jiang et al., 2020). Note also that the polarizations under zero field computed in the 1 × 1 AlN/ScN superlattice experiencing a compressive strain of −3% and the ones measured in the Al$_{0.57}$Sc$_{0.43}$N system were found to be very close to each other (see Figure 12A), which explains why we decided to determine the renormalization factor of the theoretical fields by comparing the $P$-$E$ loops of these two compounds.
Regarding the magnitude of the (renormalized) fields to be considered here, it is first worthwhile to indicate that a recent experiment reported a feasible electric field as high as ~5 MV/cm in Al$_{1-x}$Sc$_x$N films (Fichtner et al., 2019). Moreover, one can also estimate the intrinsic breakdown field of such systems via the universal expression (Wang, 2006), that is $E_{\text{BI}} = 1.36 \times 10^5 \left( \frac{E_g}{1.5} \right) ^{\frac{3}{2}}$ (V/m), where $E_g$ is the band gap, and $\alpha = 1$ for insulators, and $\alpha = 3$ for semiconductors. In such expression, a theoretical corrected band gap of ~3.1 eV is considered for the 1 × 1 AlN/ScN superlattice ground state (Jiang et al., 2019b). An intrinsic breakdown field electric field, $E_{\text{break}}$, of about 6.3 MV/cm is obtained, which is the maximal value of applied electric fields that will be considered below.

Several features are remarkable in Figure 12B and Figure 13A. First of all, the P-E loops of Figure 12B are those typical of ferroelectrics with first-order transitions (between two wurtzite-derived structures) for some values of polarization changing of sign under the application of initially opposite electric fields, but with the magnitude of the critical fields of such transitions being very strongly strain dependent. For example, the magnitude of these critical fields is 5.8 MV/cm versus 0.2 MV/cm for strains of −5% and −1%, respectively. Such a strong dependency of these fields has also been observed but with respect to the Sc composition in Al$_x$Sc$_{1-x}$N solid solutions (Fichtner et al., 2019). Consequently, varying composition in these solid solutions or changing the strain for a fixed alloy or superlattice should yield similar physics and results. Secondly and strikingly, Figure 13A reveals a nonlinear behavior of the polarization for small fields (starting from the paraelectric $R3n$ hexagonal-derived phase at a zero field), with the transition between the paraelectric hexagonal-like structure to an FE wurtzite-type phase being continuous and fully reversible upon increasing and decreasing electric fields. Note that such type of continuous and reversible transition has been mentioned in relaxor ferroelectrics (Jiang et al., 2022). As we are going to see, such latter features are indeed promising for applications in electronics and electric power systems. Moreover, larger strain makes the polarization less nonlinear at small fields and also results in a smaller out-of-plane polarization at large fields (Figure 13A), which are behaviors that can affect energy storage density (as we also discuss below).

Let us now focus on energy storage properties for the 1 × 1 AlN/ScN superlattices for misfit strains changing from −0.5% to +1%. Figure 13A shows that the energy efficiency is 100% because the charging and discharging processes are completely reversible. Regarding the calculated energy density, Figure 13D reports it as a function of epitaxial strain ranging between −0.5% and +1%, for electric fields up to two different values, namely, $E_{\text{max}} = 5$ MV/cm, which has been experimentally realized (Fichtner et al., 2019), and $E_{\text{break}} = 6.3$ MV/cm which has been estimated as the intrinsic breakdown field. The energy density can reach very large values, that is, it varies from 127 to 135 J/cm$^3$ and from 187 to 200 J/cm$^3$ when using 5 and 6.3 MV/cm for the maximal applied field, respectively. All these large energy densities with the ideal efficiency of 100% thus indicate that the 1 × 1 AlN/ScN superlattices are highly promising for high-power energy storage applications.

To understand these energy storage results of Figure 13D, we can also use Eqs 11–13 to describe the behaviors in initially nonpolar 1 × 1 AlN/ScN superlattices. Figure 14A displays the E-P data for electric field applied along the pseudocubic [001] direction at a 0.25% strain. The yellow area represents the energy density. The E-P data can be well fitted by Eq. 12 for all the considered strains ranging from −0.5 to +1%.

Figure 14B displays the $a$ and $b$ fitting parameters versus strain for fields up to the intrinsic breakdown field $E_{\text{break}} = 6.3$ MV/cm. It is worth noting that the $a$ parameter linearly increases with strain ranging from −0.5 to +1%. In contrast, the $b$ parameter linearly decreases with strain. Note that the change in $a$ is much larger in percentage than the change in $b$. Figure 14C shows the maximum polarization $P_{\text{max}}$ as a function of strain obtained from DFT calculations and the Landau model at $E_{\text{max}} = 6.3$ MV/cm. For all considered strains, the DFT and Landau model provide nearly identical results. In order to understand the results of Figure 13D and Eq. 13 is used to obtain the energy density at $E_{\text{max}} = 6.3$ MV/cm for strain ranging...
FIGURE 13 | (A) $P$-$E$ hysteresis curves for different strains with the ground state being a hexagonal-derived phase in $1 \times 1$ AlN/ScN superlattices. (B,C) represent the crystal structures of 1% tensile strain under electric fields of 0 and 5 MV/cm, respectively. (D) Energy density as a function of strain for two different maximum fields of 5.0 and 6.3 MV/cm. Reprinted figure with permission from (Jiang et al., 2021a). Copyright 2021 by the American Physical Society.

FIGURE 14 | (A) $E$-$P$ data for the strain at 0.25%, with the yellow area showing the energy density (the solid green line represents the fit of the DFT results by Eq. 12). (B) Evolution with strain of fitting parameters $a$ and $b$. (C,D) The strain dependence of $P_{\text{max}}$ and energy density obtained from DFT and Eq. 13. These data correspond to $E_{\text{max}} = 6.3$ MV/cm. Reprinted figure with permission from (Jiang et al., 2021a). Copyright 2021 by the American Physical Society.
between $-0.5$ and $+1\%$. Figure 14D shows that the Landau model and DFT-obtained energy density behave in a similar qualitative and even quantitative way with the strain, implying that the Landau model can be trusted.

Once again, Eq. 13 indicates that the energy density can be decomposed into two terms. The first term relies on the product of the fitting parameter $a$ and $P_{\text{max}}^2$, while the second term depends on the product between the $b$ parameter and $P_{\text{max}}^4$. Figures 15A,B display the total and decomposed energy densities versus strain obtained from Eq. 13 for two different maximum fields $E_{\text{max}} = 5.0$ and 6.3 MV/cm, respectively. Figure 15 shows that the Landau model predicted total energy density exhibits a maximum at 0 and 0.25% misfit strain when the largest applied fields are 5.0 and 6.3 MV/cm, respectively. Such numerical findings agree very well with the DFT-obtained results of Figure 13D. The strain dependency of $\frac{1}{2}aP_{\text{max}}^2$ and $\frac{1}{4}bP_{\text{max}}^4$ eventually give rise to a maximum value of the total energy density occurring at different specific strain for each considered maximal electric field.

### 4 SUMMARY AND PERSPECTIVE

This review summarizes and discusses the energy storage properties in ferroelectrics, lead-free antiferroelectrics, relaxor ferroelectrics, and epitaxial AlN/ScN superlattices using direct first-principles and first-principles-based effective Hamiltonian schemes. Ultrahigh energy densities and efficiencies are predicted in 1) rare-earth substituted BiFeO$_3$ AFE compounds; 2) bulks and films made of the lead-free Ba(Zr$_{0.5}$Ti$_{0.5}$)$_3$O$_3$ relaxor ferroelectrics; and 3) epitaxial AlN/ScN superlattices with initially nonpolar states. Note that an ideal 100% efficiency is predicted in Ba(Zr$_{0.5}$Ti$_{0.5}$)$_3$O$_3$ relaxor ferroelectrics and epitaxial AlN/ScN superlattices due to the second-order character of the field-induced transition toward an FE state. For the studied AFE materials, a simple phenomenological model was proposed to describe the energy density and efficiency, which should be useful in the search for other high energy storage performance in other antiferroelectrics. Another simple Landau model was developed to analyze and understand the energy storage results in BZT relaxor ferroelectrics and epitaxial AlN/ScN superlattices, which reproduces very well the numerical results. The proposed Landau model can also be easily employed for other relaxor ferroelectrics and nonlinear dielectrics, providing insight that there is a trade-off to maximize the energy density: the system should neither be too close nor too far from an FE phase transition.

Note also that one very recent work using high-throughput second-principles calculations (Aramberri et al., 2020) indicated that FE/paraelectric superlattices can be promising for energy storage as well. Other systems can also be investigated by first-principles-based effective Hamiltonian methods, or other ab initio techniques, in the near future for energy storage. Examples include the prototypical relaxor ferroelectrics Pb(Mg$_{1/3}$Nb$_{2/3}$)$_3$O$_3$ and Pb(Mg$_{1/3}$Nb$_{2/3}$)$_3$O$_3$-PbTiO$_3$, and (Bi,R)FeO$_3$ antiferroelectrics with R being a rare-earth species different from Nd. We thus hope that this review is useful to the scientific community and deepens the field of energy storage.

### AUTHOR CONTRIBUTIONS

ZJ wrote the original manuscript. LB supervised the study. BX, SP, JÍ, HX and LB revised the manuscript. All authors contributed to the interpretation of the results.

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