First-principles investigation of the ferroelectric, piezoelectric and nonlinear optical properties of LiNbO$_3$-type ZnTiO$_3$

Jing Zhang$^{1,*}$, Bin Xu$^1$, Yu-Sheng Wang$^1$, Zhen Qin$^1$ & San-Huang Ke$^2$

The newly synthesized LN-type ZnTiO$_3$ (J. Am. Chem. Soc. 2014, 136, 2748) contains cations with the electronic configurations nd$^{10}$ (Zn$^{2+}$: 3d$^{10}$) along with second-order Jahn-Teller (SOJT) nd$^0$ (Ti$^{4+}$: 3d$^0$) cations. This is different from traditional ferroelectrics with the electric configurations of d$^0$ transition metal ions or/and lone pair electrons of ns$^2$. Using a first-principles approach based on density functional theory, we investigate the electronic structure, zone-center phonon modes, piezoelectric and nonlinear optical properties of the LiNbO$_3$-type ZnTiO$_3$. The electronic structure indicates that this compound is a wide direct-band-gap insulator. The results reveal that this compound is a good ferroelectric material with a large spontaneous polarization of 90.43 μC/cm$^2$. The Raman scattering peaks of $A_1$ and $E$ modes are assigned to their zone-center optical modes. Additionally, the large piezoelectric and nonlinear optical susceptibilities reveal that LiNbO$_3$-type ZnTiO$_3$ is a high-performance lead-free piezoelectric and nonlinear optical crystal.

In recent years, noncentrosymmetric (NCS) compounds have attracted great interest in physics and material science because of their symmetry-dependent ferroelectric, piezoelectric and second-order nonlinear optical (NLO) properties, etc. When searching for other polar oxides, researchers pay special attention to two classes of compounds, specifically those that include second-order Jahn-Teller distorted (SOJT) cations (Te$^{4+}$, Sn$^{4+}$, Ti$^{4+}$, Mo$^{6+}$, Nb$^{5+}$, V$^{5+}$, etc.) and cations with stereoactive lone pair electrons of ns$^2$ (Bi$^{3+}$, Pb$^{2+}$, Se$^{4+}$, etc.)3–12. For the NCS compounds, there are two famous structures: perovskite-type (Pv-type) and LiNbO$_3$-type (LN-type) phases. Taking into account the structural relationship between the above two, the LiNbO$_3$-type structure can be regarded as the derivative of the perovskite structure 13. In general, most of the LN-type compounds cannot be synthesized under general conditions and instead require high temperature and high pressure.

In 2014 a new NCS compound, the LN-type ZnTiO$_3$, was synthesized by Inaguma et al. under high temperature and high pressure14. Their results show that LN-type ZnTiO$_3$ has a large spontaneous polarization and greater second harmonic generation (SHG) response compared to LiNbO$_3$ and LN-type ZnSnO$_3$. According to Bartram et al.15, Ito et al.'s reports16, two paraelectric phases of ZnTiO$_3$ are ilmenite (IL)-type (hexagonal space group R3) and Pv-type (orthorhombic space group Pnma) structures, respectively. Ito et al. reported that IL-type ZnTiO$_3$ decomposes into ZnO and TiO$_2$ under a pressure of 20~25 GPa16; inspired by this, Inaguma et al. successfully synthesized LN-type ZnTiO$_3$ at less than 20 GPa. As discussed by Navrotsky13 and Linton et al.'s reports17, the LN-type compounds such as ZnSnO$_3$, FeTiO$_3$, MnTiO$_3$, and ZnGeO$_3$, etc. are metastable and quenched products from the high-pressure perovskite phases18–24. This means that LN-type ZnTiO$_3$ is regarded as a retrograde product from the high-pressure perovskite phase on pressure release14. The crystal structures of ZnTiO$_3$ in the ferroelectric and two paraelectric phases are presented in Figs. 1 and 2, respectively.

Notice that recently-synthesized LN-type ZnSnO$_3$ and CdPbO$_3$ are novel polar oxides (hexagonal space group R3c) that include only the cations with the electronic configurations of nd$^{10}$ (Zn$^{2+}$: 3d$^{10}$, Cd$^{2+}$: 4d$^{10}$, Sn$^{4+}$: 4d$^{10}$, Pb$^{2+}$: 5d$^{10}$) and provide a new strategy for synthesizing new polar compounds. The LN-type ZnTiO$_3$ contains not only Zn$^{2+}$ (3d$^{10}$), but also Ti$^{4+}$ (3d$^0$), the former and later belonging to nd$^{10}$ and SOJT nd$^0$ cations, respectively. Although LN-type ZnTiO$_3$ and ZnSnO$_3$ have the similar crystal structures, experimental results have shown

$^1$School of of Physics and Electronics, North China University of Water Resources and Electric Power, ZhengZhou, 450045, China. $^2$School of Physics Science and Engineering, Tongji University, 1239 Siping Road, Shanghai, 200092, P.R. China. *email: zhangjing@ncwu.edu.cn
that the SHG intensity of LN-type ZnTiO$_3$ is 24 times greater than that of LN-type ZnSnO$_3$\textsuperscript{14}. The space group of LN-type ZnTiO$_3$ belongs to the 3m polar point group, so this compound is a promising candidate as a piezoelectric and nonlinear optical material. Therefore, LN-type ZnTiO$_3$ provides a perfect example for comparing the influence that the nd$^{10}$ and SOJT nd$^{0}$ cations have in producing the ferroelectric, piezoelectric and nonlinear optical behavior.

Nowadays, first-principles calculations based on density functional theory (DFT) play an important role in meeting the needs of experimenters because they can accurately predict the properties of new materials at the atomic scale. In general, the measurements of piezoelectric and nonlinear optical properties require very high crystal quality, specialized laboratories, and are expensive, so first-principles calculations provide an alternative to predicting optical and piezoelectric properties, and can be microscopically explain the relationship between

Figure 1. The crystallographic structures of LiNbO$_3$ (LN)-type ZnTiO$_3$ (left, space group R3c) and ilmenite (IL)-type ZnTiO$_3$ (right, space group R3) along the z-axis.

Figure 2. A view of the crystal structure of perovskite(Pv)-type ZnTiO$_3$ (space group Pnma) along the y-axis.
structure and properties. First-principles calculations including the modern theory of polarization, linear corresponding approaches, as well as the density functional perturbation theory (DFPT), can help us study the ferroelectric, piezoelectric, and nonlinear optical properties of materials. In addition to traditional ferroelectrics, first-principles calculations have made great progress in predicting and investigating new nonlinear optical crystal, multiferroic materials, two-dimensional ferroelectrics, and ferroelectric metal, etc. In order to study the intrinsic correlation from the paraelectric to ferroelectric phase transition, we have investigated the zone-center phonon modes of the ilmenite, perovskite and LiNbO$_3$-type ZnTiO$_3$ phases, respectively. Additionally, there have been no prior reports on the piezoelectric and nonlinear optical properties, including nonlinear optical susceptibilities and electro-optical coefficients, of LN-type ZnTiO$_3$, and so in this paper we carry out first-principles calculations to investigate the origin of the ferroelectric behavior, and analyze the piezoelectric and nonlinear optical properties of LN-type ZnTiO$_3$ for the first time. Since the piezoelectric and nonlinear optical properties of this type of novel material with nd$^8$ and SOJT nd$^6$ cations have not been investigated previously, our calculations provide an important complement to experimental research.

Method

Our calculations are based on the framework of density functional theory (DFT). We mainly used the ABINIT package. In order to calculate the electronic structure, spontaneous polarization, zone-center phonon modes, piezoelectric and nonlinear optical properties, we adopt norm-conserving pseudopotentials based on the local density approximation (LDA) as exchange-correlation potentials. An 8 $\times$ 8 Monkhorst-Pack k-point mesh is used with a plane wave cut-off of 45 hartrees. The Zn 3d, 4s and Ti 3d, 4s, as well as O 2s, 2p electrons are regarded as valence states to construct the pseudopotentials. The electronic structures are also calculated by adopting ultrasoft pseudopotentials based on the Vienna ab initio simulation package (VASP), and the exchange-correlation potentials are based on LDA and the general gradient approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) functional, respectively. Additionally, due to DFT systematically underestimate band gaps with respect to experiment, the Hedin-Sjölander-Ernzerhof (HSE) screened hybrid functional (with the version HSE06) is used to calculate the band structures.

The calculations of the polarization and piezoelectric properties are based on linear response functions, while the computations of nonlinear optical properties are based on nonlinear response functions. The linear and nonlinear response calculations are performed using density functional perturbation theory (DFPT). In order to calculate the above physical properties, the homogeneous electric fields, atomic displacements and stresses are regarded as perturbations. When stress is applied to a piezoelectric crystal, its interior will produce a polarization phenomenon where opposing positive and negative charges appear on its two opposite surfaces. This phenomenon is called the positive piezoelectric effect. On the contrary, when the electric field is applied in the polarization direction, the piezoelectric crystal disappears. This phenomenon is called the reverse piezoelectric effect. In this work, we calculate the piezoelectric stress tensor from the zero-field derivative of polarization by using stress as a perturbation:

$$\epsilon_{ij} = \frac{\partial P_i}{\partial \eta_j}$$

(1)

where $\eta$ and $i$ represent second-rank stress tensor and the Cartesian coordinate direction. In the actual computation, the piezoelectric stress tensor comes from the response from fixed ions and relative displacement of the ions:

$$\epsilon_{ij} = \frac{\partial P_i}{\partial \eta_j} + \sum_k \frac{\partial P_i}{\partial \mu_k} \frac{\partial \mu_k}{\partial \eta_j}$$

(2)

where $\mu$ represents the displacement of the ions. For an insulator, the relation between the polarization and macroscopic electric field can be described as follows:

$$P_i = P_i^s + \sum_{j=1}^3 x^{(1)}_{ij} \varepsilon_j + \sum_{j=1}^3 \sum_{j=1}^3 x^{(2)}_{ijl} \varepsilon_j \varepsilon_l + \ldots$$

(3)

where $P_i^s$ represents spontaneous polarization in zero electric field; $x^{(1)}_{ij}$ are linear dielectric constants, and $x^{(2)}_{ijl}$ are second-order nonlinear optical (NLO) coefficients. The NLO and electro-optic (EO) coefficients can be calculated from third-order energy derivatives within the 2n+1 theorem. Like LiNbO$_3$ and LN-type ZnSnO$_3$, we use the more convenient d tensor to represent NLO coefficients $x^{(2)}_{ijl} (d_{ijl} = \frac{1}{2} x^{(2)}_{ijl})$. When applying an electric field to some crystals, especially piezoelectric crystals, their refractive index changes. This characteristic of a crystal can be described by refractive index ellipsoids. The phenomenon is known as the linear electro-optic (EO) effect or Pockels Effect:

$$\Delta \left( \frac{1}{n^2} r_{ij} \right) = \sum_{j=1}^3 x_{ij} \varepsilon_j$$

(4)

where $n$ and $r_{ij}$ represent refractive index and linear EO coefficients ($i = 1 \sim 6$, and $j = 1 \sim 3$), respectively. Pockels effect exists only in the NCS crystals. The electro-optical (EO) tensor arises from the sum of three contributions: the electronic part, ionic contribution and piezoelectric effects.
Results and Discussions

Electronic structure. Firstly, we perform the full geometry optimization to determine the crystal parameters in the paraelectric and ferroelectric phases. According to the optimized geometry (see Table 1), we have performed the electronic structure calculations of the LiNbO$_3$-type ZnTiO$_3$ based on ultrasoft and norm-conserving pseudopotentials and Heyd-Scuseria-Ernzerhof screened hybrid functional (HSE06).

![Energy band structure of LiNbO$_3$-type ZnTiO$_3$](image)

**Figure 3.** The band structures of LiNbO$_3$-type ZnTiO$_3$ along the high symmetry directions in the Brillouin zone based on norm-conserving pseudopotentials within GGA.

Table 1. The calculated lattice constants and volumes of the ilmenite (IL)-type (space group $R_3$) and Perovskite (Pv)-type (space group Pnma) and LiNbO$_3$-type (space group $R_3c$) ZnTiO$_3$ based on norm-conserving (NC), ultrasoft pseudopotentials and Heyd-Scuseria-Ernzerhof screened hybrid functional (HSE06).

| Compound | Space Group | a (Å) | b (Å) | c (Å) | V (Å$^3$) |
|----------|-------------|-------|-------|-------|-----------|
| ZnTiO$_3$ ($R_3$) | Expt ref. | 5.079 | 5.079 | 13.927 | 311.1319 |
| Present (LDA-NC) | 5.0564 | 5.0564 | 13.9001 | 307.7801 |
| Present (GGA-NC) | 5.1647 | 5.1647 | 14.3519 | 331.5384 |
| Present (GGA-PBEsol-NC) | 5.1169 | 5.1169 | 14.1530 | 320.9172 |
| ZnTiO$_3$ (Pnma) | Present (LDA-NC) | 5.2026 | 7.4146 | 5.0631 | 195.3118 |
| Present (GGA-NC) | 5.3258 | 7.5722 | 5.18200 | 208.9797 |
| Present (GGA-PBEsol-NC) | 5.2751 | 7.4955 | 5.135123 | 202.8997 |
| ZnTiO$_3$ ($R_3c$) | Present (LDA-NC) | 5.09452(12) | 5.09452(12) | 13.7177(3) | 308.332(12) |
| Present (GGA-NC) | 5.2089 | 5.2089 | 13.9559 | 327.9307 |
| Present (LDA-NC) | 5.0878 | 5.0878 | 13.5610 | 304.0071 |
| Present (GGA-PBEsol-NC) | 5.1579 | 5.1579 | 13.7210 | 316.1275 |
| Present (GGA-ultrasoft) | 5.1384 | 5.1384 | 13.9478 | 318.9250 |
| Present (LDA-ultrasoft) | 5.0211 | 5.0211 | 13.5725 | 296.3407 |
| Present (HSE06) | 5.0678 | 5.0678 | 13.6395 | 303.3668 |
and is about 1 eV higher than that of GGA based on norm-conserving pseudopotentials. From Table 1, one can see that the lattice parameters of LDA and GGA are slightly lower and higher than the experimental values. The difference in the band gaps between GGA and LDA result from the difference in calculated lattice parameters. Compared with the results of LDA and GGA, the lattice parameters based on HSE06 are the lowest, however the band gap is the largest. Until now, as far as we know there is no experimental report on the band gap of LN-type ZnTiO$_3$. Although the band gap of HSE06 is relatively larger than that of LDA and GGA, the agreement with the experimental band gap needs further verification.

Figure 4 shows the band structures of LiNbO$_3$-type ZnTiO$_3$ along the high symmetry directions in the Brillouin zone based on HSE06.

Figure 5 shows the total and partial density of states (DOSs) of LN-type ZnTiO$_3$ based on norm-conserving pseudopotentials within GGA with the Fermi levels at 0 eV.
the charge populations of the s and p orbitals are 1.85 and 4.85. In addition, the calculated charge populations between nearest-neighboring (1.8652 Å) and next nearest-neighboring (2.1589 Å) Ti-O bonds are 0.56 and 0.30; the charge populations between the nearest-neighboring (2.0421 Å) and next nearest-neighboring (2.2671 Å) Zn-O bonds are only 0.29 and 0.04. The number of charges on the different bonds can reflect the covalent and ionic properties. Obviously, the chemical bonding of the Ti-O and nearest-neighboring Zn-O bonds is of mixed covalent-ionic character, however the next nearest-neighboring Zn-O bonds show ionic character. As discussed above, the hybridization of Zn-O bonds and Ti-O bonds mainly occurs in their 3d and 2p orbitals. The charge distribution of Zn-O and Ti-O bonds indicates that the empty 3d orbital in Ti4⁺ (3d⁰) more easily forms a covalent bond with O atoms than the fully occupied 3d orbital in Ti4⁺ (3d¹⁰). This may be the reason why the piezoelectric and nonlinear optical properties of LN-type ZnTiO₃ are superior to those of the LN-type ZnSnO₃ and LN-type ZnGeO₃ (see the results below). In the latter two compounds, it is noted that the all the cations are fully occupied 3d orbitals.

**Spontaneous polarization.** The most basic characteristics of ferroelectric materials is the existence of spontaneous polarization over certain temperature ranges, and the fact that the polarization can be reversed by the external electric field. Using the Berry-phase approach proposed by R. D. King-Smith and D. Vanderbilt25,26, we have calculated the spontaneous electric polarization of LN-type ZnTiO₃ based on finite electric field calculations. The results show that the polarizations of Pₓ and Pᵧ are almost equal to zero, so the polarization lies mainly along the z-axis direction. The total polarization is composed of the ionic (P⁺) and electronic (P₋) contributions. The results based on LDA show that the total polarization is 90.43 μC/cm², and the values of P⁺ and P₋ are 89.07 μC/cm² and 1.36 μC/cm², respectively. Therefore, the electric polarization mainly arises from the ionic contribution. Based on the result of our GGA calculation, the total polarization is 93.14 μC/cm², and the values of P⁺ and electronic P₋ are 91.73 μC/cm² and 1.41 μC/cm². According to ref. 14, the values of polarization obtained by Born effective charges and nominal charge are 88μC/cm² and 75μC/cm². Our results are slightly larger than their values and consistent with their results based on Born effective charges.

The Born effective charges of the LN-type ZnTiO₃ are presented in Table 2. The nominal charges of Zn, Ti and O are +2, +4 and −2, respectively. By comparing the Born effective charges of these ions and their nominal values, it is found that charge numbers Z⁺ of Zn, Ti and O (especially for Zxx in Ti atom, Zyy in O1, and Zzz in O2 atoms) are obvious anomalous, which is an important characteristic in ferroelectric materials. From Table 2, one can see that Z⁺ of Zn and Ti atoms mainly occur on the diagonal elements, and the values of the non-diagonal elements are small or equal to zero. This is in consistent with the spontaneous polarization being mainly along the z-axis direction. Compared with Z⁺ of Zn and Ti atoms, the Z⁻ tensor of O atoms displays strong anisotropy, and this should be attributed to the structural distortions caused by the Zn 3d-O 2p and Ti 3d-O 2p orbital hybridizations.

**Zone-center phonon modes.** In ferroelectric crystals that have undergone the paraelectric to ferroelectric transition, the relative displacements of anions and cations will lower the symmetry and lead to spontaneous polarization. This phenomenon can be explained by the theory of soft zone-center phonon modes. Firstly, we perform the symmetry analyses in ZnTiO₃ and divide its zone-center phonon modes into irreducible representations. The two paraelectric phases of ZnTiO₃ are ilmenite (IL)-type (hexagonal space group R3) and Perovskite (Pv)-type (orthorhombic space group Pnma) structures, and the ferroelectric phase is LiNbO₃-type structure (hexagonal space group R3c). In this compound, there exists a continuous phase transition from ilmenite-type structure to perovskite-type, and then to LiNbO₃-type structure.

In high-symmetry IL-type ZnTiO₃ (space group R3), there are 10 atoms in the primitive cell. All the 30 modes (including 3 acoustic modes) are composed of 4 irreducible representations (irreps).

\[
\Gamma (R3) = 5A_g \oplus 10E_g \oplus 5A_u \oplus 10E_u
\]

(5)

In these modes, the three acoustic modes are composed of one Aₚ and two Eₚ modes. In the optical modes, Aₚ and Eₚ are Raman active, while Aₘ and Eₘ are infrared (IR) active. The corresponding zone-center optical phonon modes are presented in Table 3. In its perovskite-type paraelectric phase (space group Pnma), there are 20 atoms in the primitive cell. All the 60 phonon modes at Γ point (including three acoustic modes) are composed of 8 irreps.

\[
\Gamma (Pnma) = 7A_g \oplus 5B_{1g} \oplus 7B_{2g} \oplus 5B_{3g} \oplus 8A_u \oplus 10B_{1u} \oplus 8B_{2u} \oplus 10B_{3u}
\]

(6)

Among them, three acoustic modes are in B₁u, B₂u and B₃u, respectively. The optical modes of Aₚ, B₁g, B₂g and B₃g are Raman active; the optical modes of B₁u, B₂u and B₃u are IR active, while the Aₘ modes are silent. We present

| Atom | Zxx | Zyy | Zzz | Ax₁ | Ax₂ | Ay₁ | Ay₂ | Az₁ | Az₂ |
|------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Zn   | 2.59| 2.59| 2.29| 0.24| 0.24| 0.00| 0.00| 0.00| 0.00|
| Ti   | 6.16| 6.16| 3.34| −0.54| 0.54| 0.00| 0.00| 0.00| 0.00|
| O₁   | −2.19| −3.64| −2.54| −0.58| −0.55| −0.31| −0.35| −1.28| −1.32|
| O₂   | −3.77| −2.06| −2.54| −0.35| −0.34| 1.27| 1.32| 0.37| 0.37|
| O₃   |−2.79| −3.04| −2.54| 0.90| 0.92| −0.96| −0.96| 0.97| 0.91| 0.95|

Table 2. The calculate Born effective charge of Zn, Ti, O₁−₃ in LN-type ZnTiO₃.
the corresponding zone-center optical phonon modes in Table 4. From this table, it is found that there are two imaginary frequencies in $B_{2u}$ ($124.12i$) and $B_{3u}$ ($101.57i$), respectively. However, in its high-symmetry IL-type ZnTiO$_3$, according to Table 3, it is found that there are no imaginary frequencies in the zone-center phonon optical modes; additionally, we also calculated its phonon dispersion spectrum, and it is found that there are no imaginary frequencies in these phonon modes. In order to verify the stability of the R3c and R-3 structures, we also carried out the phonon dispersion relationship based on GGA. Figures 6 and 7 present the phonon dispersion relations of the ilmenite (IL)-type ZnTiO$_3$ (space group R3) along high symmetry directions based on GGA.

**Table 3.** The calculated frequency (cm$^{-1}$) of zone-center optical phonon modes of ilmenite (IL)-type ZnTiO$_3$ (space group R3).

| $A_g$ | $A_u$ | $B_{1g}$ | $B_{2g}$ | $B_{3g}$ | $B_{1u}$ | $B_{2u}$ | $B_{3u}$ |
|-------|-------|----------|----------|----------|----------|----------|----------|
| 182.88 | 137.31 | 187.49 | 172.99 |
| 368.25 | 213.20 | 267.39 | 248.74 |
| 469.14 | 356.79 | 387.31 | 309.73 |
| 660.88 | 442.07 | 481.90 | 453.06 |
| 678.17 | 578.94 | |

**Table 4.** The frequencies (cm$^{-1}$) of zone-center optical phonon modes in the perovskite (Pv)-type ZnTiO$_3$.

| $A_g$ | $A_u$ | $B_{1g}$ | $B_{2g}$ | $B_{3g}$ | $B_{1u}$ | $B_{2u}$ | $B_{3u}$ |
|-------|-------|----------|----------|----------|----------|----------|----------|
| 105.09 | 74.20 | 173.82 | 137.82 | 131.12 | 63.56 | 124.12i | 101.57i |
| 153.48 | 102.07 | 244.52 | 163.07 | 304.52 | 111.09 | 74.88 | 95.45 |
| 241.88 | 113.28 | 356.88 | 250.55 | 454.52 | 183.91 | 127.15 | 178.83 |
| 300.53 | 151.47 | 467.27 | 370.45 | 462.60 | 305.34 | 219.98 | 232.22 |
| 434.00 | 283.65 | 654.80 | 467.71 | 747.05 | 332.94 | 397.35 | 325.38 |
| 451.84 | 379.67 | 509.34 | 370.06 | 413.30 | 366.11 |
| 509.22 | 394.47 | 729.64 | 440.83 | 472.24 | 430.89 |
| 490.47 | 461.78 | 489.77 |
| 516.84 | 457.12 |

**Figure 6.** The phonon dispersion relations of the ilmenite (IL)-type ZnTiO$_3$ (space group R3) along high symmetry directions based on GGA.
−8321.0790 (R3c) eV within GGA. The results show that the energy of its IL-type paraelectric phase is the lowest, the energy of Pv-type paraelectric phase is the highest, and the energy of LN-type ferroelectric phase lies in the middle. In order to verify whether it is due to the inaccuracy of the exchange correlation, we have carried out total energy calculation based on PBEsol, which is intended to improve on PBE for equilibrium properties such as bond lengths and lattice parameters. The calculated lattice parameters of PBEsol are also presented in Table 1. The results show that total energies are −8302.8974 (R3c), −8302.3911 (pnma) and −8302.5810 (R3c) eV based on PBEsol. This is consistent with the above conclusion E(R3c) < E(R3c) < E(pnma). This should be attributed to the synthesis of LN-type ZnTiO3 under high pressure.

In the ferroelectric phase (space group R3c) in ZnTiO3, the primitive cell contains 10 atoms, so there are 30 phonon modes at the Г point. The three zero-frequency acoustic modes comprise one in A1 and two in E. The zone-center phonon optical modes are as follows:

\[
\Gamma = \bigoplus (R3c) 4 A_5 A_9 E (7) 12
\]

In these modes, A1 and E optical modes are both Raman and infrared (IR) active, while A2 modes are silent. The optical modes of the LN-type ZnTiO3 (see in Table 5) infer that the imaginary frequencies disappear from perovskite-type paraelectric phase to LiNO3-type ferroelectric phase. Due to A1 and E optical modes being IR active, these frequencies are splitting into LO and TO modes described by the Lyddane–Sachs–Teller (LST) relation\(^5\). Generally, the large Bern effective charge corresponds to a large LO-TO splitting. From Table 5, one can see that three A1 modes (281.53~325.71 cm\(^{-1}\), 387.55~436.30 (cm\(^{-1}\), and 653.83~826.10 cm\(^{-1}\)) and three E modes (142.56~194.64 cm\(^{-1}\), 343.16~436.96 cm\(^{-1}\), and 577.30~848.01 cm\(^{-1}\)) show large LO-TO splitting. In Table 6, we present the mode effective charges and mode-oscillator strengths corresponding to the zone-center transverse optical (TO) modes of LN-type ZnTiO3.

**Piezoelectric properties.** In order to investigate the structural stability and piezoelectric properties of LN-type ZnTiO3, we calculate the elastic and piezoelectric constants by treating homogeneous strains as perturbations based on DFPT. According to the calculated results, the six independent elastic coefficients (Voigt notations) of this compound are C11, C12, C13, C14, C15, and C16 respectively. Additionally, it should be pointed out

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**Table 5.** The frequencies (cm\(^{-1}\)) of transverse optical (TO) and longitudinal optical (LO) zone-center optical phonon modes of the LiNbO3-type ZnTiO3.

| A1 (TO) | A1 (LO) | E (TO) | E (LO) | A2 |
|---------|---------|--------|--------|----|
| 142.56  | 165.26  | 141.16 | 152.71 | 120.69 |
| 281.53  | 325.70  | 194.64 | 204.87 | 363.21 |
| 387.55  | 436.30  | 223.63 | 223.88 | 417.04 |
| 653.83  | 826.10  | 265.30 | 267.41 | 468.54 |
| 321.53  | 325.71  | 839.51 |
| 343.16  | 428.20  |
| 436.96  | 479.11  |
| 639.91  | 656.14  |
| 657.30  | 848.01  |

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Figure 7. The phonon dispersion relations of the LN-type ZnTiO3 (space group R3c) along high symmetry directions based on GGA.
that $C_{66} = (C_{11} - C_{12})/2$. In Table 7, we give the corresponding elastic stiffness coefficients (relaxed ion) of LN-type ZnTiO$_3$. The point group of LN-type ZnTiO$_3$ belongs to the triangle crystal. As discussed in refs. 51,52, the triangle crystals need to satisfy the following Born mechanical stability criterion.

\[
\begin{align*}
C_{11} - |C_{12}| & > 0 \\
(C_{11} + C_{12})C_{33} - 2C_{13}^2 & > 0 \\
(C_{11} - C_{12})C_{44} - 2C_{15}^2 & > 0 \\
\end{align*}
\]

(8)

The results presented in Table 7 reveal that the elastic constants of the LN-type ZnTiO$_3$ satisfy the constraints of the Born stability condition. Therefore, the structure of LN-type ZnTiO$_3$ is stable. By using homogeneous strains and electric fields as perturbations, we can calculate the piezoelectric properties of LN-type ZnTiO$_3$. The obtained piezoelectric tensor of this compound has the four independent elements (Voigt notations) $e_{11}$, $e_{15}$, $e_{31}$, $e_{33}$:

\[
\epsilon = \begin{pmatrix}
-\epsilon_{11} & -\epsilon_{15} & 0 & 0 & e_{31} & 0 \\
0 & 0 & e_{15} & 0 & 0 & 0 \\
e_{31} & 0 & 0 & 0 & 0 & 0 \\
\end{pmatrix}
\]

(9)

Obviously, this tensor is the same as that of LN-type ZnSnO$_3$ and ZnGeO$_3$, however it is a little different from that of LiNbO$_3$ and LiTaO$_3$ since independent elements of the piezoelectric tensor in LiNbO$_3$ and LiTaO$_3$ are $e_{22}$, $e_{15}$, $e_{31}$, and $e_{33}$. In Table 8, we present the piezoelectric stress constants of LN-type ZnTiO$_3$, ZnSnO$_3$ and ZnGeO$_3$.

Table 6. The calculated mode effective charges (|$e$|), and mode-oscillator strengths (within $10^{-4}$ atomic units) corresponding to the zone-center transverse optical phonon modes of LiNbO$_3$-type ZnTiO$_3$.

| $\omega$ (cm$^{-1}$) | $Z_m^+$ | $S_m$ | $\omega$ (cm$^{-1}$) | $Z_m^+$ | $S_m$ |
|---------------------|---------|-------|---------------------|---------|-------|
| 142.56              | 3.61    | 1.97  | 141.16              | 2.47    | 1.09  |
| 281.53              | 6.51    | 10.05 | 194.64              | 2.50    | 1.01  |
| 387.55              | 0.50    | 0.08  | 223.63              | 0.30    | 0.02  |
| 653.83              | 5.63    | 10.35 | 265.30              | 1.18    | 0.40  |
|                     |         |       | 321.53              | 3.68    | 2.54  |
|                     |         |       | 343.16              | 6.02    | 10.07 |
|                     |         |       | 436.96              | 1.33    | 0.59  |
|                     |         |       | 639.91              | 6.15    | 12.06 |
|                     |         |       | 657.30              | 1.73    | 0.84  |

Table 7. The Elastic stiffness coefficients of LN-type ZnTiO$_3$.

| Material          | $C_{11}$ (10$^{11}$N/m$^2$) | $C_{12}$ | $C_{13}$ | $C_{15}$ | $C_{33}$ | $C_{44}$ | $C_{66}$ |
|-------------------|-----------------------------|---------|---------|---------|---------|---------|---------|
| ZnTiO$_3$         | 3.675                       | 1.875   | 1.442   | 0.031   | 2.877   | 0.800   | 0.899   |
| ZnSnO$_3$ ref. 43 | 1.94                        | 0.63    | 1.01    | 0.001   | 1.69    | 1.17    | 0.92    |
| ZnGeO$_3$ ref. 43 |                            |         |         |         |         |         |         |
| LiNbO$_3$ ref. 44 |                            |         |         |         |         |         |         |
| LiTaO$_3$ ref. 44 |                            |         |         |         |         |         |         |

Table 8. The piezoelectric stress constants (relaxed ion) of LN-type ZnTiO$_3$, it is noted that a and b in PbTiO$_3$ represents DFPT finite strain method, respectively.

| Material          | $e_{11}$ (C/m$^2$) | $e_{15}$ | $e_{31}$ | $e_{33}$ |
|-------------------|-------------------|---------|---------|---------|
| ZnTiO$_3$         | $-0.93$           | 1.00    | 1.01    | 2.51    |
| PbTiO$_3$ ref. 54 | 6.63              | 2.06    | 4.41    |
| PbTiO$_3$ ref. 54 | 6.66              | 2.07    | 4.48    |
| ZnSnO$_3$ ref. 43 | $-0.15$           | 0.26    | 1.23    | 0.29    |
| ZnGeO$_3$ ref. 43 | $-0.27$           | 0.36    | 0.65    | 2.81    |
| LiNbO$_3$ ref. 44 | 2.43              | 3.76    | 0.23    | 1.33    |
| LiTaO$_3$ ref. 44 | 1.67              | 2.72    | $-0.38$ | 1.09    |
together with LiNbO3 and LiTaO3. From this table, the piezoelectric constants $e_{11}$, $e_{15}$, $e_{31}$, $e_{33}$ are $-0.93$, 1.00, 1.01 and 2.51 C/m², respectively. It is well known that lead titanate (PbTiO3) piezoelectric ceramics have excellent piezoelectric properties. By comparing the piezoelectric coefficients of LN-type ZnTiO and that of PbTiO3 calculated by density functional perturbation theory and finite strain method (see Table 8), it is found that values of $e_{31}$, $e_{33}$ of LN-type ZnTiO3 are close to and exceed one-half of that of PbTiO3, and the value of $e_{15}$ is relatively small compared to that of PbTiO3. The large piezoelectric constants reveal that LN-type ZnTiO3 is a promising candidate piezoelectric material.

Nonlinear optical properties. As mentioned above, the zone-center phonon optical modes of ferroelectric phase ZnTiO3 can be divided into $4A_1 \oplus 5A_2 \oplus 9E$, and $A_1$ and $E$ modes are both Raman and infrared active. The Raman scattering efficiencies of the phonon modes can be calculated using the following formula:

$$\frac{dS}{d\Omega} = \frac{(\omega_0 - \omega_m)^4}{c^4} |\mu_0 \cdot \alpha_m \cdot e_0|^2 \frac{\hbar}{2\omega_m} (n_m + 1)$$

where $\alpha_m$, $c$, $\hbar$ and $n_m$ are the Raman susceptibility, the speed of light in vacuum, the Planck constant and Bose-Einstein factor, respectively; $\omega_0$ and $\omega_m$ are the frequencies of an incoming photon and the $m$th zone-center phonon mode, the frequency of scattered outgoing photon is $(\omega_0 - \omega_m)$, $e_0$ and $e$ indicate incoming and outgoing polarizations within an angle $\Omega$. According to the structural symmetry, the Raman tensors of $A_1$ mode (along $z$ axis) and $E$ mode (in the $x$-$y$ plane) of LN-type ZnTiO3 are similar to that of LiNbO3 and described as follows:

$$A_1(x) = \begin{pmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & b \end{pmatrix}$$

$$E(x) = \begin{pmatrix} c & 0 & d \\ 0 & -c & 0 \\ d & 0 & 0 \end{pmatrix} \quad E(y) = \begin{pmatrix} 0 & c & 0 \\ c & 0 & -d \\ 0 & -d & 0 \end{pmatrix}$$

Figure 8 displays the calculated Raman spectrum of LiNbO3-type ZnTiO3 for the $x(zz)y$ scattering configuration. In this configuration, as in the case of LiNbO3 or PbTiO3, only the transverse $A_1$ modes can be detected. In order to see the peaks of TO1 and TO3 clearly, we have made two enlarged small illustrations in this figure. The results show that TO2 and TO4 modes have a very strong Raman scattering efficiency. In comparison, the Raman scattering efficiencies of TO1 and TO3 are very weak and are much smaller than that of the TO2 and TO4 modes. As presented in Tables 5 and Table 6, notice that TO2 and TO4 of $A_1$ modes have large LO-TO splittings and oscillator strengths, and the two frequencies just correspond to large Raman peaks. Figure 9 presents the calculated Raman spectrum of LiNbO3-type ZnTiO3 for the $x(yz)y$ configuration. In this configuration, the same as LiNbO3, only the TO and LO of $E$ modes can be detected. From this figure, it is found that five transverse modes (TO3, TO4, TO6 and TO7 and TO8) and five longitudinal modes (LO2, LO3, LO4, LO7 and LO9) have strong Raman scattering efficiency. Due to the LO-TO splittings of LO3(223.63 cm⁻¹)-TO3(223.88 cm⁻¹) and LO4(265.30 cm⁻¹)-TO4(267.41 cm⁻¹) being very small, the two Raman intensity peaks almost completely overlap.
The LN-type ZnTiO₃ belongs to the 3 m point group, therefore this compound is a candidate promising nonlinear optical material. As discussed by Inaguma et al., the SHG response of LN-type ZnTiO₃ is 24 times greater than that of LN-type ZnSnO₃ and has about 5% of the SHG response of LiNbO₃. By using electric fields and atomic displacements as perturbations based on DFPT, we have calculated the nonlinear optical (NLO) susceptibilities and electro-optic (EO) coefficients of LN-type ZnTiO₃. According to reports by M. Veithen, et al., the NLO properties of various semiconductors, such as LiNbO₃, PbTiO₃, and AlAs, etc. were calculated by DFPT based on the ABINIT package. The comparison between the theoretical results of NLO and EO coefficients with the experimental data shows that the method is reliable. The calculated results show that the three independent elements of the NLO tensor of this compound are \( d_{12} \), \( d_{15} \), and \( d_{33} \) (Voigt notations).

\[
\begin{bmatrix}
-d_{12} & d_{12} & 0 & 0 & d_{15} & 0 \\
0 & 0 & 0 & d_{15} & 0 & d_{12} \\
-d_{15} & d_{15} & d_{33} & 0 & 0 & 0
\end{bmatrix}
\]  

(13)

The NLO tensor form of LN-type ZnTiO₃ is the same as that of LN-type ZnSnO₃ and ZnGeO₃, but it is not the same as that of LiNbO₃ and LiTaO₃ since the independent elements of NLO tensor of the latter are \( d_{22}, d_{31}, \) and \( d_{33} \). The calculated NLO susceptibilities of LN-type ZnTiO₃ together with those of LN-type ZnSnO₃, LiNbO₃, and LiTaO₃ are presented in Table 9. From this table, the NLO susceptibilities \( d_{12}, d_{15} \), and \( d_{33} \) are 1.37, 1.46 and \(-20.18\) Pm/V, respectively, and one can see that the biggest susceptibility (\( d_{33} \)) of this compound is larger than that of ZnSnO₃, and lower than that of LiNbO₃. For the electro-optic (EO) coefficients of LN-type ZnTiO₃, the results reveal that its independent elements are \( \gamma_{11}, \gamma_{13}, \gamma_{33}, \) and \( \gamma_{51} \).

\[
\gamma = \begin{bmatrix}
\gamma_{11} & 0 & \gamma_{13} \\
0 & 0 & \gamma_{13} \\
0 & 0 & \gamma_{33} \\
0 & 0 & \gamma_{51} \\
\gamma_{51} & 0 & 0 \\
0 & \gamma_{11} & 0
\end{bmatrix}
\]  

(14)
As can be seen, the EO tensor is the same as that of LN-type ZnSnO₃ and ZnGeO₃, but is different from that of LiNbO₃ and LiTaO₃, since the independent elements of latter are $\gamma_{111}$, $\gamma_{112}$, and $\gamma_{122}$. The EO coefficients can be divided into three contributing parts: electronic, ionic, and piezoelectric. In Table 10, we give the calculated EO coefficients of LN-type ZnTiO₃. For ease of comparison, the EO coefficients of LN-type ZnGeO₃, LN-type ZnSnO₃, LiNbO₃, and LiTaO₃ are also listed in this table. Our obtained EO coefficients $\gamma_{111}$, $\gamma_{112}$, and $\gamma_{122}$ for LN-type ZnTiO₃ are 0.46, 3.71, 17.17 and 1.62 Pm/V, respectively. Obviously, the coefficients $\gamma_{122}$ are much larger than that of LN-type ZnSnO₃ and ZnGeO₃. The large NLO susceptibilities and EO coefficients reveal that the LN-type ZnTiO₃ is a high performance lead-free nonlinear optical crystal.

### Conclusions

In this work, the electronic structure, zone-center phonon modes, piezoelectric and nonlinear optical properties of LN-type ZnTiO₃ are investigated by first-principles calculations based on DFT. The electronic structure shows that this compound is a wide direct-band-gap insulator. By investigating the zone-center phonon modes of the paraelectric and ferroelectric phases, it is found that there are two imaginary frequencies in $B_{2g}$ and $B_{3g}$ in the perovskite paraelectric phase, and subsequently the imaginary frequencies disappear in the ferroelectric phase. The calculated spontaneous polarizations are 90.43 μC/cm² and 93.14 μC/cm² based on LDA and GGA, respectively. Our results are in good agreement with the experimental results, and the large spontaneous polarization reveals that this compound is a good ferroelectric material.

The elastic constants of LN-type ZnTiO₃ satisfy the constraints of the Born stability condition, and therefore this compound has a stable structure. The obtained piezoelectric tensor has four independent elements $e_{111}$, $e_{112}$, $e_{122}$, $e_{333}$, with values $-0.93, 1.00, 1.01$ and $2.51$ C/m². This shows that this compound is a promising piezoelectric crystal. Like LiNbO₃, the calculated Raman spectrum for the $x(zz)y$ and $x(yz)y$ configurations correspond to A₁ and E modes, and the Raman scattering peaks of A₁ and E modes are assigned to their zone-center optical modes, respectively. The independent nonlinear optical susceptibilities of this compound are $d_{11}$, $d_{15}$, and $d_{33}$, with values $1.37, 1.46$ and $-20.18$ Pm/V, respectively. For the EO coefficients, the independent elements are $\gamma_{111}$, $\gamma_{112}$, $\gamma_{122}$, and $\gamma_{333}$ with values $0.46, 3.71, 17.17$ and $1.62$ Pm/V, respectively. The results show that LN-type ZnTiO₃ exhibits better nonlinear optical properties than LN-type ZnSnO₃. The large piezoelectric and nonlinear optical susceptibilities reveal that this compound is a high-performance lead-free piezoelectric and nonlinear optical crystal.

### Table 10. The calculated Electro-optic tensor of LN-type ZnTiO₃.

| Electro-optic tensors $\gamma_{ij}$ (Pm/V) | $\gamma_{111}$ | $\gamma_{112}$ | $\gamma_{122}$ | $\gamma_{333}$ |
|-----------------------------------------|----------------|----------------|----------------|----------------|
| ZnTiO₃ ref. | 0.46           | 3.71           | 17.17          | 1.62           |
| ZnSnO₃ ref. | 1.23           | 1.57           | $-2.78$        | 0.54           |
| ZnGeO₃ ref. | 0.44           | 1.68           | 5.56           | 0.85           |
| LiNbO₃ ref. | $\gamma_{111}$ | $\gamma_{112}$ | $\gamma_{122}$ | $\gamma_{333}$ |
| LiTaO₃ ref. | 8.6            | 30.8           | 3.4            | 28             |
| LiTaO₃      | 35             | 8.2            | 20             | 0.5            |

Received: 21 June 2019; Accepted: 29 October 2019

Published online: 26 November 2019

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Acknowledgements
This work was supported by the National Natural Science Foundations of China (Nos. 11104072, U1404108, 11404112, 11174220, 19ZR1459100 and 11374226), the Key scientific research projects in Colleges and Universities of Henan province (Nos. 17A140009) and Innovative Talent of University in Henan Province (17HASTIT013). We also thank very much to Dr. Zhansheng Lu for providing assistance in calculations and to Dr. Derwyn. A. Rowlands in the polish of English.

Author contributions
Jing Zhang and San-Huang Ke designed calculational model; Bin Xu and Yu-Sheng Wang carried out calculations of electronic structures and ferroelectric properties; Jing Zhang and Zhen Qin carried out calculations of piezoelectric properties and nonlinear optical properties; Jing Zhang and San-Huang Ke analyzed the theoretical results; Jing Zhang wrote the manuscript.

Competing interests
The authors declare no competing interests.

Additional information
Correspondence and requests for materials should be addressed to J.Z.

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