Forecast of Piezoelectric Properties of Crystalline Materials from First Principles Calculation

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Abstract. In this paper, forecast of piezoelectric tensors are presented. Piezo crystals including quartz, quartz-like crystals, known and novel crystals of langasite-type structure are treated with density-functional perturbation theory (DFPT) using plane-wave pseudopotentials method, within the local density approximation (LDA) to the exchange-correlation functional. Compared with experimental results, the ab initio calculation results have quantitative or semi-quantitative accuracy. It is shown that first principles calculation opens a door to the search and design of new piezoelectric material. Further application of first principles calculation to forecast the whole piezoelectric properties are also discussed.

1. Introduction
Piezoelectric materials have very important role in modern industries. They are widely used as key material in resonator, filter, sensor, and so on. Until now, forecast of piezoelectric properties of materials remains as not easy task. From 1970’s, scientists are keeping on theoretic effort to make the forecast feasible[1]. Due to fast increasing of the calculation velocity and memory capacity of supercomputer and establish of modern polarization theory[2,3], direct quantitative calculation of piezoelectric coefficient of some relative simple piezoelectric systems and qualitative forecast of piezoelectric coefficient of some ferroelectric system from first principles are possible now[4].

The method of density-functional theory[5] (DFT) and density-functional perturbation theory[6,7] (DFPT) have been shown to give a successful description of the dielectric and piezoelectric properties of a wide range of materials in which electronic correlation are not too strong.[8,9] The use of DFPT methods is becoming increasingly popular because they can be used to compute the response properties directly. In recent years, improved DFPT capabilities have been implemented in several of the compute code packages commonly used by the computational electronic-structure community[10-12]. This development has been most thorough in the case of the open-source ABINIT computer package [10], in which the capability for handling atomic-displacement, electric-field, and strain is now available. This development opens the prospect for a systematic treatment of three kinds of perturbations in insulating crystals on an equal footing: periodicity-preserving atomic displacements (i.e., zone-center phonons), homogeneous electric fields, and homogeneous strains[13].

Now, more and more works are reported in which treated either simple structure binary compounds, such as III-V semiconductor[14], or complex compounds of ferroelectrics, such as PMN-PT[15]. Although the calculation of the piezoelectric properties is still semi-quantitative or qualitative when comparing with experiment results, the forecast of piezoelectric properties of all semiconductor is now feasible and this opens a door to the search and design of new piezoelectric material.

In this work, we use this approach to calculation the piezoelectric properties of the most common piezoelectric crystals without ferroelectricity, mostly with point group of 32, i.e., quartz, Sr,NbGa,Si,O$_{10}$, Ca,NbGa,Si,O$_{10}$, Sr,TaGa,Si,O$_{10}$, and Sr,Ga,Ge,O$_{10}$. The main purposes of this manuscript are to test the theoretical calculation accuracy, and illustrate its usefulness in forecast of piezoelectric properties.
2. Methods and Details of the Calculations
The ab initio calculations were carried out using the ABINIT code package[6,15]. Technical details on the computation of responses to atomic displacements and homogeneous electric fields can be found in Ref.16, while Ref.17 presents the subsequent computation of dynamical matrices, Born effective charges, dielectric permittivity tensors, and interatomic force constants. Details on the computation of responses to the strain perturbation can be found in Ref.18, which describes the computation of the elastic, piezoelectric, and internal force-response tensors. Specifically, we first carried out full structural relaxations or atomic position relaxations for all the materials. Next, response-function calculations were carried out in order to obtain first derivatives of the occupied wavefunctions with respect to the perturbations of atomic displacements (i.e., phonons at q=0), uniform electric field, and strain. These were then used to compute the elementary second-derivative response-function tensors. Finally, from these elementary response tensors, the various secondary response tensors are obtained according to the formulas given in Ref. 13. All calculations are at zero temperature.

The DFT and DFPT calculations for all materials were carried out using FHI98PP Troullier-Martins type pseudopotentials and a plane-wave energy cutoff of 40-50 hartree. Various Brillouin-zone k-point sampling were used for different materials respectively. Table I lists the grids used. The exchange and correlation effects were treated within the local-density approximation (LDA) in the Ceperley-Alder[19] form with the Perdew-Wang[20] parametrization.

| Material          | Quartz, GeO₂ | Sr₃NbGa₅Si₅O₁₄, Ca₃NbGa₅Si₅O₁₄, Sr₃Ga₅Ge₅O₁₄ | Sr₃Ga₅Ge₅O₁₄ |
|-------------------|--------------|-----------------------------------------------|--------------|
| Grid              | 4x4x4, 6x6x6 | 4x4x6                                         |              |

It is well known that the usual underestimation of the equilibrium lattice constant associated with the local-density approximation has an unusually profound influence on the ferroelectric distortion, which is very sensitive to cell volume[18]. Here, the influence on the piezoelectric response of the cell volume was also performed by carrying out the initial structural relaxation with the cell volume constrained to be that of the experimental structure at zero temperature, i.e., using of a “negative fictitious pressure” on the cell.

3. Results
Quartz is the most important piezoelectric crystal widely used in mechanical actuators and SAW filters applications, while Sr₃NbGa₅Si₅O₁₄, Ca₃NbGa₅Si₅O₁₄, and Sr₃TaGa₅Si₅O₁₄ belong to a piezoelectric family of langasite recently found, which have order atom occupations in lattice sites. The space group is P321. Its structure could be presented as A₃BᵥC₃D₂O₁₄. Sr₃(Ga₃₋ₓGeₓ₀.₄₅)(GaₓGeₓ₋₀.₄₅)₃Ge₂O₁₄ (Sr₃Ga₅Ge₅O₁₄ or SGG) also belongs to this family but the atom occupations in lattice sites are disorder[23]. It consists of four types of polyhedra, a distorted Thomson cubes with coordination number 8 (3e site, A) occupied by Sr₂+, an octahedron (1a site, B) occupied by Ga³⁺₀.₄Ge⁴⁺₀.₄, and two types of tetrahedra (3f site, C, and 2d site, D) occupied by Ga³⁺₀.₅₃Ge⁴⁺₀.₄₇ and Ge⁴⁺.

Due to the limit of paper length, the optimization of crystal structures, the dielectric constants, elastic constants, zone-center phonon frequencies, etc, are reported elsewhere. Here, the piezoelectric tensors of the above crystals obtained by calculation are presented compared with available experimental results. The clamped piezoelectric tensors which represents the electronic contribution, internal piezoelectric tensors which represents the lattice contribution and relaxed piezoelectric tensors which is the sum of these two tensors are all shown in table II for quartz. And in table III and IV, the relaxed piezoelectric tensors of crystals of A₃BᵥC₃D₂O₁₄ structure are presented and compared with the experimental ones.

It is shown in table II that the clamped piezoelectric tensor $\varepsilon_{11}$ and internal piezoelectric tensor $e_{11}$, in have the opposite effects on the final piezoelectric tensors. Internal one is nearly twice as larger as the clamped one and it means that the dominated contribution comes from the internal lattice, i.e., atomic positions relaxation after imposing a homogenous strain on the lattice. For Sr₃NbGa₅Si₅O₁₄, Ca₃NbGa₅Si₅O₁₄, and Sr₃TaGa₅Si₅O₁₄, the same thing happens to $\varepsilon_{11}$, while internal one is nearly ten times larger than the clamped one. The detail results is not shown here. The relaxed piezoelectric tensors of the above three crystals using experimental lattice constants and those of Sr₃NbGa₅Si₅O₁₄ and Ca₃NbGa₅Si₅O₁₄ crystals using
fully relaxed structures are given in table III, and the available experimental tensors are also presented for comparison. From the results, it is obviously that the structure parameters influence the piezoelectric tensors calculated at the extent of about 20%. Unlike ferroelectricity, the experimental structure doesn’t give more accurate results than the relaxed structure does. The accuracy of calculation of piezoelectric tensor using experimental results as refers is about 11% for $e_{11}$ of Sr$_3$NbGa$_3$Si$_2$O$_{14}$ and about 0.9% for that of Ca$_3$NbGa$_3$Si$_2$O$_{14}$ using the fully relaxed structure.

| Present work | Experiment | Remark |
|--------------|------------|--------|
| Sr$_3$NbGa$_3$Si$_2$O$_{14}$ | -0.429 | -0.486$^a$ | Experimental structure |
| Sr$_3$TaGa$_3$Si$_2$O$_{14}$ | -0.483 | --- | Experimental structure |
| Ca$_3$NbGa$_3$Si$_2$O$_{14}$ | -0.409 | -0.335$^b$ | Experimental structure |
| -0.338 | --- | Relaxed structure |

$^a$Reference [24]  
$^b$Reference [25]

The piezoelectric coefficients of SGG have been computed by using the alchemical pseudo-potentials technique. The piezoelectric coefficient $e_{11}$ calculated from experimental structure is presented in table IV. The signs of clamped and internal piezoelectric tensor are the same. The accuracy of calculation is about 30% referred to the experimental result.

| A$_3$BC$_3$D$_2$O$_{14}$ | Present work | $e_{11}$ | Experiment | Remark |
|------------------------|--------------|--------|------------|--------|
| Sr$_3$NbGa$_3$Si$_2$O$_{14}$ | -0.429 | -0.486 | --- | Experimental structure |
| Sr$_3$TaGa$_3$Si$_2$O$_{14}$ | -0.483 | --- | --- | Experimental structure |
| Ca$_3$NbGa$_3$Si$_2$O$_{14}$ | -0.409 | -0.335$^b$ | --- | Experimental structure |
| -0.338 | --- | --- | Relaxed structure |

$^a$Reference [23]  
$^b$Reference [25]

Table II. Clamped, internal and relaxed piezoelectric tensors of quartz (Unit:C/m$^2$)

| Present work | $\tilde{e}_{11}$ | $\tilde{e}_{14}$ | $e_{11,\text{in}}$ | $e_{14,\text{in}}$ | $e_{11}$ | $e_{14}$ |
|--------------|----------------|----------------|----------------|----------------|----------|----------|
| Expt$^*$     | -              | -              | -              | -              | 0.171    | -0.0436  |

$^*$Reference [22]
4. Summary

It is shown in this work that first principles calculation opens a door to the search and design of new piezoelectric material. The calculation accuracy of piezoelectric tensors referred to experiments could as better as within 10% to 40%.

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