# Structural, electronic, and elastic properties of tetragonal $Sr_{0.5}Be_{0.5}TiO_3$: Ab-initio calculation

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In this theoretical study, we present for the first time, to the best of our knowledge, the structural, electronic, and elastic properties of perovskite $Sr_{0.5}Be_{0.5}TiO_3$ type structure (Tetragonal), P4/mmm, space group, 123, using the full potential linearized augmented plane wave (FP-LAPW) method based on density functional theory (DFT) integrated into the Wien2k code . The generalized gradient approximation (GGA-PBEsol) and local density approximation have been used for the exchange correlation potential. The electronic properties represented by the band structure (BS) and DOS as well as the (PDOS) partial density of states, allowed to obtain semiconductor compounds, which have been calculated with mBJ approximation. The elastic constants were reported, and we verified the stability conditions of our materials elastically. These theoretical results open the way for experimental and other theoretical studies of this compound.

## 1. Introduction

The importance of technology and technological applications are the main reason for most experimental and theoretical physical studies. Materials having Chemical formula ABO3 materials have been of interest to many researchers to discover their physical and chemical properties and the extent of their technological applications [1,2]. It has a structure of cubic perovskite with space group 221 pm-3m, at room temperature. This ideal structure displays a wide variety of structural instabilities in the various materials. The interaction between these instabilities represents a rich group of photoelectric and ferroelectric and antiferroelectric behaviors. Useful properties of the ABO3 type perovskite can be obtained by some modifications of the ideal structure. In 2001, Shende *et al.* claim that SrTiO3 can be used in high voltage applications because of their high breakdown strengths [7], and Semiconductive ceramics, Pyroelectric far-infrared detectors. The effects of doping and alloying on the electronic structure of strontium titanate SrTiO3 have been discussed in previous experimental and theoretical studies [3-5] but, ab initio calculations of Sr(1-x)Be(x)TiO3 properties have not been performed yet (to our best knowledge). Beryllium has become an increasingly important material for a wide range of commercial and governmental applications because of its unmatched combination of qualities [6]. The simple cubic structure of SrTiO3 crystal is described mainly using the Pm3m space group [7.8]. The beryllium is potentially effective, which can improve the electrical or catalytic properties of SrTiO3. So, the results of FP-LAPW DFT calculations, elastic properties, and the electron density carried out for the structures of beryllium doped strontium titanate provide additional theoretical information that may aid in elucidating experimental results in the future. A few perovskites solid solutions were experimentally synthesized by the mean of the foreign ions substitution (see cations between parentheses), like (Ba, Sr)TiO3, Ca(Ti, Zr)O3, and (La, Sr)(Co, Fe)O3,etc. [9-10]. $Sr_{0.5}Be_{0.5}TiO_3$ is one of them. The anal-

ysis of mechanical properties remains an untreated subject on such materials. The calculations of bandgap depict a possible use of the investigated compound in many UV device applications. In this study, the coordinate origin has been placed in Sr vacancy, which corresponds to the P4/mmm space group (Fig. 1). The purpose of this work is to provide information regarding Sr(1-x)Be(x)TiO3, $x = 0.5$ properties. Section 2 concerns the procedure calculation. The results are reported and discussed in Sec. 3. Finally, we present our conclusions in Sec. 4.

## 2. Theoretical method

Density functional theory (DFT) has been very popular for calculations in the ground-state properties of electronic systems (metals, semiconductors, and insulators) since the 1970s. At the beginning of the 1990s, DFT was considered accurate enough for calculations in quantum chemistry, when the approximations used in the theory were greatly refined to better model the exchange and correlation interactions [11,12].

In the current research worksheets, we have calculated the structural, electronic, electronic charge density, and elastic properties of pure (Sr,Be)TiO3 perovskite using the full potential linearized augmented plane wave (FP-LAPW) method implemented in the WIEN2k code as part of the DFT [13,14]. We used the generalized gradient approximation (PBEsol-GGA) Perdew 08 *et al.,* [15]. And the modified Becke-Johnson (mBJ) potential [16] is an empirical potential of the form (1)

$$v_x^{mBj}(r) = cv_x^{BR}(r) + (3c - 2)\frac{1}{\pi}\sqrt{\frac{5}{12}}\sqrt{\frac{2t(r)}{\rho(r)}} \qquad (1)$$

$$c = -0.012 + 1.023\left(\frac{1}{v_{cell}}\int\limits_{V_{cell}}\frac{|\nabla\rho(r)|}{\rho(r)}dr\right)^{1/2} \qquad (2)$$
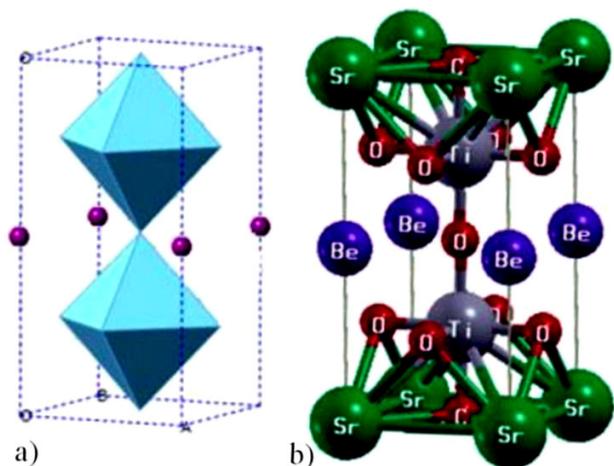
FIGURE 1. Structure of tetragonal $Sr_{0.5}Be_{0.5}TiO_3$. a) cell polyhedral and b) cell primitive.

TABLE I. The electronic configuration and chemical composition of $Sr_{0.5}Be_{0.5}TiO_3$.

| Element | Content (%) |
|---|---|
| Strontium [Kr] $5s^2$ | 30.38 |
| Beryllium $1s^2$ $2s^2$ | 03.12 |
| Titanium [Ar] $3d^2$ $4s^2$ | 33.20 |
| Oxygen [He] $2s^2$ $2p^4$ | 33.30 |

where, $c = 1 \Rightarrow$ Original $v_x^{BJ}$. $c > 1 \Rightarrow$ Less negative potential in low $\rho$ regions $Eg$ increases monotonically with respect to $c$. $V_{cell}$ is the volume of the unit cell. $\rho(r) \equiv \sum_i^N \mid \psi(r) \mid^2$ is the electron density, and $(\nabla \rho(r))$ the density gradient [17].

For the electronic properties and electronic charge density: A $1 \times 1 \times 2$ supercell was constructed from the primitive cell of SrTiO3 cubic structure (space group $Pm3 - m$); the first atom Sr was replaced by beryllium atom (Be). The new compound $Sr_{0.5}Be_{0.5}TiO_3$ has space group P4/mmm (N°123), a (Å) = b(Å), and $c > a$. The electronic configuration and chemical composition of strontium beryllium titanate are given in Table I. The cell of $Sr_{0.5}Be_{0.5}TiO_3$ can be schematically described by a sequence of successive layers perpendicular to the $c-$axis (see Fig. 1a), b). Input data is essential for Wien2K code such as: the elements in the materials. The crystalline lattice system of bravais, (space group). Radius of the atomic spheres $R_{MT}$ (MT: muffin-tin). The positions of the atoms.

These input parameters are grouped in Table II. The wave functions in the interstitial parts were developed in plane waves with a cutoff of $R_{MT}$. $K_{max} = 7$ and set $18 \times 18 \times 9$ Monkhorst and Pack grid point in the (IBZ) Brillouin zone sampling with smearing occupations [18], corresponding to 3000 points in the (IBZ). We optimized the structures for the value of remaining force which was less than 0.0001 Ry/Bohr. We performed a self-consistent calculation of total energy as a function of volume and $c/a$ ratio. The

TABLE II. Wyckoff positions, space group, and the atomic sphere radii of $Sr_{0.5}Be_{0.5}TiO_3$.

| Material | Space group | Atom | $R_{MT}$ (Bohr) | Atomic position | | |
|---|---|---|---|---|---|---|
| | | | | $x$ | $y$ | $z$ |
| $Sr_{0.5}Be_{0.5}TiO_3$ | P4/mmm | Sr | 2.50 | 0.0 | 0.0 | 0.0 |
| | (N°123) | Be | 1.50 | 0.0 | 0.0 | 0.5 |
| | | Ti | 1.87 | 0.5 | 0.5 | 0.75 |
| | | O 1 | 1.69 | 0.0 | 0.5 | 0.25 |
| | | O 2 | 1.69 | 0.5 | 0.5 | 0.0 |
| | | O 3 | 1.69 | 0.5 | 0.5 | 0.5 |
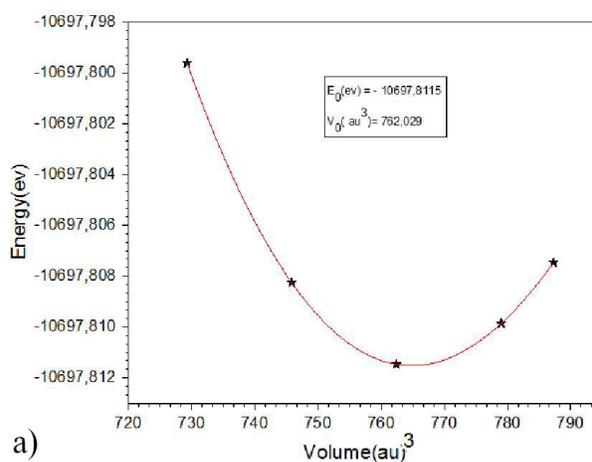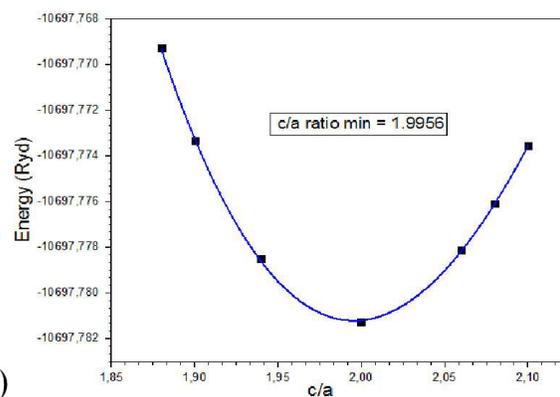


FIGURE 2. Variations of the energy with the unit cell volume and $c/a$.

lattice constants ($a = b$ and $c$), bulk modulus (B), and its pressure derivative (B') for $Sr_{0.5}Be_{0.5}TiO_3$ are determined after adjusting the total energy E(V) obtained from the Murnaghan state equation [19].

To evaluate the elastic parameters (elastic constants, bulk, shear, Young's moduli, Poisson's ratio, etc.) of $Sr_{0.5}Be_{0.5}TiO_3$, for tetragonal symmetry. We have used the IRelast method developed by J. Morteza integrated into the Wien2K code [20] called Tetra-elastic.
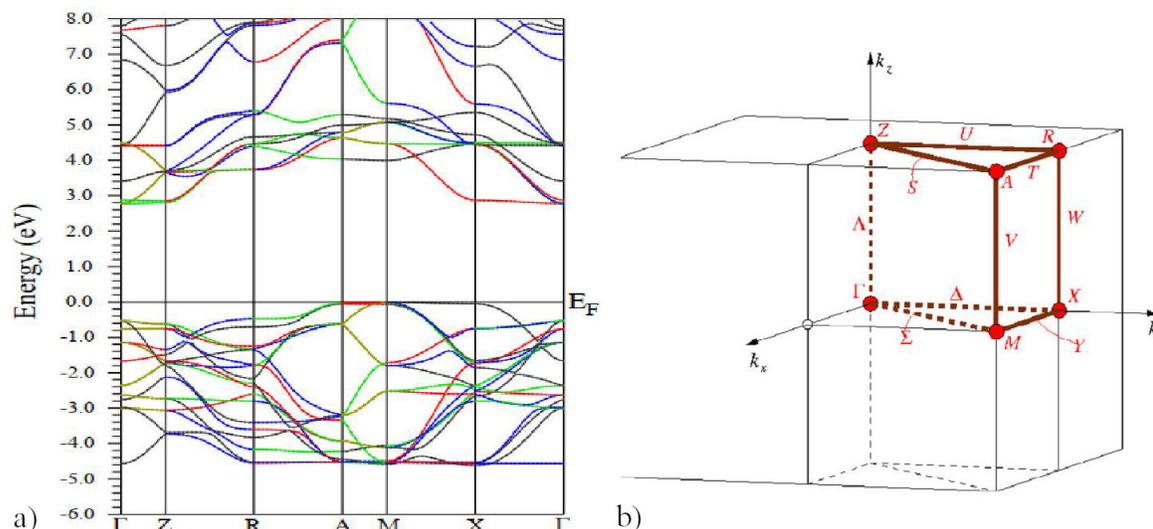
FIGURE 3. Electronic band structure of $Sr_{0.5}Be_{0.5}TiO_3$ by using mBj-GGA potential. And the the high-symmetry points in the Brillouin zone, $\Gamma$, Z, R, A, M, X.

TABLE III. Volume optimized (A$^\circ$) , The lattice parameters $(a, b, c)$ (Å), bulk modulus B(GPa) and its pressure derivative B'.

| Material | Approximation | optimized volume | Parameters | | | | |
|---|---|---|---|---|---|---|---|
| | | $V_{0p}$ | $a = b$ | $c$ | $c/a$ | B | B' |
| $Sr_{0.5}Be_{0.5}TiO_3$ | GGA-PBEsol | 113.837 | 3.849 | 7.684 | 1.996 | 191.996 | 4.92 |
| | LDA | 111.057 | 3.819 | 7.615 | 1.994 | 203.95 | 2.00 |
| | averaged value | 112.447 | 3.834 | 7.649 | 1.995 | | |

## 3. Results and discussion

### 3.1. Structural and electronic properties

Using the data shown in Table II as the starting point for geometrical optimization for the Compound $Sr_{0.5}Be_{0.5}TiO_3$. The total energy volume and $c/a$ curves are shown in Fig. 3. Our results are reported in Table III. We note, for the calculations using (GGA-PBEsol, LDA) approximations of $Sr_{0.5}Be_{0.5}TiO_3$, that there are any theoretical or experimental data for comparison, but we remark that the substitution of atom Sr by atom Be. Causes a noticeable decrease in the lattice parameter a(Å). We know that for SrTiO3, $a_{exp} = 3.91$ A$^\circ$[21] for cubic structure. This is acceptable considering that the ionic radius of $Sr^{2+}$ (1.18 Å) bigger than $Be^{2+}$ (0.45 Å). To the best of our knowledge, there were no comparable studies done on the $SrBeTi_2O_6$ compound. And so, we calculated the formation energies ($E_{form}$) of the proposed systems according to the equation of the reaction considered for the creation of the system.

Which defined as the difference between the total energy of $SrBeTi_2O_6$ phase and the total energy of isolated atoms Sr, Be, Ti, and O. Using the following equation:

$$E_{form}(SrBeTi_2O_6) = E_{tot}(SrBeTi_2O_6)$$
$$- E_{tot}(Sr) - E_{tot}(Be) - 2E_{tot}(Ti) - 6E_{tot}(O), \quad (3)$$

where Etot(Sr), Etot(Be), and Etot(Ti), Etot(O) correspond to the total energy per atom for Sr, Be, and Ti, O atoms, respectively, calculated by the same method used for E total ($SrBeTi_2O_6$). We found that the calculated formation energy is -4.757 Ry, which indicates that the ($SrBeTi_2O_6$) alloy is thermodynamically stable due to its negative formation energy. The calculation of the electronic properties is very important to determine the other physical properties. For accuracy, we have applied the possibility of using the averaged value as the volume optimized, $V_{Avg}$, where $V_{Avg} = (V_{op}LDA + V_{op}GGA )/2$, and the averaged value for the ratio $c/a$ (avg) in Table III. Here VLDA (VGGA-PBEsol) is the volume optimized obtained from an LDA (GGA-PBEsol) optimization procedure.

When V Avg and $c/a$ (avg) ratio is used as input into the Wien2k code implemented with the mBJ potential, a better agreement of the bandgap value is obtained as compared to the results with either approximation LDA or GGA-PBEsol. So this procedure turns out to give better results than the one recommended by Tran and Blaha, and its extra computational cost is relatively low [22]. The band structure calculated with this approach obtained along with the high symmetry directions for space group P4/mmm(N$^\circ$123) in the zone Brillouin, with k-vector. Description with the following [23]: GM(0,0,0); Z(0;0;1/2); R(0,1/2,1/2); A(1/2,1/2,1/2);M(1/2,1/2,0); X(0,1/2,0) of $Sr_{0.5}Be_{0.5}TiO_3$ is schematized in Fig. 3. We note that our calculations outputted
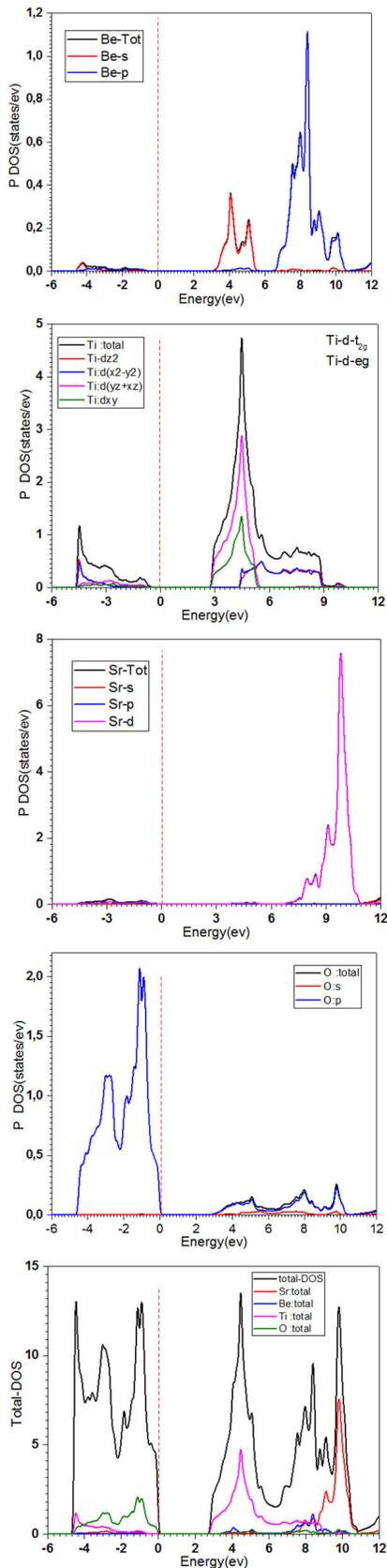
FIGURE 4. Total and partial DOS of $Sr_{0.5}Be_{0.5}TiO_3$ by using mBj-GGA potential.
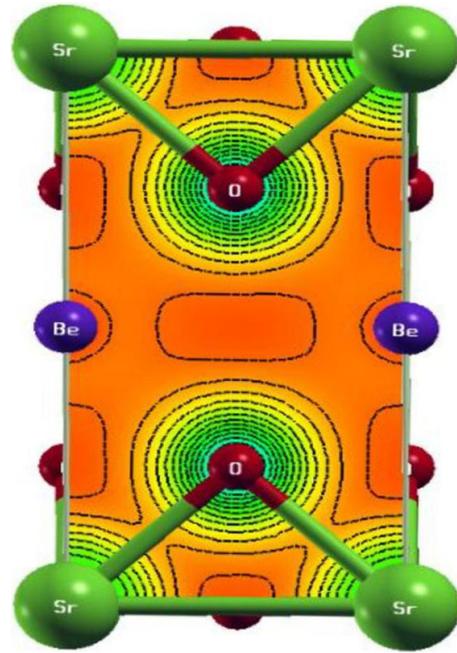


FIGURE 5. Electron density contour plots along (100) directions.

an indirect bandgap ($\Gamma - X$) equal to 2.77 eV, using mBj approximation, which indicates a semiconductor behavior. The contribution of atomic total densities to the total crystal density is shown in Fig. 4. This shows that the DOS and PDOS of $Sr_{0.5}Be_{0.5}TiO_3$ consist bandgap ($E_g = 2.77$ ev) and we note that the density of states at Fermi level is zero, which gives a material having a semiconductor character, the valence bands formed by the hybridization between O-2p and Ti-3d. The conduction bands are dominated by three-fold degenerate Ti-3d-t 2g orbitals, which hybridize with Sr-3d and O-2s and Be-3s Table IV, show the Comparison of our calculated bandgap values with different types of approximations. Electron density indicates the nature of the bond among different atoms [27]. Figure 5 exposures the charge density behaviors in 2D, which is determined in the (100) plane for our compound, indicating the sign of the covalent bond in the studied compound.

## 3.2. Elastic properties

To obtain the elastic constants Cij, we used in the calculations the equilibrium structure of the standard volume [24]. The calculated elastic constants for several tetragonal structure compounds using the Tetra-elastic package are presented in Table V, the focus was on the Voigt-Reuss-Hill (VRH) approximation for its widely used [28]. The Pugh's criterion (G/B ratio) was proposed as an empirical malleability measure of polycrystalline materials [27]: if G/B< 0.5, a material behaves in a ductile manner, and vice versa, if G/B> 0.5, a material demonstrates brittleness. In our case, according to this indicator (G/B∼ 0.7), $Sr_{0.5}Be_{0.5}TiO_3$ will behave as a Brittle material. The stability criteria for tetragonal crystals are:

TABLE IV. Show Comparison of our calculated band gap values with different types of approximations.

| | | band gap Eg (ev) | | | |
|---|---|---|---|---|---|
| Material | | SrTiO3 | | | Sr$_{0.5}$Be$_{0.5}$TiO$_3$ |
| (with space group N°123 P4/mmm) | | Experiment | | | |
| Different types of approximations | .GGA-PBEsol | 1.87 | 1.73a | 3.4a | 1.25 |
| | .LDA | 1.82 | | | 1.34 |
| | . mBj- GGA | 2.80 | | | 2.77 |

TABLE V. Elastic constants (Cij, in Gpa).bulk modulus (B, in GPa), compressibility ($\beta$, in GPa$^{-1}$), shear modulus (G, in GPa), Pugh's indicator (G/B), Young's modulus (Y, in GPa), Poisson's ratio ($\nu$), with in the Voigt-Reuss-Hill (VRH) approximation.

| Method | XC | C11 | C12 | C13 | C33 | C44 | C66 |
|---|---|---|---|---|---|---|---|
| Sr$_{0.5}$Be$_{0.5}$TiO$_3$FP-LAPW | PBE | 300.91 | 55.85 | 196.83 | 490.12 | 61.26 | 122.53 |
| | | B$_{VRH}$ | G$_{VRH}$ | $\beta$ | Y$_{VRH}$ | $\nu_{VRH}$ | G/B |
| | | 199.18 | 86.46 | 0.0084 | 226.59 | 0.31 | 0.72 |

$$C11 > 0, \; C33 > 0, \; C44 > 0, \; C66 > 0,$$

$$(C11 - C12) > 0, \; (C11 + C33 - 2C13) > 0.$$

$$\text{and} \quad \{2(C11 + C12) + C33 + 4C13\} > 0 \quad [25].$$

The calculated elastic constants are positive and satisfy the criteria of generalized elastic stability [26]. We can confirm that Sr$_{0.5}$Be$_{0.5}$TiO$_3$ is mechanically stable.

## 4. Conclusions

According to the calculations in tetragonal space group n°123 structure of at zero temperature, using the full-potential linear augmented plane-wave method (FP-LAPW) within the known Wien2k code. Has been exercised to probe the ground state properties such a structural, electronic, and elastic constant stability of the compound. The conclusions we can observe are:

(a) The new compound Sr$_{0.5}$Be$_{0.5}$TiO$_3$ represented by forming a supercell $2 \times 1 \times 1$ of SrTiO$_3$ cubic structure is a tetragonal structure with space group P4/mmm n°123.

(b) The narrowing of Sr$_{0.5}$Be$_{0.5}$TiO$_3$ lattice calculated with PBEsol-GGA was inferred from the sharp decrease in unit cell volume $V_0$, due to the small ionic radius of Be$^{+2}$ compared with the ionic radius of Sr$^{+2}$.

(c) An additional hybridization between Be-2s and Ti-3d-2g in the conduction band narrowed the band gap calculated from 2.80 ev for SrTiO$_3$ to 2.77 ev for Sr$_{0.5}$Be$_{0.5}$TiO$_3$.

(d) From Pugh's ratio (B/G) we classify Sr$_{0.5}$Be$_{0.5}$TiO$_3$ as brittle material while to that Poisson's ratio suggests (0.3) Sr$_{0.5}$Be$_{0.5}$TiO$_3$ its brittle nature.

(e) The elastic constants $C_{ij}$ satisfy the mechanical stability criterion for tetragonal structure.

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