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Mechanical properties of CaN, SrN, and BaN compounds by density functional theory

Homa Sadat Sharifzadeh[1*], Sima Sadat Sharifzadeh[1], Faramarz Kanjouri[2] and Amirhosein Esmailian[1]

Abstract

Using density functional theory, a systematic study of the elastic properties of CaN, SrN, and BaN compounds is performed. As a result, the optimized lattice parameters and independent elastic constants are calculated within the generalized gradient approximation. We have also derived bulk and shear moduli, Young's moduli, Poisson's ratio, and brittle/ductile behavior for CaN, SrN, and BaN. The estimated anisotropy parameter, *A*, shows that SrN has higher degree of elastic isotropy in comparison to CaN and BaN.

Keywords: Elastic properties, Density functional theory, First principles calculations

Background

In the last decade, half-metallic ferromagnets, in which one of the two spin channels presents metallic properties while the other is a semiconductor, resulting in complete (100%) spin polarization around the Fermi level, have been extensively studied due to their potential application in spintronic devices. Recently, it was proposed that spin polarization may exist in solids that do not contain transition-metal or rare-earth atoms. The rock-salt CaN, SrN, and BaN compounds are the sample of half-metallic systems that do not contain any transition-metal atoms, wherein their electronic structure and magnetism were completely investigated. Recent theoretical studies indicate that for these three binary nitrides, the rock-salt structure is energetically more stable than other structure, which makes them more promising candidates for the fabrication of HM thin films with rock-salt structure on suitable substrates [1-3], and further experiments confirm the existence of self-assembled metastable CaN nanostructures. In addition, to extend the previous studies on alkaline-earth mononitrides, the surfaces of rock-salt CaN and SrN and their interfaces with semiconductors were investigated by Gao et al.[4].

As it is known, the elastic properties of crystals are closely related to many fundamental properties, such as equation of state, thermal expansion, melting point, and some others. From elastic parameters, valuable information can be obtained about intra-atomic bonding, structural stability, etc.

The present study illustrates the computational procedure employed to obtain the three independent elastic constants of the rock-salt CaN, SrN, and BaN from first-principles calculations on the basis of computational implementation of the density functional theory of electronic structure. One of the objectives is to evaluate the effectiveness of these approaches in providing accurate elastic constants of CaN, SrN, and BaN. Using Voight-Reuss-Hill approximation, bulk and shear moduli, Young's moduli, and Poisson's ratios for this component are also calculated [5-7].

Computational method

CaN, SrN, and BaN compounds are half-metallic ferromagnets. Our calculation has been performed using the full-potential linearized augmented plane wave method to solve the Kohn-Sham equations as implemented in Wien2k code [8]. In this code, the crystal structures were devided under the condition that the total energy is minimized for all atomic configurations. Exchange and correlation effects are treated using the generalized gradient approximation (GGA) [9]. The plane wave cutoff $K_{\mathrm{MAX}} = \frac{7.5}{R_{\mathrm{MT}}}$ (R_{MT} is the smallest muffin-tin radius in the unit cell) is chosen for the expansion of the wave functions in the interstitial region, while the charge density is Fourier expanded up to $G_{\mathrm{MAX}} = 14, 12, 12(\mathrm{Ryd})^{1/2}$ for CaN, SrN, and BaN, respectively. The integration in the

*Correspondence: homa.sharifzadeh@gmail.com
[1]Department of Physics, Islamic Azad University, Qom Branch, Qom 37185-364, Iran
Full list of author information is available at the end of the article

Brilloun zone is done on the special k points determined from the Monkhorst-Pack scheme [10]. In order to obtain the best equilibrium crystal structure and to ensure the accuracy of the subsequent calculation, the convergence tests for the total energy were strictly implemented.

The calculated lattice parameters are in good agreement with the calculated values in [1,2,11]. Our calculated lattice parameters are compared to those obtained in the previous research in Table 1.

Elastic properties

Hooke's law is applied to small strains (δ), and the elastic energy E can be approximated by a quadratic function of the strain components:

$$E \propto V_0 \sum_{i,j=1}^{6} \frac{1}{2} C_{ij} e_i e_j, \tag{1}$$

where C_{ij} are the elastic constants, V_0 is the equilibrium volume of the unit cell, and e_j is the components of the strain tensor. In the case of the cubic system, there are only three independent elastic constants, namely, C_{11}, C_{12}, and C_{44} [12]. So, a set of three equations is needed to determine all the constants, which means that three types of strain must be applied to the starting crystals. The first equation involves calculating the bulk modulus B, which is related to the elastic constants by the following formula:

$$B = \frac{(C_{11} + 2C_{12})}{3}.$$

The second one involves performing the volume-conservative tetragonal strain tensor:

$$\begin{bmatrix} \delta & 0 & 0 \\ 0 & \delta & 0 \\ 0 & 0 & \frac{1}{(1+\delta)^2} - 1 \end{bmatrix}.$$

Using the above strain tensor has an effect on the total energy from its unstrained value, as follows:

$$E(\delta) = E(0) + 3\,(C_{11} - C_{12})\,V_0\delta^2 + O(\delta^3),$$

where V_0 is the volume of the unit cell. Finally, for the last type of the deformation, we use the volume-conserving rhombohedral strain tensor given by

$$\frac{\delta}{3} \begin{bmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \\ 1 & 1 & 1 \end{bmatrix}.$$

This changes the total energy to

$$E(\delta) = E(0) + \frac{1}{6}\,(C_{11} + 2C_{12} + 4C_{44})\,V_0\delta^2 + O(\delta^3).$$

The calculated values of elastic constants are listed in Table 2. The mechanical stability conditions

$$C_{11} - C_{12} > 0, \quad C_{11} > 0, \quad C_{44} > 0, \quad C_{11} + 2C_{12} > 0$$

Table 1 Calculated lattice constant and comparison with other works

	CaN	SrN	BaN
a (Å) (present work)	5.016	5.379	5.677
a (Å) [1]	5.091	5.34	-
a (Å) [2]	5.03	5.40	5.69
a (Å) [11]	5.0	5.40	5.55

Table 2 GGA calculated elastic constants (C_{11}, C_{12}, and C_{44}) for CaN, SrN, and BaN in rock-salt structures

	CaN	SrN	BaN
C_{11}(GPa)	145.48	106.16	96.65
C_{12}(GPa)	50.03	43.04	32.89
C_{44}(GPa)	6.76	25.05	4.09

Table 3 Calculated mechanical parameters values of CaN, SrN, and BaN using Voight, Ruess, and Hill approximations

	CaN	SrN	BaN
A	0.14	0.79	0.13
$1-A$	0.86	0.21	0.87
A_G	0.38	0.01	0.42
$B_V = B_R = B_H$(GPa)	81.85	64.08	54.14
$\beta_V = \beta_R = \beta_H$($10^{-3}$/GPa)	0.0122	0.0156	0.0185
G_V (GPa)	23.14	27.67	15.21
G_R(GPa)	10.29	27.31	6.28
G_H(GPa)	16.72	27.49	10.75
E_V(GPa)	63.45	72.55	41.71
E_R(GPa)	29.62	71.74	18.14
E_H(GPa)	46.54	72.15	29.93
ν_V	0.3708	0.3113	0.3716
ν_R	0.4397	0.3134	0.4442
ν_H	0.4052	0.3123	0.4079
λ_V(GPa)	33.21	22.82	22.00
λ_R(GPa)	37.51	22.94	24.99
λ_H(GPa)	35.36	22.88	23.50
μ_V(GPa)	23.14	27.66	15.21
μ_R(GPa)	10.29	27.31	6.28
μ_H(GPa)	16.72	27.49	10.75
B_V/G_V	3.54	2.32	3.56
B_R/G_R	7.96	2.35	3.56
B_H/G_H	4.90	2.33	5.04

A, anisotropy factor; A_G, anisotropy in shear moduli; B, bulk moduli; β, compressibility; G, shear moduli; E, Young's modulus; ν Poisson's ratio; λ and μ, Lame's constants.

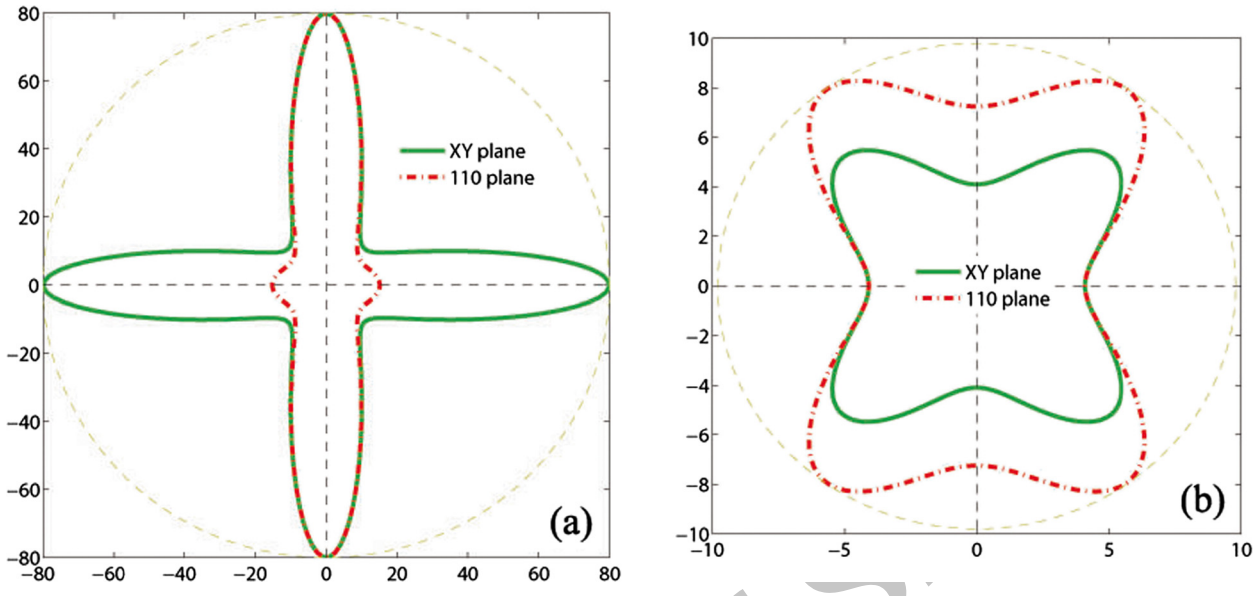

Figure 1 Projections of directional dependence of (a) Young's and (b) shear moduli in different planes for CaN.

can lead us to the validity of the elastic moduli [13,14]. The calculated elastic constant values satisfy all these stability conditions, including the fact that $C_{12} < C_{11}$. Furthermore, the calculated elastic moduli also satisfy the cubic stability condition, i.e., $C_{12} < B < C_{11}$. Thus, our calculated values of elastic moduli are justified.

There are two approximation methods to calculate the polycrystalline modulus, namely the Voight method and the Reuss method. Using energy considerations, Hill showed that the Voight and Reuss equations represent upper and lower limits of realistic polycrystalline constants and recommended that a practical estimate of the bulk and shear moduli should be the arithmetic means of the extremes. Elastic properties (such as bulk modulus, shears modulus, Young's modulus, and Poisson's ratio) are studied in the Voight-Reuss-Hill approximation, and their values are accumulated in Table 3. As far as we know, there are no reports in literature about these parameters for comparison.

The elastic anisotropy of crystals is an important factor in material science. There are different ways to estimate

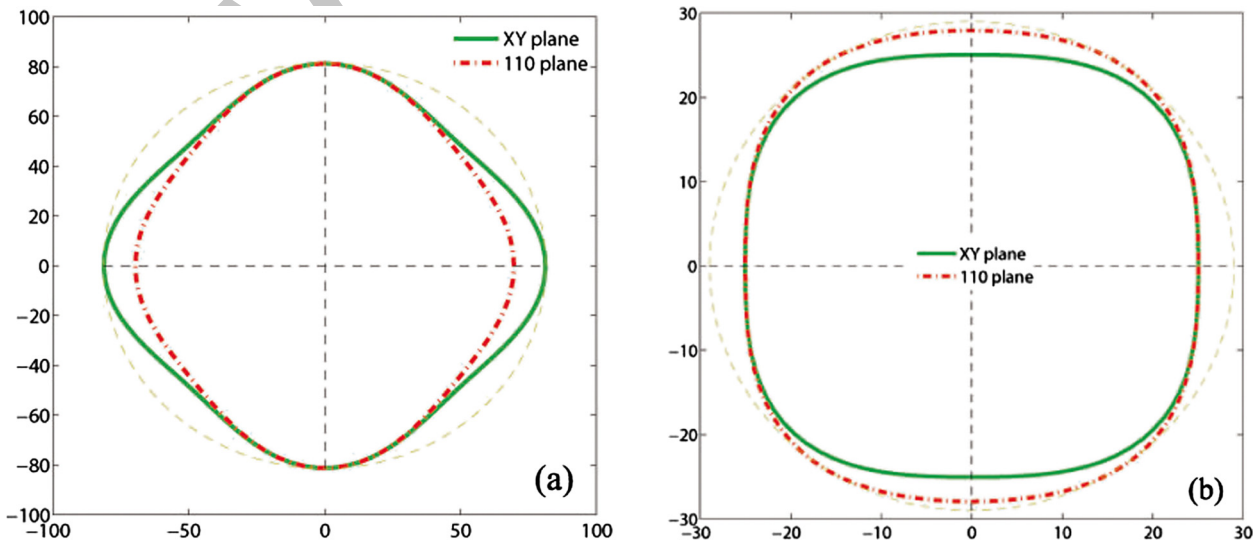

Figure 2 Projections of directional dependence of (a) Young's and (b) shear moduli in different planes for SrN.

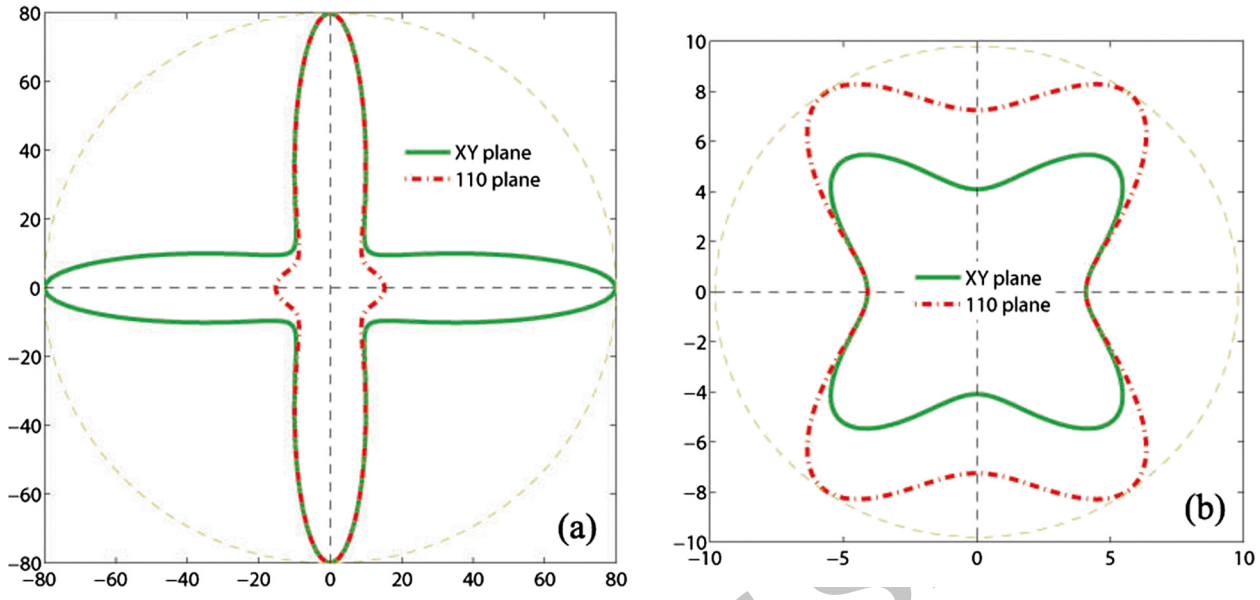

Figure 3 Projections of directional dependence of (a) Young's and (b) shear modulus in different planes for BaN.

elastic anisotropy theoretically. For example, the so called Zener's anisotropy parameter $A = 2C_{44}/(C_{11} - C_{12})$ is widely used for this purpose [15,16]. The degree of deviation of Zener's anisotropy parameter from unity 1 indicates the degree of elastic anisotropy. SrN is nearly elastically isotropic with A = 0.79, and a higher degree of elastic anisotropy is found in BaN with A = 0.13, as listed in Table 3.

It is known that a high (low) B/G value is associated with ductility (brittleness), and the critical value which separates ductile and brittle materials is approximately 1.75 [17]. The calculated ratios B/G are 4.90, 2.33, and 5.04 for CaN, SrN, and BaN, respectively. These values classify the three materials as ductile and show that SrN is the most brittle among them. An additional argument for the variation in the brittle/ductile behavior follows directly from the calculated Poisson's ratio ν. Indeed, for brittle materials, these values are small enough, whereas for ductile materials, ν is typically 0.33 [17]. In our study, CaN and BaN with ν=0.4052 are more ductile than SrN with ν=0.4079.

Young's modulus is defined as the ratio of stress to strain and is used to provide a measure of stiffness. SrN with E_H=72.15 (GPa) is more stiff than CaN (E_H=46.54 (GPa)) and BaN (E_H=29.93 (GPa)).

The directional dependence of Young's modulus E and shear modulus G for a cubic system are given by [18,19]

$$\frac{1}{E} = S_{11} - 2\left(S_{11} - S_{12} - \frac{S_{44}}{2}\right)\left(l_1^2 l_2^2 + l_2^2 l_3^2 + l_3^2 l_1^2\right) \quad (2)$$

and

$$\frac{1}{G} = S_{44} + 4\left(S_{11} - S_{12} - \frac{S_{44}}{2}\right)\left(l_1^2 l_2^2 + l_2^2 l_3^2 + l_3^2 l_1^2\right), \quad (3)$$

where S_{ij} are the elastic compliance constants, and l_1, l_2, and l_3 are the directional cosines to the X, Y, and Z axes, respectively.

Directional dependence of Young's modulus and shear modulus in XY and ⟨110⟩ planes for three different compounds are shown in Figures 1, 2 and 3. As it can be seen from these figures, the projection curves for SrN are nearly circular, while the curves for CaN and BaN significantly deviate from the circular shape. Therefore, we conclude that the elastic isotropy degree of SrN is higher than the elastic isotropy degree of CaN and BaN. This result is consistent with the result obtained by Zener's anisotropy parameter.

On the other hand, the Debye temperature, T_D, is a fundamental parameter of a material which is linked to many physical properties, such as specific heat, elastic constants, and melting point. At low temperatures, the vibrational excitations arise solely from acoustic vibrations. Debye temperature corresponds to the upper limit of

Table 4 Mass density and Debye temperature of CaN, SrN, and BaN

	CaN	SrN	BaN
ρ (g/cm^3)	2.85	4.34	5.49
T_D (K)	319	299	163

phonon frequency in a crystal lattice. Hence, at low temperatures, the Debye temperature calculated from elastic constants is the same as that determined from specific heat measurements. It can be obtained from the average wave velocity by use of the following equation [20,21]:

$$T_{\mathrm{D}} = \frac{h}{k}\left[\frac{3n}{4\pi}\left(\frac{N_A\,\rho}{M}\right)\right]^{\frac{1}{3}}\upsilon_m. \tag{4}$$

Here h is the Planck constant, k is the Boltzmann constant,N_A is the Avogadro number, ρ is the mass density, M is the molecular mass per formula unit, and n is the number of atoms per formula unit. The average sound velocity in polycrystalline systems υ_m, is evaluated by [22,23]:

$$\upsilon_m = \left[\frac{1}{3}\left(\frac{2}{\upsilon_t^3} + \frac{1}{\upsilon_l^3}\right)\right]^{\frac{-1}{3}} \tag{5}$$

where υ_t and υ_l are the mean transverse and longitudinal sound velocities, which can be related by the shear and bulk moduli from Navier's equation [22-24]:

$$\upsilon_l = \left(\frac{3B + 4G}{3\rho}\right)^{\frac{1}{2}} \tag{6}$$

$$\upsilon_t = \left(\frac{G}{\rho}\right)^{\frac{1}{2}} \tag{7}$$

The results are summarized in Table 4. Debye temperatures for CaN, SrN, and BaN are 319, 299, and 163 K, respectively. It is clear from these results that the Debye temperature decreases from CaN to BaN due to the effect of the increase in the anion weight.

Conclusions

The elastic properties of CaN, SrN, and BaN were obtained using Voight-Reuss-Hill approximation. Our calculated Zener's anisotropy parameter, A, shows that SrN has the lowest degree of elastic anisotropy. According to the critical values of B/G, the three compounds are classified as ductile materials. SrN with E_{H}=72.15 GPa is more stiff than CaN and BaN compounds. The Debye temperature decreases from CaN to BaN due to the effect of the increase in the anion weight.

Competing interests

The authors declare that they have no competing interests.

Author details

[1]Department of Physics, Islamic Azad University, Qom Branch, Qom 37185-364, Iran. [2]Department of Physics, Kharazmi University, Karaj 31979-37551, Iran.

Authors' contributions

HSH and SSH have developed the theoretical part and the simulation program; in addition, they performed the calculations and also analyzed the data and the results. FK and AE provided guidance at various stages of the study, reviewed the manuscript, and participated in the editing of the manuscript. All the authors read and approved the final manuscript.

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