The first principles structural study on the Barium Oxonitrido silicate ($BaSi_4O_6N_2$) compound

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ABSTRACT

By means of first principles calculations, we have studied the structural, electronic, elastic and anisotropy properties of the Barium Oxonitrido silicate ($BaSi_4O_6N_2$) compounds. The recent study showed that it's crystal structure is in the hexagonal (P6/mmm, SPG No: 191) where *1a* and *1b* sites partially occupied by Ba atom with 0.871 and 0.129 ratio, respectively [1]. The elastic constants and lattice dynamical properties of this compound are calculated and its stability is discussed.

1. INTRODUCTION

Nitrido- and oxonitridosilicates (i.e. γ-Si3N4, $SiAlON_s$, $M_2Si_5N_8:Eu^{2+}$ {M = Ca, Sr, Ba}, $Eu_2Si_5N_8$, $MSi_2O_2N_2:Eu^{2+}$ {M = alkaline earth}, ...) have interesting physical and luminescence properties [1, 2]. Most of them are used for high power (2-100 W) LED applications. Scientists have shown intense assiduities to improve alternative Nitrido- and oxonitridosilicates [3].

Firstly, Braun et al. discovered green phosphor $Ba_3Si_6O_{12}N_2:Eu^{2+}$ [2]. Then, $BaSi_4O_6N_2$ synthesized by starting from $BaSi_2O_2N_2$ in a hexagonal unit cell [1]. In this study, we used DFT-based first principles method to investigate the structural and mechanical properties of $BaSi_4O_6N_2$ compound in experimentally determined structure (Hexagonal, P6/mmm).

The structure of the study; the method of calculation is given in Section 2, the results and discussion overall conclusions are presented in Section 3.

2. METHOD

All calculations have been carried by using the VASP code [4-6] based on the density functional theory (DFT). The electron–ion interaction was considered in the form of the projector-augmented-wave (PAW) method with plane wave up to an energy of 520 eV [7]. GGA-PBE type XC functional has been used for the electron–electron interaction. 9x9x6 Gamma-centered k-grids been used [8]. The stress-strain method, implemented in the VASP code, was used to predict the second order elastic constants [9]. Also, DFPT & Phonopy have been used for vibrational calculations [10, 11].

3. RESULTS AND DISCUSSION

3.1. Structural properties

The experimental findigns for the titled compound given in Table 1. Here, Space Group is P6/mmm (no. 191) and the lattice parameters are a = 5.3512, c = 7.5235 (1a and 1b Wyckoff sites are occupied by Ba atom with 87% and 13%, respectively) [1]. We propose three model for calculation.While 1a site fully accopied by Ba atoms in Model-I, 1b site occupied in Model-II. For Model-III, we create 2x2x2 supercell and Ba atoms have an occupancy of 87.5% and 12.5% in the 1a and 1b sites. The fully accopied structural view of the crystal structure given in Fig. 1. The calculated structural parameters and atomic sites for the proposed models with experimental data are given in Table 2.

Table 1. Experimental Crystallographic data for hexagonal $BaSi_4O_6N_2$.

Atom	Wyckoff	*x*	*y*	*z*	site occupation factor
Ba1	1a	0	0	0	0.871
Ba2	1b	0	0	1/2	0.129
Si1	4h	1/3	2/3	0.2866	1.0
O2	6i	1/2	0	0.2064	1.0
N1	2d	1/3	2/3	1/2	1.0

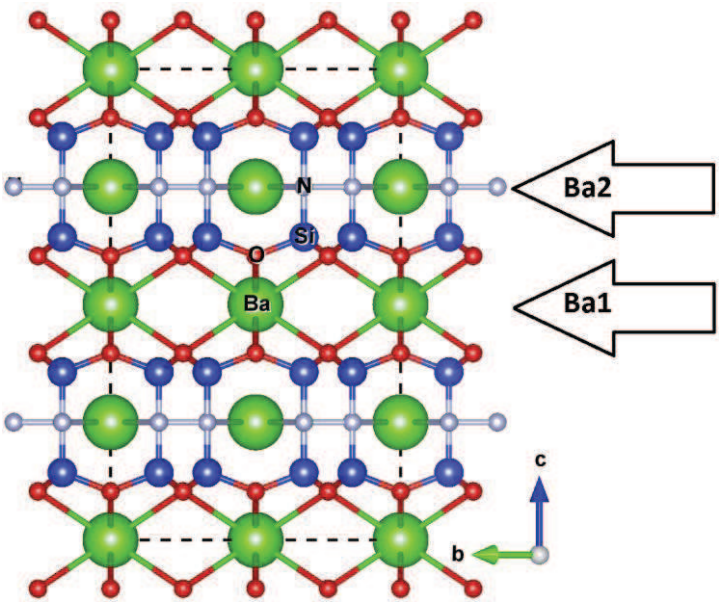


Figure 1. The crystal view of fully occupied sites.

Table 2. The calculated lattice parameters (a, c in Å), ground state energy (E_0 in eV/f.u.), and volume (V_0 in Å^3/fu) with available experimental values.

	a	*c*	E_0	V_0
Model-I	5.2254	7.9387	-99.9755	187.72
Model-II	5.3370	8.2995	-99.1387	204.73
Model-III	5.2414	7.9643	-99.8481	189.48
Experimental [1]	5.3512	7.5235		186.57

The calculated parameters for Model-I and Model-III best fit for experimental values than Model-II.

3.2. Mechanical properties

We have used the "stress-strain" method [9] to compute the elastic constants, and the findings are given in Table 3.

The Born's mechanical stability conditions for hexagonal crystals on the elastic constants are known as [12, 13];

$$C_{11}>0,\ C_{11}-C_{12}>0,\ C_{44}>0,\ (C_{11}+C_{12})C_{33}-2C_{12}^2>0$$

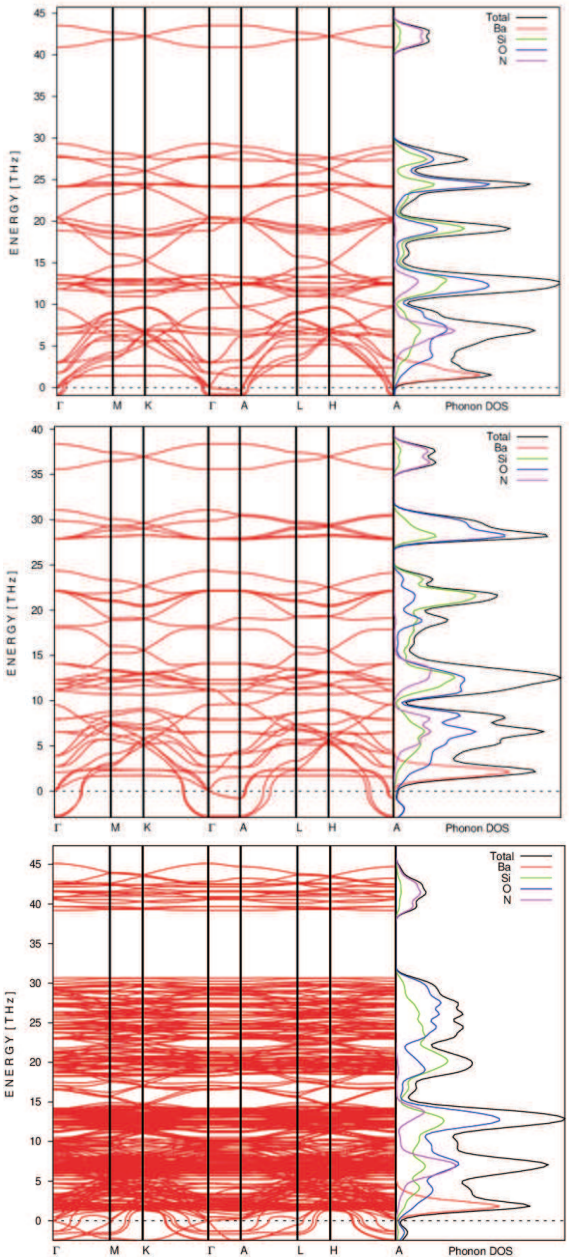
Our results are given in Table 3 satisfy Born's stability conditions [13] for Model-I and Model-III. We found that the titled compound mechanically unstable in Model-II.

Table 3. The calculated elastic constants (C_{ij} in GPa).

C_{ij} (GPa)	C_{11}	C_{12}	C_{13}	C_{33}	C_{44}	C_{66}	*Stability*
Model-I	229.9	93.7	26.4	126.7	12.7	68.1	Yes
Model-II	244.5	103	0.2	8.9	**-1.2**	70.8	No
Model-III	229.9	95.1	22.1	103.1	4.9	67.4	Yes

3.3. Dynamical Properties

The check the structural stability, we have been performed the DFPT calculation using the Phonopy code [10, 11]. The results are illustrated in Fig. 2. It is found that Model-I is dynamically more stable structure for the titled compound.



Model-I

Model-II

Model-III

Figure 2. The calculated phonon distribution for the considered models

4. CONCLUSION

We have performed the first principles total energy calculation for hexagonal $BaSi_4O_6N_2$ compound using the plane-wave pseudopotential approach to the density-functional theory within the generalized gradient approximation. The calculated lattice parameters are consistent with the experimental values. The calculated second order elastic constants and phonon dispersions show that the compound mechanically and dynamically more stable in Model-I then Model-II and Model-III.

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