Parameterized Empirical Potentials For BaF_2 From Ab-Initio Methods Applied To The Study Of Superionic Transition Of C-BaF_2

P.W.O. Nyawere
Department of Physical Sciences
Rongo University
P.O. Box 103, 40404,
Rongo, Kenya
pnyawere@gmail.com

***Abstract*—Potentials for BaF_2 have been generated from the ab-initio methods and tested to determine its applicability in classical dynamics. The minimization process for this force field was stopped at 17% where forces, stresses and energies were close enough to the ab-initio results. Using the steepest descent approach, this potential was used to calculate the lattice constant of BaF_2 and inter-atomic bond length. The lattice parameter for BaF_2 using this force field was found to be 6.13 Å comparable to 6.10 Å from DFT. Other parameters that are compared are the bond length between cations and anions and transition temperatures. The results are found to be in good agreement with the already computed results from DFT. The melting temperature calculated at 1700 K is closer to 1641 K from experiment than the already reported. This current potential therefore seems to be an improvement to the classical potentials that have previously been used in molecular dynamics study of BaF_2.**

Keywords—superionic, empirical potential, molecular dynamics

I. INTRODUCTION

Barium fluoride falls in the family of compounds called alkaline-earth fluorides. Some of the other fluorites in this category include MaF_2, CaF_2 and SrF_2. BaF_2 crystallizes into cubic, orthorhombic and hexagonal phases with cubic phase being the most stable. BaF_2 is a high density luminescent material (radiation hard material) used in gamma ray and elementary particle detectors due to its scintillation property. Both CaF_2 and BaF_2 have been used in precision vacuum ultraviolet (VUV) lithography, scintillation detection and as superionic conductors. Superionic property of BaF_2 can be improved by doping it with a small amount of appropriate dopant to create ions redistribution in the space charge region [1]. Because of its superionic property, BaF_2 can be used in high-temperature batteries, fuel cells, chemical filters and sensors.

Superionics can go through solid to solid phase transition just before reaching melting point. This transition can be type I superionics or type II superionics. Whereas type I superionics evolve to highly conducting state abruptly, type II evolve continuously [2]. Specific heat jump and high-temperature conductivity behaviour for superionics are due to diffuse phase transition at which there is a relative disordering of the anion sub lattice. Presence of a broad peak in the heat capacity curve has been observed at a temperature T_C (specific heat maximum) essentially below the melting point T_m for most of superioncs [8]. Earlier studies based on empirical potentials have focused on MgF_2, CaF_2, SrF_2 and BaF_2 [3-7]. Calculations are done using classical molecular dynamics of ref [9] has shown that BaF_2 becomes superionic at about 1250 K.

The rest of this paper is given such that section II is presentation of the methods used in obtaining the potential from *ab initio* methods and minimizing the force field, section III is the results and discussions then conclusions in section IV.

II. METHODS

In parameterization procedure, the empirical potentials were fitted into *ab-initio* data as described by Tangney and Scandolo [11] in the parameterization of the force field for silica. In this approach, the potential of Morse-Stretch [10] is used. This potential is more transferable and is given as,

$$U_{ij} = \frac{q_i q_j}{r_{ij}} + D_{ij}\left[e^{\gamma_{ij}[1-(r_{ij}/r_{ij}^0]} - 2e^{(\gamma_{ij}/2)[1-[r_{ij}/r_{ij}^0]}\right], \qquad [1]$$

where the interaction between atom types *i* and *j* is given by the parameters q_i, q_j, D_{ij}, γ_{ij}, $r_{ij}{}^0$ and r_{ij}. The second term in eqn. [1] is the short range part of the potential. This potential is more transferable between different phases compared to Born-Mayer potential [12]. This potential is improved by inclusion of polarization effects. In this force field model, dipole moments both by electrostatic forces and the short-range repulsive forces between anions and cations are introduced. The short-range contribution is described by the approach of Madden et al [13] and is given as;

$$\mathbf{P}_{\mathbf{i}}^{sr} = \alpha \sum_{j \neq i} \frac{q_i r_{ij}}{r_{ij}^3} f_{ij}(r_{ij}), \qquad [2]$$

where

$$f_{ij}(r_{ij}) = c_{ij}\sum_{k=0}^{4}\frac{(br_{ij})^k}{k!}e^{-br_{ij}} \qquad [3]$$

and $r_{ij} = r_i - r_j$, while b and c are parameters of the model [11]. The dipole moments are charge-dipole and dipole-dipole interactions and are calculated using the Ewald summation scheme [14]. The dipoles on each ion are found self-consistently at each step by iterating to self-consistency the equation

$$\mathbf{P}_i^n = \alpha\mathbf{E}\left(r_i;\left\{\mathbf{p}_j^{n-1}\right\}_{j=1,N}\right)+\mathbf{p}_i^{sr}, \qquad [4]$$

where the dipole moment on ion *i*, $\boldsymbol{p}_i$ depends on the electric field $\mathbf{E}(\mathbf{r}_i)$ at position r_j which in turn depends on the positions and the dipole moments of all the other ions and on the short-range dipole, $\mathbf{p}_i^{sr}$. For the empirical approach to be accurate, the force field used should be able to represent the electronic effects which are important for ionic motions. A good force field should thus properly capture the electronic effects necessary for ionic motions. A classical polarizable potential with fixed point charges and atomic polarizable as implemented in the Asap Code [11] was used in the parameterization of the potentials. Conditions for fitting were chosen at 1200 K with pressure set at zero. This temperature was chosen so as to give BaF_2 amorphous form and therefore different number of configurations that were used in the fit. Starting from a suitable potential (here Buckingham potentials [16] were used), a molecular dynamics run to obtain the initial configurations was done. The configurations are supposed to be apart to minimize similarities between them. These configurations from molecular dynamics runs were used in the *ab initio* studies to do a self-consistent calculation. The parameters of the potential were fitted to forces, stresses and total energies taken from these configurations using the force-matching approach [17]. In *ab-initio* calculations, density functional theory (DFT) using pseudopotentials method with generalized gradient approximation [18] was employed. All calculations were done on a supercell of 32 barium and 64 fluorine atoms. An energy cut-off of 50 Ry was used for the convergence of the calculations of stress. In this scheme of potential parameterization, the function;

$$\Gamma = w_f\Delta F + w_s\Delta S + w_E\Delta E, \qquad [5]$$

was minimized to get the force field parameters ΔF, ΔS and ΔE which are the differences between the classical and *ab ignition* forces, stresses and energies respectively [11]. The values w_f, w_E and w_E are the corresponding weights of the forces, stresses and energies respectively.

III. RESULTS AND DISCUSSIONS

A. The Potential

The final force field at the lowest minimization value attained is shown in Table 1 and Table 2. At the minimum, the charge *q* for Ba was 1.612 C while fluorine was -0.806 C. These values were very close to the exact charge values of 2 and -1 C for Ba and F anions, respectively, and hence suitable for the simulations. The comparison between the structural parameters of molecular dynamics of *C*-BaF_2 and those obtained from density functional theory are given in Table I. The results obtained from molecular dynamics simulations were found to be in good agreement with those obtained from the DFT calculations. The parameters shown in Table I was then used to run molecular dynamics simulation of BaF_2 in order to calculate some of its thermal properties. Some of these properties studied include the phase transition and melting temperatures of BaF_2 which are important in determining the superionic transition temperatures.

Fig. 1 shows the force matching between quantum espresso and the parameterized one.

TABLE 2

Force field parameterized for BaF_2. $D_{F\text{-}F}$, $D_{Ba\text{-}F}$ and $D_{Ba\text{-}Ba}$ are parameterization constants between F-F, Ba-F and Ba-Ba atoms, respectively, $\gamma_{F\text{-}F}$, $\gamma_{Ba\text{-}F}$ and $\gamma_{Ba\text{-}Ba}$ are the short polarization parameters, respectively. $r_{F\text{-}F}$, $r_{Ba\text{-}F}$ and $r_{Ba\text{-}Ba}$ are the distances between different atoms and α is the polarization constant. The constants *b* and *c* are fitting parameters of the model

Parameter	Value
q_F	-0.80595
$D_{Ba\text{-}Ba}$	-1.7294 x 10^{-2}
$\alpha_{F\text{-}F}$	7.0831
$\alpha_{Ba\text{-}Ba}$	4.6537
q_{Ba}	1.6.1189
α	4.828142
$D_{Ba\text{-}F}$	1.2765 x 10^{-2}
$\alpha_{Ba\text{-}F}$	8.4838
$r_{Ba\text{-}F}$	8.0098
b	1.76615
c	8.68333
$D_{F\text{-}F}$	8.2344x10^{-02}
$\alpha_{Ba\text{-}Ba}$	5.5049
$\alpha_{F\text{-}F}$	3.6812

TABLE 1: PARAMETERS COMPARISON

Parameter	Molecular Dynamics	DFT
Lattice parameter, a_0	6.125	6.10
Ba – Ba	4.31	4.31
Ba – F	2.66	2.64
F-F	3.08	3.05

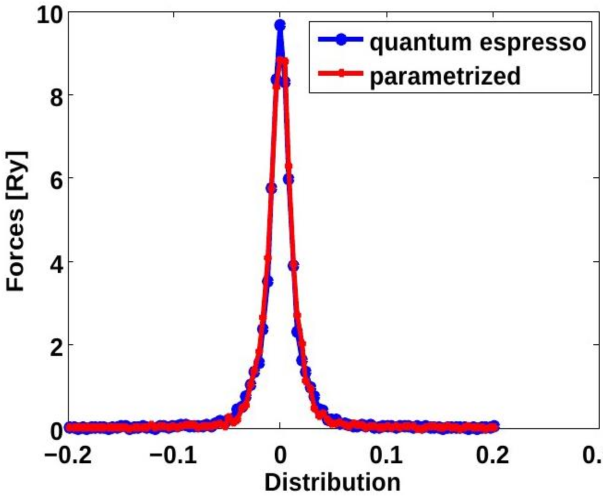

FIG 1: Forces against distribution in force matching minimization between quantum espresso and parameterized potential

The variation of energy with respect to temperature is generally the specific heat capacity of the material. Fig. 2 therefore shows that there are peaks, C_P, at T = 1000K and at T = 1700 K. The first peak is the superionic transition temperature and the second is the estimated melting temperature of BaF_2. These two temperatures are lower than those calculated by Ivanov-Shitz et al [16] which are reported as 1285 K and 1800 K, respectively. The difference is attributed to their use of classical molecular dynamics which tends to overestimate the melting point, since the experimental melting temperature of BaF_2 is 1641 K [15], a value which is much closer to our calculated value of 1700K than the 1800 K predicted earlier by Ivanov et al [16]. This lower deviation is attributed to the fact that the empirical potential constructed in this current work considering the polarization effects on BaF_2 which play an important role in the properties of fluorides unlike in the classical molecular dynamics.

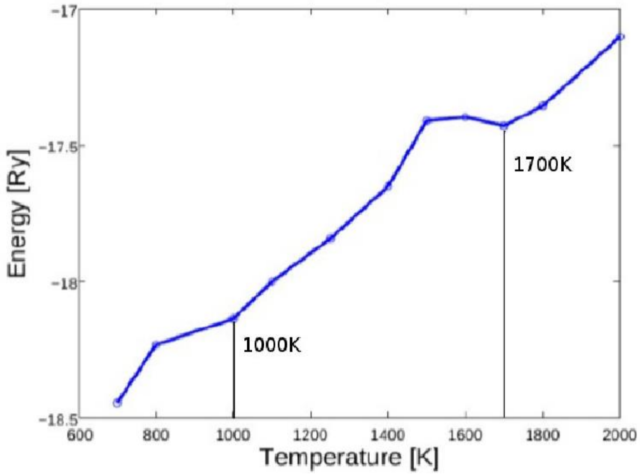

FIG 2: The temperature dependence of the total energy for the c-BaF_2

B. Ionic Motion

At low temperatures, the cations and anions are in vibrational thermal motion, with the vibrational amplitude of the fluorine atoms being higher than those of Barium atoms due to their differences in sizes and weights. Barium atoms continue vibrating in their equilibrium positions at higher temperatures while fluorine anions begin diffusing between nearest neighboring sites. It is therefore correct to assume that most of the thermodynamic properties of BaF_2 are a result of the motion of the anions and to some extent this applies to other fluorite structures e.g. CaF_2. In the following section we discuss the cation and anion motion using radial distribution function and anion motion using mean square displacement.

C. The Radial Distribution Function, g(r)

The radial distribution function gives the probability of finding a particle at a distance *r* from another particle. In Fig 3 the first (and large) peak occurs at around $r = 4.20$ Å with the radial distribution function $g(r)$ having an intensity of about 2.25.

This value of 2.25 implies that it is 2.25 times more likely that two Ba-Ba ions would be found at this separation. This separation distance is in agreement with the value of 4.31 Å found from steepest descent calculations reported in Table 2. The distance between Ba-F is about 2.62 Å and that between F-F is 3.07 Å. At this temperature of 800 K and 1000K as shown in Fig 3 and Fig 4, it was found that both ions were still vibrating at their mean lattice positions, since the Ba-Ba, F-F and Ba-F distances were unchanged.

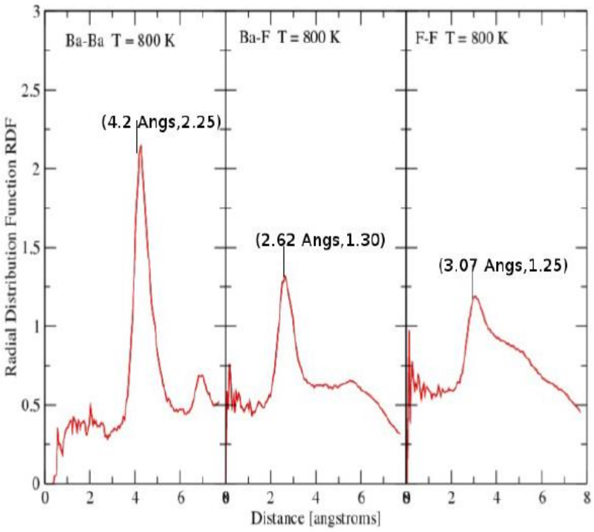

FIG 3: The radial distributions function at 800K. Both cation and anion are within their lattice site positions.

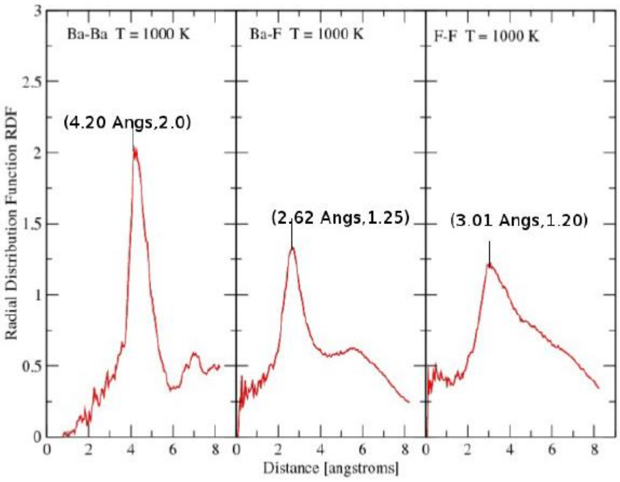

FIG 4: The radial distributions function at 1000K. Cations and anions are still at their mean lattice positions.

Radial distribution function on the other hand is reduced to 2.0 for Ba-Ba, 1.25 for Ba-F and 1.20 for F-F. Fig 3 gives the distance between Ba-F ions as about 2.62 Å with low $g(r)$ (intensity) value of about 1.30 while the F-F distance at this temperature is 3.07 Å with radial distribution function whose intensity is 1.25. The low intensity of F-F peaks when compared to those of Ba-Ba (2.25) and Ba-F (1.30) implies that fluorine ions vibrate more and therefore the chances of finding F-F close to each other is the lowest. This is in agreement with the fact that anions diffuse more than cations.

In Fig 5, where the temperature is 1400 K, the distance between Ba-Ba appears still to be 4.2 Å but radial function is reduced from 2.25 to 1.80. Ba-F and F-F radial distribution functions are 1.4 and 1.0, respectively.

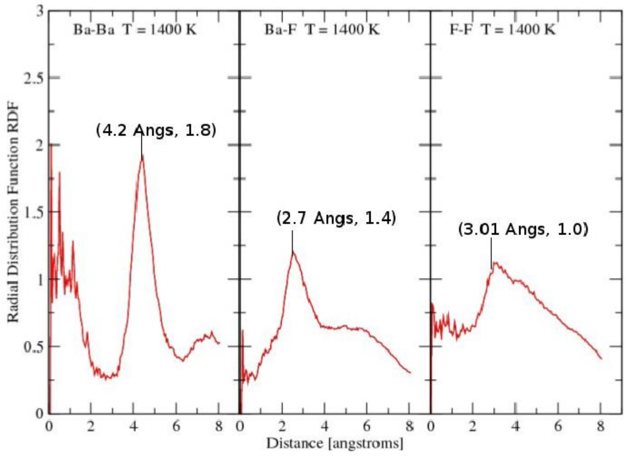

FIG 5: Radial distributions at 1400 K. There is noticeable variation in the positions of both cations and anions.

Therefore, the chances of finding these two cations close to each other has somewhat reduced with increase in temperature. The intensity of Ba-F radial distribution function is below 1.4 at 1400 K while that of the F-F radial distribution function is below 1 (Fig. 2). It still appears that the distance between F-F is 3.01 Å with the low radial distribution discussed in the next section, it is apparent that fluorine ions have started diffusing at 1000 K. In Fig. 6 and Fig 7, it is seen that the intensity of $g(r)$ for Ba-F and F-F is tending to one while that of Ba-Ba is at around 1.75.

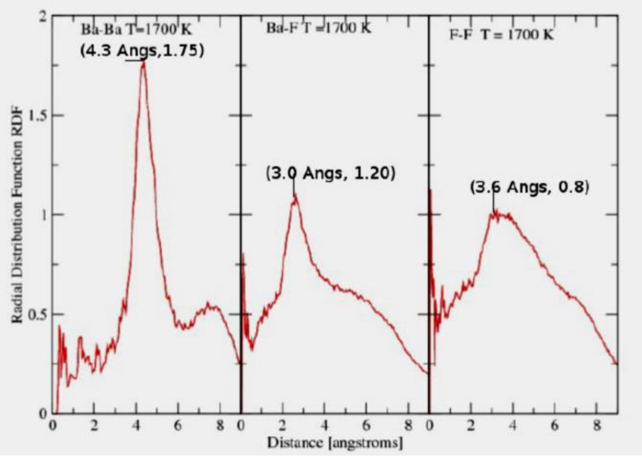

FIG 6: Radial distributions at 1700 K.

A radial distribution function of 1 indicates the absence of long-range forces. This is not the case in BaF_2 given that the interactions of cation-cation, cation-anion and anion-anion give values that are more than one even after melting point at 1700 K which is near experimental value of 1641 K.

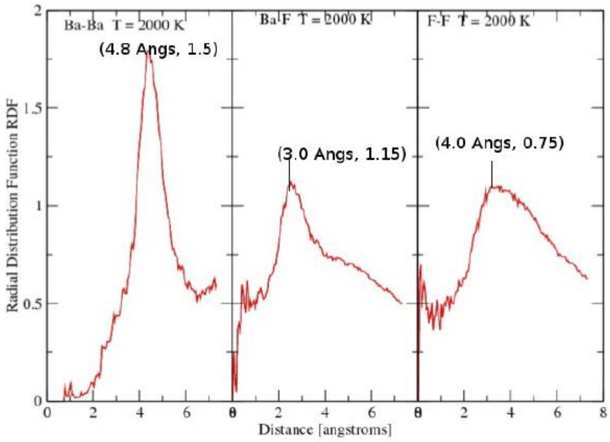

FIG 7: Radial distribution functions at 2000 K.

This is an indication of presence of long-range forces in BaF_2 which exists even after the F anions have transformed to molten form while Ba cations are still in their equilibrium lattice positions. This is in good agreement with classical molecular dynamics reported by Ivanov et al [16].

D. Mean Square Displacement, MSD

Fig 8 shows a plot of the mean square displacement MSD against time. The figure shows that at about 1000 K, there is a jump which corresponds to the superionic phase transition predicted to start at 1000 K.

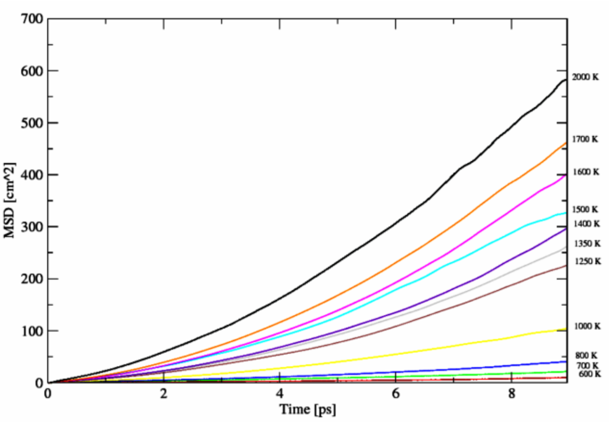

FIG 8: Mean square displacement $\left\langle \Delta r^2 \right\rangle$ as a function of time in picoseconds

There is another appreciable gap at 1700 K which is in agreement with the results shown in Fig 2 where superionic conductivity is predicted to start at 1000 K. There is another appreciable gap at 1700 K, which is in agreement with the results presented previously in Fig 2 for the melting temperature of BaF_2. This gap is the liquid phase of BaF_2 where the anions are diffusing more freely.

This study reveals that the anions motion in the low temperature phase of up to 1000 K is vibrational in nature but are diffusing in the high temperature phase. The diffusion constant is in the range of 4.55 x 10^{-5}cm^{2}s^{-1} at 500 K to 1.52 x 10^{-4}cm^{2}s^{-1} at 1500 K. These values are typical of superionic conductor which is about 10^{-5}cm^{2}s^{-1}[16].

IV.. CONCLUSIONS

Parameterized potential for BaF_2 have been generated from the *ab initio* methods to improve on the results of molecular dynamics that have been done previously. With this new potential, polarization effects have been taken into account. These effects improve the results for the lattice constant and bond lengths. These results are close to the *ab initio* ones, a sign that the electronic interactions are crucial in the dynamics of atoms. Our melting point is 1700 K comparable to 1641 K from the experimental data. This is an error of 3.6% compared to previous study of 1800 K and an error of 9.7%. The current transition temperature is here reported at 1000 K in comparison to 1250 K. The current potential is therefore an improvement of the classical potentials previously used to do simulations of molecular dynamics of BaF_2.

REFERENCES

[1] N. Sata et al Mesoscopic fast ion Conduction in nanometer-scale, Nature vol.408, pp.946-948, 2000.

[2] J.B. Boyce and B.A. Huberman Superionic Conductors; transitions, structures, dynamics. Physics Reports, vol 51 (4) pp 189-265, 1979

[3] Chakravorty D, J. Phys. and Chem. Solids, vol 32, pp 1091, 1971

[4] M.J Gillan and P.W.M Jacobs., Phys. Rev. B vol 28, pp.759, 1983

[5] S. Keeton and W. Wilson Phys. Rev B vol 7, pp. 834, 1973

[6] Norgett, J. Phys. C: Sol. Sta. Phys. 4, 298 1971.

[7] Franklin A, J. Phys and Chem of Sol. vol 29, pp. 823 1968

[8] C.E. Derrington, A. Lindner and O'kee eM, Ionic Conductivity of some alkaline earth halides. J. of Solid State Chem., vol 15(2): pp 171-174, 1975

[9] Ivanov-Shitz, A.K, Aityan S.K, and Kohler H.H, Molecular Dynamics Simulation of the superionic conductor BaF_2, App. Physics A: Materials Science & Processing, vol 54(3): pp 251-257, 1992.

[10] Demiralp E, Cagin T., and Goddard II W.A., Morse Stretch potential charge equilibrium force field for ceramics: Application to the quartz-stishovite phase transition and silica glass. Physical Review letters, vol 82(8), pp.1708- 1711, 1999.

[11] Tangney P. and Scandolo S., Ab initio parameterized interatomic force field for silica. The Journal of chemical Physics, vol 117: pp 88-98, 2002

[12] Tersoff J. et all. Modelling solid-state chemistry: Interatomic potentials for multicomponent systems. Physical Review B, vol 39(8): pp 5566-5568, 1989

[13] Rowley A.J. et al Evaluation of the many body contributions to the interionic interactions in MgO. The Journal of chemical physics, vol 108: pp 102-109, 1998

[14] Tom D., Darrin Y., and Lee P Particle mesh Ewald: N-log (N) method of Ewald Sum in large systems. Journal of chemical Physics, vol 98: pp 100-109, 1993

[15] Chemexper;http://www.chemexper.com/chemical/supplier/cas/7787-32-8.html, Catalog of Chemical Supplies, Accessed July2018

[16] Ivanov-Shitz A.K., Buchstab A.S., Aityan S.K., and Kohler H.H. Molecular Dynamics simulation of the superionic conductor BaF_2 . Applied Physics A: Materials Science & Processing, vol 54(3): pp 251-257, 1992

[17] Ercolessi F. and Adams J.B. Interatomic potentials from first principles calculations; force-matching method. Europhysics Letters, vol. 26: pp 583-586, 1994

[18] Perdew J.P., Burke K., and Wang Y. Generalized Gradient approximation for the exchange-correlation hole of a many-electron system. Physical Review B, vol 54(23);pp165-168, 1996