

**Lattice Dynamics of Alkaline-Earth Hafnates BaHfO<sub>3</sub> And SrHfO<sub>3</sub>**M. M. Sinha<sup>1,\*</sup><sup>1</sup>*Department of Physics, Sant Longowal Institute of Engineering and Technology,  
Longowal, Sangrur (Punjab) – 148106, India*

(Received April 14 2010)

The perovskite-type oxides have the potential to be attractive functional materials because they have various unique properties in spite of their relatively simple crystal structure. Alkaline-earth hafnates (MHfO<sub>3</sub> with M = Ba, Sr) doped with a low level of cerium are suitable materials for high-energy nuclear medical applications. The luminescence properties of the cerium-doped hafnates have been investigated extensively; little study was done on dynamical and electronic properties of the MHfO<sub>3</sub> host due to the unavailability of single crystal. The knowledge of the dynamical properties of the materials is very important in order to understand the possible applications of its properties in different branches of new engineering. In this work, the results of my theoretical investigation on the phonon properties of BaHfO<sub>3</sub> and SrHfO<sub>3</sub> in its cubic phase is being presented by applying lattice dynamical simulation method based on de Launey angular force (DAF) constant model to understand the role of phonon in this system. The calculated zone center phonon frequencies agree well with available results. The phonon spectrum of BaHfO<sub>3</sub> and SrHfO<sub>3</sub> are calculated along the three symmetry directions. All the phonon modes of BaHfO<sub>3</sub> have positive frequency, indicating the stability of cubic phase in BaHfO<sub>3</sub>. Some modes of SrHfO<sub>3</sub> are coming out negative. The imaginary frequencies are associated with unstable mode and in agreement with other calculations.

PACS numbers: 61.3, 63.3, 78.3

**I. INTRODUCTION**

The perovskite oxides ABO<sub>3</sub>, with a transition metal on their B-sites, display a wide variety of complex structural instabilities and electronic properties, depending on the combination of A and B cations. Owing to their varied structure and composition, these materials are the subject of extensive investigation both because of their technical importance and the fundamental interest in the physics of their phase transitions [1]. Among them, alkaline rare-earth hafnates, (MHfO<sub>3</sub>, M = Ba, Sr, or Ca) have been reported [2] as promising candidates as scintillators used in  $\gamma$ -ray imaging fields, such as positron emission tomography. Besides, SrHfO<sub>3</sub> is a promising candidate high-k dielectric oxide for the next generation of CMOS devices due to its good physical and electrical properties [3].

Strontium titanate (SrTiO<sub>3</sub>) is a typical perovskite dielectric with a wide range of technological applications. Because of its special properties related to ferroelectricity, semi-conductivity, superconductivity and catalytic activity, it has been extensively studied over the past several years. SrHfO<sub>3</sub> is a compound that has a composition and lattice structure similar to SrTiO<sub>3</sub> [4]. Although the perovskite compound SrHfO<sub>3</sub> has been well known

for a long time, theoretical studies on this compound are few.  $\text{MHfO}_3$  ( $M = \text{Ba}, \text{Sr}, \text{or Ca}$ ) compounds are a new class of scintillator host materials with  $\text{ABO}_3$  perovskite crystal structure [5]. Low level  $\text{Ce}^{+3}$  was found to be an efficient dopant for the desirable luminescent properties of the material. It revealed that  $\text{SrHfO}_3:\text{Ce}$  is the most efficient emitter among  $\text{MHfO}_3:\text{Ce}$  ( $M = \text{Ba}, \text{Sr}, \text{or Ca}$ ), and its light output is almost twice that of the two others [2]. Although the characters of the luminescent centres have been well investigated, the properties of the host themselves have been little studied due to the unavailability of large-sized single crystals.

$\text{SrHfO}_3$  that adopts the orthorhombic  $\text{Pnma}$ -type perovskite structure under ambient conditions undergoes structural transitions to the cubic perovskite structure at elevated temperatures. From their X-ray diffraction measurements on  $\text{SrHfO}_3$  powder samples, Cuffini *et al.* [6], reported an orthorhombic structure at room temperature and two phase transitions around 700 K ( $\text{Pnma} \leftrightarrow \text{Imma}$ ) and around 1000 K ( $\text{Imma} \leftrightarrow \text{Pm3m}$ ). In another experimental work, however, using the powder neutron diffraction data, Kennedy *et al.* [7] concluded that  $\text{SrHfO}_3$  undergoes three phase transitions: From 300 K to approximately 670 K, the structure of  $\text{SrHfO}_3$  is orthorhombic with space group  $\text{Pnma}$ . By 870 K, it adopts a second orthorhombic structure with space group  $\text{Cmcm}$ . It then undergoes a further phase transition and is tetragonal with space group  $\text{I4/mcm}$  from  $\sim 1000$  to 1353 K. At higher temperatures, the structure is the ideal cubic perovskite with space group  $\text{Pm3m}$ . Thus, there are controversial results about structural phases of  $\text{SrHfO}_3$  [8], whereas  $\text{BaHfO}_3$  is cubic at room temperature [9]. The knowledge of the dynamical properties of the  $\text{MHfO}_3$  ( $M = \text{Ba}, \text{Sr}, \text{or Ca}$ ) is very important in order to understand the optoelectronic processes such as scintillation. It is therefore in the present investigation the calculations of phonon frequencies and eigenvectors for the zone centre modes and phonon dispersion curves in three symmetric directions of cubic phase of  $\text{MHfO}_3$  ( $M = \text{Ba}$  and  $\text{Sr}$ ) have been made by applying a short-range force constant model [10] in order to obtain a more quantitative picture of the possible lattice instabilities.

## II. CRYSTAL STRUCTURE AND METHODOLOGY

In the ideal cubic perovskite  $\text{ABX}_3$  (fig. 1), the B cation is surrounded by six anions making up regular  $\text{BX}_6$  octahedra. These octahedra share corners, creating the twelve coordinated site which is occupied by the A cation. Alternatively, the structure may be considered to have cubic close packed  $\text{AX}_3$  layers with the B cations occupying one quarter of the interstitial octahedral sites (those surrounded by anions only). Tilting of the  $\text{BX}_6$  octahedra about their tetrad and diad axes (equivalent to tilting about the triad axis) reduces the symmetry from cubic to orthorhombic and the coordination of the A cations from twelve to eight. In the cubic cell, we have a Sr/Ba atom at  $(a/2, a/2, a/2)$ , a Hf atom at  $(0, 0, 0)$ , an oxygen at  $(a/2, 0, 0)$  ( $\text{O}_1$ ), a second at  $(0, a/2, 0)$  ( $\text{O}_2$ ) and a third at  $(0, 0, a/2)$  ( $\text{O}_3$ ). As is known, zone centre phonon vibration modes ( $\Gamma(\text{O}_h)$ ) in cubic  $\text{ABO}_3$  perovskites are split by symmetry into three  $\text{T}_{1u}$  modes and one  $\text{T}_{2u}$  mode (all of which are triply degenerate). The  $\text{T}_{1u}$  modes are active only in the infrared, while the  $\text{T}_{2u}$  mode

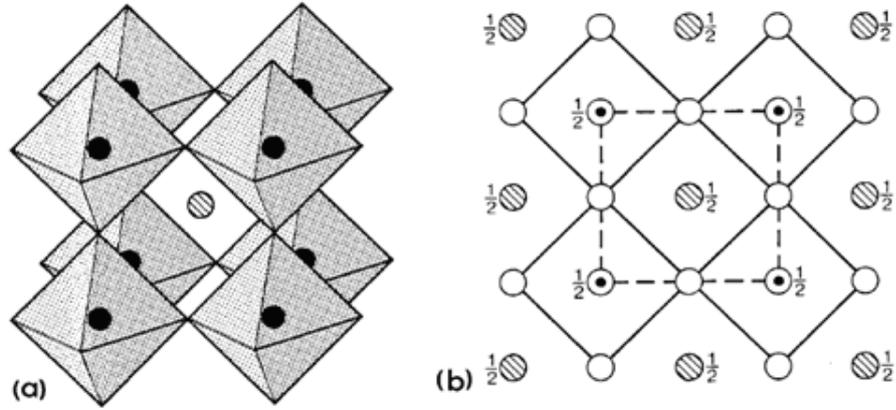


FIG. 1: The ideal perovskite structure  $ABX_3$ . (a) Perspective view of the framework of octahedra: black circles B cations, hatched circles A cations. (b) Projection of the structure on to (001): the octahedra are outlined by solid lines, the unit cell by broken lines, and open circles represent X anions.

is inactive both in the infrared and Raman spectra (silent mode). The symmetry of these phonons at the  $\Gamma$  point (in terms of the  $O_h$  representation) is

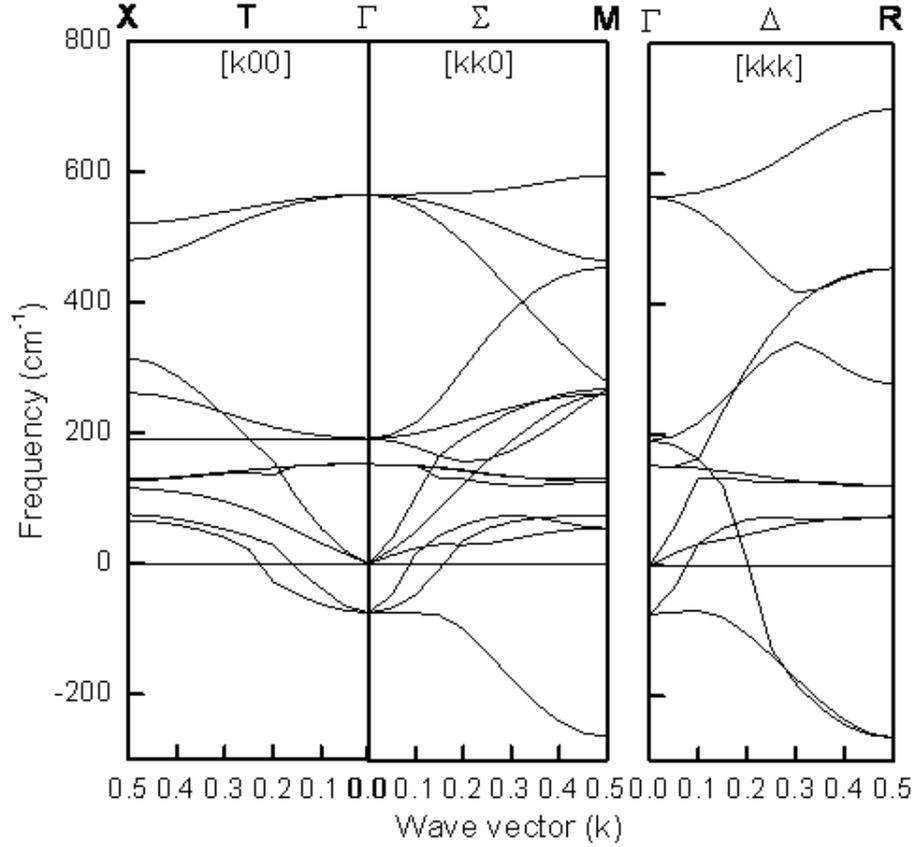
$$\Gamma(O_h) = 4T_{1u} + T_{2u}.$$

There are possibilities of occurrence of some imaginary frequencies at the zone boundary. The imaginary frequency corresponds to unstable mode. The unstable mode determines the nature of the phase transitions and the dielectric responses of the compounds.

TABLE I: Values of force constants ( $10^3$  dyne  $\text{cm}^{-1}$ )

Force constants	SrHfO <sub>3</sub>	BaHfO <sub>3</sub>
$\alpha_1$ (Hf-O)	-11.0	6.5
$\alpha_1'$ (Hf-O)	0.5	1.0
$\alpha_2$ (Sr/Ba-O)	-10.0	-9.5
$\alpha_2'$ (Sr/Ba-O)	6.0	6.0
$\alpha_3$ (Sr/Ba-Hf)	20.0	67.0
$\alpha_3'$ (Sr/Ba-Hf)	5.0	5.0
$\alpha_4$ (O-O)	58.0	33.7
$\alpha_4'$ (O-O)	-7.4	-1.0

In the present investigation, a de Launey angular force (DAF) constant model [11] has been used to study the phonons in the these hafnates to check whether softening of phonons are there or not in some crystal symmetry directions as it is supposed to be connected to phase changes in these compounds. In DAF model, the relative displacement of the reference atom and one of the neighbors is considered. The restoring force on the reference atom is

FIG. 2: Phonon dispersion curves (PDCs) of SrHfO<sub>3</sub>TABLE II: Calculated zone centre phonon frequencies in cm<sup>-1</sup>

Phonons modes	ZC phonons of SrHfO <sub>3</sub>				ZC phonons of BaHfO <sub>3</sub>	
	Present work	Vali [8]	Stachiotti <i>et al.</i> [13]	Hou [14]	Present work	Vali [12]
T <sub>1u</sub>	565	564	574	603.6	496	496
T <sub>1u</sub>	192	195	182	178.2	276	194
T <sub>1u</sub>	75i	61i	76i	66.9i	93.5	93.5
T <sub>2u</sub>	153	150	119	79.7	214	214

taken to be proportional to the component of the relative displacement perpendicular to the line joining the two atoms at their equilibrium positions. The forces due to all neighbors are calculated separately and summed up together. Different force constants are used for the various categories of neighbors, and the net force on the reference atom is obtained by summing over the contribution from all the neighbors. The present calculation involves

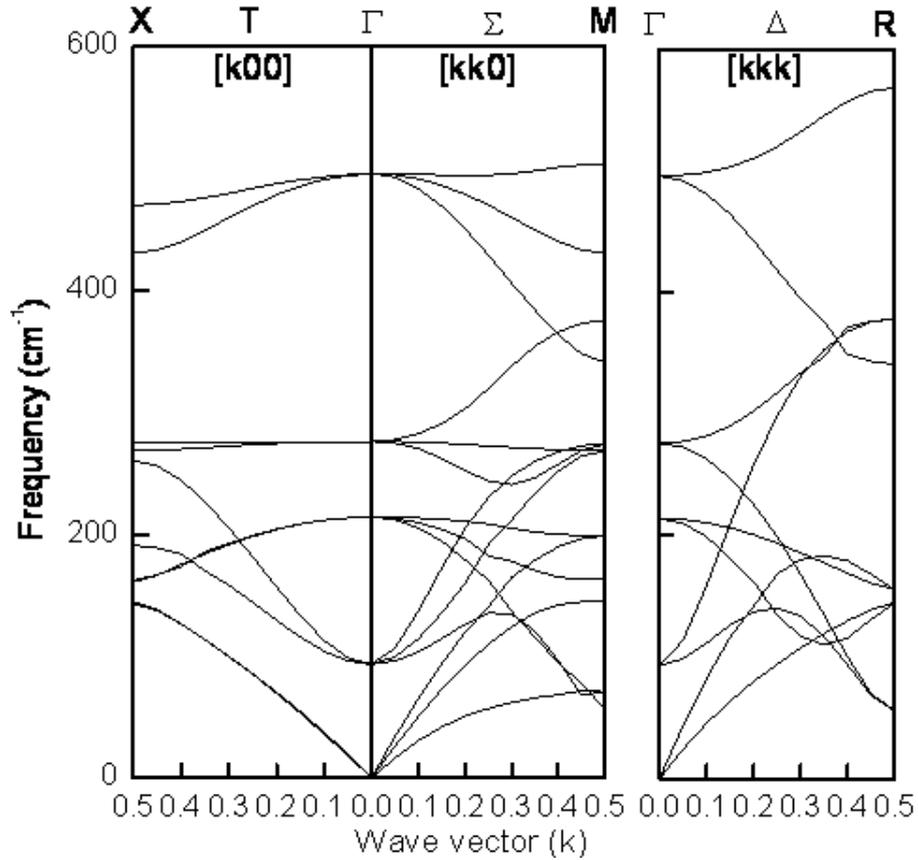


FIG. 3: Phonon dispersion curves (PDCs) of BaHfO<sub>3</sub>

four central force constants  $\alpha_1, \alpha_2, \alpha_3, \alpha_4$  and four angular force constants  $\alpha_1', \alpha_2', \alpha_3'$  and  $\alpha_4'$  between Hf-O, Sr/Ba-O, Sr/Ba-Hf and O-O atoms, respectively, up to the third nearest neighbor. The calculated dynamical matrix of  $(15 \times 15)$  is reduced to three matrices of the order  $(5 \times 5)$  at zone center (ZC) [11]. R. Vali [8, 12] has performed lattice dynamics calculation of cubic phase of SrHfO<sub>3</sub> and BaHfO<sub>3</sub> by using density functional theory with the local density approximation. In the present calculation, the interatomic force constants are obtained by fitting the calculated results of R. Vali [8, 12] at the ZC for TO mode of infrared-active phonon frequencies. The force constants thus calculated are listed in table I. Taking these force constants as input parameters, the dynamical matrix is solved at the ZC as well as along three symmetric directions  $(k00)$ ,  $(kk0)$  and  $(kkk)$ . The ZC phonons thus obtained are listed in table II along with other results [8, 12–14]. The phonon dispersion curves thus obtained in three symmetric directions for SrHfO<sub>3</sub> and BaHfO<sub>3</sub> are shown in figures 2 and 3, respectively.

### III. RESULTS AND DISCUSSIONS

Table I presents the inter-atomic force constants with reference to Hf atom along Hf-O chain in SrHfO<sub>3</sub> and BaHfO<sub>3</sub>. It is observed that force constant  $\alpha_1$  between Hf-O atoms in SrHfO<sub>3</sub> has a considerable negative value, indicating a sizable coupling between Hf and O atoms along Hf-O chain, which does not allow the displacement of Hf atom against O atoms and is in agreement with the other calculation [8]. The force constant  $\alpha_3$  between Ba-Hf is strongest among all other interatomic interactions in BaHfO<sub>3</sub>. This suggests that the covalent bonding between (Ba-Hf) is strongest than that between (Hf-O), (O-O) and (Ba-O) in BaHfO<sub>3</sub>. Since the modes at zone centre are degenerate with respect to displacements in the x, y or z directions, it is convenient to select a reference one, say z, where atoms are displaced by an amount u. Symmetry requires that  $u(O_1)=u(O_2)$  for the T<sub>1u</sub> modes and  $u(O_1)=-u(O_2)$  for the T<sub>2u</sub> mode. It is obvious from table II that the present calculation of zone centre phonons of cubic SrHfO<sub>3</sub> gives an unstable TO mode appears as an imaginary frequency mode with the value of  $-75 \text{ cm}^{-1}$ , which is in good agreement with one  $-76 \text{ cm}^{-1}$  predicted by Stachiotti *et al.* [13],  $-61 \text{ cm}^{-1}$  by Vali [8] and  $-66.9 \text{ cm}^{-1}$  by Hou [14]. The other zone centre phonons are in good agreement with other theoretically calculated results. Whereas, no zone centre phonon mode is found to be imaginary in cubic BaHfO<sub>3</sub>. This suggests that cubic phase of BaHfO<sub>3</sub> is stable, whereas SrHfO<sub>3</sub> is unstable in cubic phase. Unfortunately, there are no experimental results available to compare the present calculation. However, it is expected that the present calculation have the same accuracy as given by other theoretical results [8, 13, 14]. The phonon dispersion curves of SrHfO<sub>3</sub> and BaHfO<sub>3</sub> are calculated along high symmetry directions in the Brillouin zone and are shown in figures 2 and 3. It is seen from figure 3 that all the phonon modes of BaHfO<sub>3</sub> have positive frequency, indicating the stability of the cubic phase of BaHfO<sub>3</sub>, and they are in agreement with the other calculation [12]. The phonon spectrum of SrHfO<sub>3</sub> along high symmetry lines are shown in figure 2. Negative frequencies in the plot show the imaginary frequencies associated with unstable mode. The T<sub>1u</sub> soft mode of SrHfO<sub>3</sub> could induce a P4mm phase, which allows for a ferroelectric state, according to the following subduction diagram [15]: Pm3m ( $z = 1$ )  $\rightarrow$  ( $\Gamma_4^-$ )  $\rightarrow$  P4mm ( $z = 1$ ). However, as can be seen from Fig. 2, this instability coexists with the nonpolar zone boundary soft mode extending along the Brillouin zone edges (R-M lines). The  $\Gamma$ -point instability is less unstable than zone boundary, implying that an anti-ferroelectric relaxation could lead to a lower-energy structure than a ferroelectric relaxation. The unstable phonons of the cubic phase of SrHfO<sub>3</sub> are there at Brillouin Zone boundary, and no such instabilities are found in BaHfO<sub>3</sub> perovskite. This suggests that cubic form of BaHfO<sub>3</sub> is stable relative to low symmetry distortions, whereas distortion is possible in SrHfO<sub>3</sub> perovskite.

### IV. CONCLUSION

The zone centre phonons and phonon dispersion curves of SrHfO<sub>3</sub> and BaHfO<sub>3</sub> have been calculated by applying a short-range force constant model. All the phonon modes of

BaHfO<sub>3</sub> are found to be positive, indicating the stability of cubic phase of BaHfO<sub>3</sub>. We found a soft mode of T<sub>1u</sub> symmetry at the  $\Gamma$ -point in SrHfO<sub>3</sub>. This soft mode corresponds to a displacement pattern in which Hf moves in the same direction as that of the oxygen tetrahedron displacement. We observed that the longitudinal inter-atomic force constant between nearest neighbor Hf and O atoms has a considerable negative value, indicating a sizable coupling between Hf and O atoms along the Hf–O chain, which explains the observed displacement pattern in SrHfO<sub>3</sub>. The T<sub>1u</sub> soft mode could induce a P4mm phase, which allows for a ferroelectric state. It is worth to mention here that the proposed force constant model, with small number of parameters, gives a satisfactory description of phonon spectra of hafnates.

### Acknowledgments

The author acknowledges financial support received from Sant Longowal Institute of Engineering and Technology, Longowal (India) under PDA grant for presenting this work at the 13<sup>th</sup> International Conference on Phonon Scattering in Condensed Matter at Taipei, Taiwan.

### References

- \* Electronic address: mm.sinha@rediffmail.com
- [1] M. E. Lines, A. M. Glass, *Principles and applications of ferroelectrics and related materials*, (Clarendon press, oxford, 1977).
  - [2] Y. M. Ji, D. Y. Jiang, Z. H. Wu, T. Feng, J. L. Shi, Mater. Res. Bull. **40**, 1521 (2005).
  - [3] C. Rossel, M. Sousa, C. Marchiori, J. Fompeyrine, D. Webb, D. Caimi, B. Mereu, A. Ispas, J. P. Locquet, H. Siegwart, R. Germann, A. Taponnier, K. abich, Microelec. Eng. **84**,1869 (2007).
  - [4] Y. X. Wang, W. L. Zhong, C. L. Wang, P. L. Zhang, Solid State Commun. **120**, 133(2001).
  - [5] Y. Ji, D. Y. Jiang, J. J. Chen, L. S. Qin, Y. P. Xu, T. Feng, J. L. Shi, Optic. Mater. **28**, 436 (2006).
  - [6] S. Cuffini, *et al.*, Ceramica **43**, 91 (1997).
  - [7] B. J. Kennedy, C. J. Howard, B. C. Chakoumakos, Phys. Rev. B **60**, 2972 (1999).
  - [8] R. Vali, Solid State Commun. **148**, 29 (2008).
  - [9] R. Sholder, D. Rade, H. Schwarz, A. Anorg. Allgem. Chem. **362**, 149 (1968).
  - [10] J. de Launey, Solid State Physics Series **2**, 219 (1956).
  - [11] M. M. Sinha and K. Wakamura, J. Phys. Chem. Solids **63**, 541 (2002).
  - [12] R. Vali, Solid State Commun. **147**, 1 (2008).
  - [13] M. G. Stachiotti, G. Fabricius, R. Alonso, C. O. Rodriguez, Phys. Rev. B **58**, 8145 (1998).
  - [14] Z. F. Hou, Phys. Status Solidi B **246**, 135 (2009).
  - [15] H. T. Stokes, D. M. Hatch, *Isotropic Subgroups of 230 Crystallographic Space Groups, Gordon and Breach*, (New York, 1965).