

Vibrational properties of $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$

A molecular dynamics study

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We present a rigid-ion model of $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ for compositions $x = 0.25$ and $x = 0.40$. Partial vibrational density of states of ions in the compounds $\text{Ba}_{0.75}\text{K}_{0.25}\text{BiO}_3$ and $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$ are reported at room temperature and 100 K. The oxygen modes dominate the vibrational spectrum from 150 up to 820 cm^{-1} . The low frequency modes are associated with the cations. The number of substituted K around an oxygen favors high frequency vibrational modes.

Qualitative agreement between the calculated phonon density of states of $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$ and available experimental data is achieved.

1. Introduction

The high temperature (high- T_c) superconducting ceramics include cuprates and bismates compounds. Despite the lower critical temperature exhibited by the bismuth oxides, they are of considerable physical and theoretical interest in understanding high- T_c superconductivity. In this paper we concentrate on the $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ compounds. The $x = 0$ compound possesses a monoclinic structure with semiconducting character. In the composition range $x = [0.04-0.13]$, the oxide changes to an orthorhombic structure. Above $x = 0.13$ the lattice is cubic. However, superconductivity does not appear before the composition $x = 0.25$ is reached with an optimum composition for superconductivity at $x = 0.40$. For this composition, $T_c \sim 30$ K. The simple cubic perovskite structure at $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ in the superconducting range of compositions has been determined by powder X-ray diffraction [1–3] and confirmed by powder neutron diffraction [4].

Recent measurements of the energy gap of the high- T_c bismuth oxide superconductor $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$ are consistent with a BCS type superconductivity [5]. In this paper, we present a

theoretical investigation of the vibrational properties of $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ compounds and an atomistic model of the cubic perovskite superconducting bismates.

Atomistic simulation methods have been successfully applied to the study of phonon behavior and defect properties in high- T_c superconducting cuprates. Available models include $\text{YBa}_2\text{Cu}_3\text{O}_7$ [6–8], $\text{YBa}_2\text{Cu}_3\text{O}_6$, La_2CuO_4 [9], and BaBiO_3 and $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$ [10]. In these latter models, the structure of the bismates is stabilized by applying steric repulsions between the atoms thus constraining bond orientation. In this paper, we introduce a purely ionic model for $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ with composition $x = 0.25$ and $x = 0.40$. Molecular dynamics (MD) calculations of these two superconducting compounds ($x = 0.25$; 0.40) were performed with interatomic interactions which included only Coulomb interactions and central ion core–ion core repulsions.

Good agreement between the calculated properties and available experimental data is achieved with the simpler model.

This paper is organized as follows. A brief description of the method and model used is given in section 2. Structural and vibrations properties of the models are presented and discussed in section 3.

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2. Model and method

The use of realistic interatomic pair potentials is critical for the generation of satisfactory MD results. For computational convenience, we have used central, pairwise additive interionic potentials to describe the interactions between ions in the cubic bismate perovskites. The interaction between an ion “ i ” and another ion “ j ” is modeled with a pair potential of the Born–Mayer–Huggins type:

$$\phi_{ij}(r_{ij}) = \frac{Z_i Z_j e^2}{4\pi\epsilon_0 r_{ij}} + A_{ij} \exp\left[-\frac{r_{ij}}{\rho_{ij}}\right] - \frac{C_{ij}}{r_{ij}^6},$$

where the total potential is the sum of a long-range Coulombic term, a short-range core–core repulsion, and a short-range Van der Waals attractive term. r_{ij} is the distance between ions i and j . Z_i is the ionic charge of ion i and C_{ij} is a Van der Waals attractive coefficient. The exponentially decaying repulsive term is composed of two parameters, A_{ij} and ρ_{ij} , which are characteristic of the size and “hardness” of the interacting ions.

For the simulation of the $Ba_{1-x}K_xBiO_3$ lattices, the cation–cation short range interactions have been neglected. The charges on the ions Ba, K and O are taken as 2+, 1+ and 2–, respectively. The charge on the Bi is adjusted with the potassium composition to balance the net charge of the lattice.

The three parameters for the oxygen–oxygen short range interaction have been taken from quantum mechanical calculations [11]. The Ba–O parameters we have used are variations of the parameter for the BaO [12].

The remaining parameter for the Bi–O and K–O bonds have been determined empirically by fitting the lattice parameters and interionic distances of the models to experimental values. The best sets of parameters are listed in table 1.

We used periodic boundary conditions in all the molecular dynamics simulations. The lattice parameters of the cells were determined by employing the constant-pressure molecular dynamics algorithm by Parrinello and Rahman [13]. To avoid artificial fluctuations of the shape

Table 1

Parameters used in the rigid-ion model of $Ba_{1-x}K_xBiO_3$. A and B stand for the compositions $x = 0.25$ and $x = 0.40$, respectively.

Ion	$Z(i)$	A_{iO^2-} (eV)	ρ_{iO^2-} (Å)	C_{iO^2-} (eVÅ)
A	Ba 2+	1252.8	0.350	0.00
	K 1+	1195.2	0.310	0.00
	Bi 4.25+	2016.0	0.353	0.00
B	Ba 2+	1252.8	0.346	0.00
	K 1+	1224.0	0.312	0.00
	Bi 4.40625+	2088.0	0.353	0.00
O	2–	22 764.3	0.149	20.37

of the simulation cell resulting from its small size, the edges of the cell were constrained to stretching only.

The summation of the long-range Coulombic forces and potential energy is conducted efficiently by the Ewald method [14]. Details of the technique can be found in ref. [7].

The $Ba_{0.75}K_{0.25}BiO_3$ and $Ba_{0.6}K_{0.4}BiO_3$ systems consisted of 320 particles in an initially cubic simulation cell. The compositions $x = 0.25$ and $x = 0.40$ are modeled by substitution of 16 and 26 Ba ions by K ions. In both cases the K ions are distributed randomly but uniformly on the Ba sites.

These systems were simulated under a constant external pressure of 1 atm. The equations of motion of the ions and boundaries of the simulation cell were numerically integrated with a finite difference scheme. We used a time integration step of 2.68×10^{-15} s.

Constant temperature was achieved by momentum rescaling [15].

3. Computational results

The stability of the $x = 0.25$ and $x = 0.40$ cubic bismate compounds at room temperature was verified in simulations lasting 20 000 integration steps (or $\sim 5.4 \times 10^{-11}$ s). The cubic lattices were found to be stable and only vibrational processes about well defined lattice sites were observed. The lattice parameter of the two model compositions are $a(x = 0.25) = 4.303 \pm 0.002$ Å and

$a(x = 0.40) = 4.294 \pm 0.002 \text{ \AA}$, were fitted to the experimental values of “4.303” [4] and “4.2932” [1].

$Ba_{0.6}K_{0.4}BiO_3$ was also simulated at a temperature of 100 K for 20 000 steps. The lattice parameter at this low temperature is $a(X = 0.40; T = 100 \text{ K}) = 4.287 \pm 0.002 \text{ \AA}$. The temperature dependence of the lattice parameter is given in a linear form as $a(\text{\AA}) = 3.5 \times 10^{-5}T(\text{K}) + 4.284$. This calculated linear expansion coefficient agrees again very well with experimental values [3]. These results demonstrate that contrary to previous models [10], T_c bismates can be stabilized within a purely ionic model and do not require necessarily bond-bending restrictions.

We report calculated anisotropic vibrational spectra of individual atoms. The vibrational spectrum of a selected ion is calculated by fast Fourier transformation of the ion's normalized velocity autocorrelation function [16]. The vel-

ocities of Ba, K, Bi and oxygen ions differing by their K environment have been followed during long simulations (10 000 integration steps) at room temperature.

The vibrational density spectra were calculated from ions located near the center of the simulation cell to avoid artifacts due to periodic boundary conditions. The projection of the normalized spectra along the cubic directions of the simulation cell are reported in figs. 1 and 2 for the potassium compositions $x = 0.25$ and $x = 0.40$.

The spectra for the composition $x = 0.25$ present no significant difference with the composition $x = 0.40$. The low-energy vibrational modes of the bismate models (below 100 cm^{-1}) are dominated by contributions from the Ba and K ions, as well as some contribution from Bi and to a smaller extent oxygen. The high density of very low frequency vibrational modes of the Ba ion near 60 cm^{-1} is in very good agreement with the

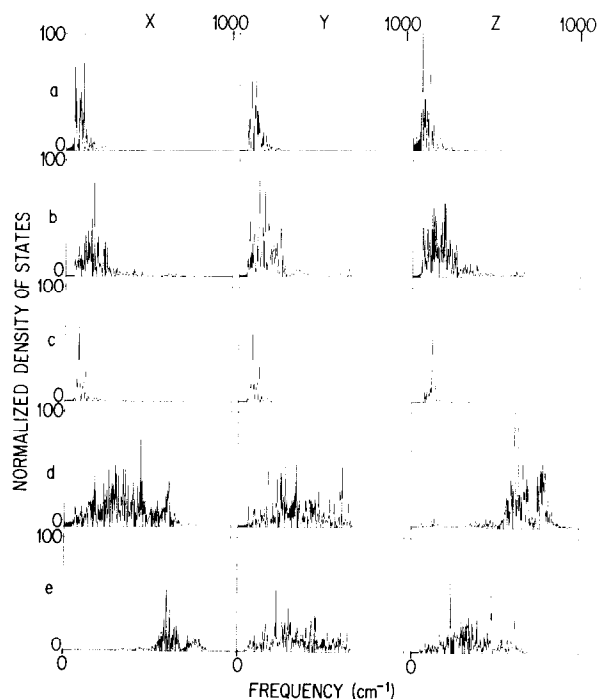


Fig. 1. Room temperature anisotropic partial vibrational density of states of $Ba_{0.75}K_{0.25}BiO_3$. a, b, c, d, e report to Ba, Bi, K, oxygen linked to Bi along the Z direction with K rich environment and oxygen linked to Bi along the X direction with K poor environment.

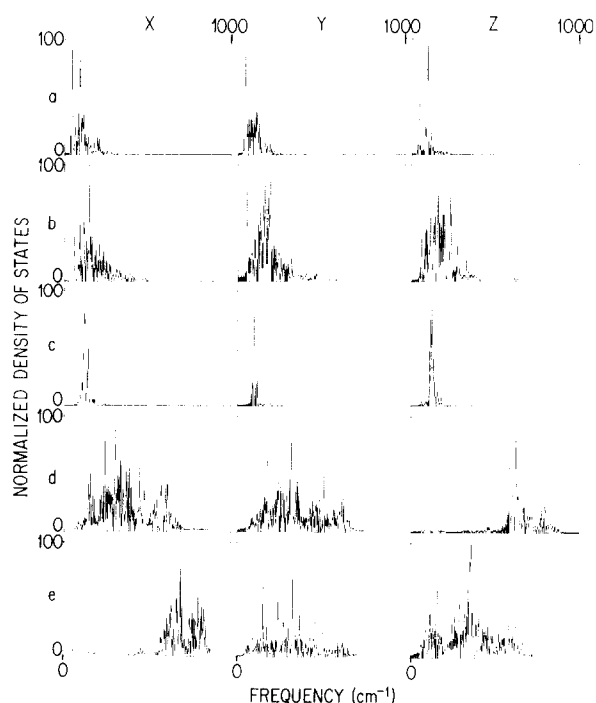


Fig. 2. Room temperature anisotropic partial vibrational density of states of $Ba_{0.6}K_{0.4}BiO_3$. a, b, c, d, e report to Ba, Bi, K, oxygen linked to Bi along the Z direction with K poor environment and oxygen linked to Bi along the X direction with K rich environment.

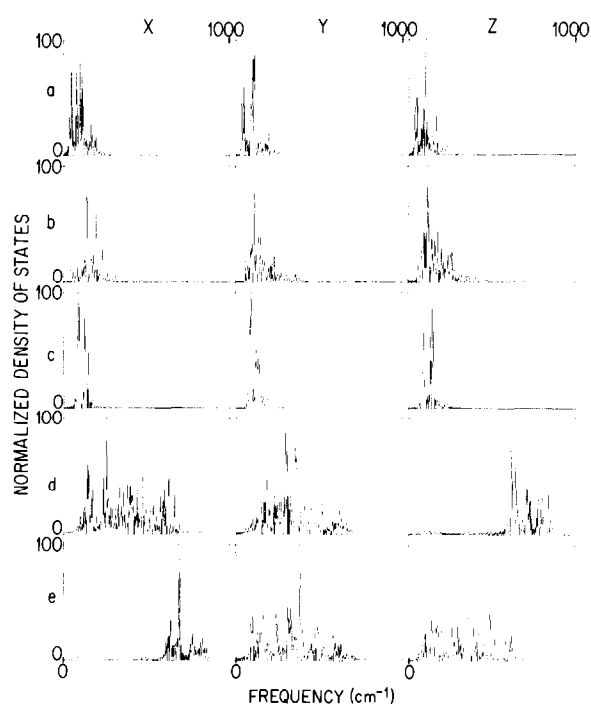


Fig. 3. Low (100 K) temperature anisotropic partial vibrational density of states of $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$. a, b, c, d, e report to Ba, Bi, K, oxygen linked to Bi along the Z direction with K poor environment and oxygen linked to Bi along the X direction with K rich environment.

acoustic modes dispersion curves for BaO [17]. The very high energy modes are essentially associated with oxygen vibration. The anisotropy of the oxygen vibration is noteworthy. The oxygen ion exhibits vibrational modes at ~ 610 and $\sim 800\text{ cm}^{-1}$ parallel to the Bi–O bond while modes of vibration perpendicular to the Bi–O bond cover a wide interval of frequencies from 125 to 600 cm^{-1} . The density of vibrational modes of the oxygen ion depends on the potassium environment. Assuming that the internal vibrational modes of the BiO_6 octahedron may be separated from the internal modes of the perovskite [18]; the high frequency oxygen vibrational mode can be ascribed to a stretching mode of the BiO_6 octahedron and the lower frequency oxygen vibrational modes to a bending mode of the octahedron. This observation is in accord with infrared absorption spectra of BaBiO_3

which exhibit bands at 265 and 440 cm^{-1} associated with the bending and stretching of BiO_6 octahedra, respectively [19]. The oxygen density of state with frequency 800 cm^{-1} may decrease from 60% to 25% relative to the density at 610 cm^{-1} depending upon the potassium environment. The proximity of potassium ions to the oxygen favors the high frequency modes. The larger the number of K neighbors, the higher the density of state at 800 cm^{-1} . This feature may be arising from a tighter Bi–O bond resulting from the substitution of the $\text{Ba}^{2+}\text{--O}^{2-}$ bonds by the weaker $\text{K}^+\text{--O}^{2-}$ Coulombic attraction.

It is, however, necessary to keep in mind that rigid ion models, because they neglect ionic polarizability, give rise to longitudinal optical (LO) modes which are too high and longitudinal optical modes–transverse optical modes splitting which are too large [20]. One, therefore, expects the frequency of the Bi–O bond stretching to be overestimated. This is particularly true for the highly polarizable oxygen ion. Improvement of the model may be made by incorporation of ionic polarizability through shell models.

The effect of temperature on the vibrational properties of the $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$ compound is investigated. We have calculated the vibrational spectra of the selected ions at 100 K. The results are reported in fig. 3.

These densities of state exhibit sharper well defined peaks as the anharmonic effects decrease with temperature. The frequencies of the oxygen vibrations along the Bi–O bond are ~ 610 , 700 and 820 cm^{-1} . The modes perpendicular to the Bi–O bond modes have the frequencies: 90 , 170 , 240 , 330 , 390 , 500 and 610 cm^{-1} .

We have calculated the total phonon density of state for $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$. At room temperature, there are three dominant features: a high density peak at 150 cm^{-1} , a broad band extending from 210 to 370 cm^{-1} and a peak at 610 cm^{-1} . Other peaks with lower density of states are present at 475 , 700 and 800 cm^{-1} .

The experimental phonon density of state [10] shows a shoulder at approximately 130 cm^{-1} as well as two broad peaks at 240 and 485 cm^{-1} . Allowing for an overestimate of the high frequency density of states in an ionic model, qual-

itative agreement with experimental data seems to have been achieved in the MD model.

Decreasing the temperature from room temperature to 100 K has for effect the lowering of the density of states at low energies and the increase of the density of states of the high energy modes by approximately 25%.

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