Molecular Dyamics Simulation
and Far Infrared Measurements of $Ba_{0.6}K_{0.4}BiO_3$

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Abstract   The vibrational behavior and the molecular dynamics of the high Tc superconductor $Ba_{0.6}K_{0.4}BiO_3$ have been studied experimentally and by atomistic computer simulation methods. For $Ba_{0.6}K_{0.4}BiO_3$, the vibrational spectrum is dominated by oxygen ion modes from $150cm^{-1}$ to $820 cm^{-1}$ including infrared absorption bands at 330, 480, 640 and 830 cm^{-1} at room temperature. Band assignments are discussed in relation to those bands predicted by simulations, and the infrared and Raman measurements reported in the literature.

1. Introduction

Molecular Dynamics (MD) simulation is a powerful tool for the study of the classical properties of high Tc superconductors (SC)[1]. Most high Tc materials discovered so far are copper oxide superconductors with d-band electrons. Atomistic simulation methods have been successfully applied to the study of phonon and defect behavior in high Tc superconductiong cuprates. Available models include $YBa_2Cu_3O_7$, $BaBiO_3$, and $Ba_{0.6}K_{0.4}BiO_3$ Understanding the normal state properties of High Tc bismates will shed light on the superconducting mechanism. Attention has also been paid to $BaBiO_3$ as an insulator material in a superconductor–insulator superconductor (SIS) junction of $Ba_{1-x}K_xBiO_3$. The high Tc bismate SC $Ba_{1-x}K_xBiO_3$ discovered by Mattheiss et al.[4] is of particular interest in the study of superconductivity in ceramic oxides[2,5]. The structure of the bismates is stabilized by applying steric repulsions between the atomics thus constraining bond orientation. MD calculations of the bismate superconductor is performed with interatomic interactions which included only Coulomb interactions and central ion core–ion core repulsions. Knowledge of the energy gap which is crucial to these studies, can be examined via infrared or Raman spectra. The energy gap of the high Tc SC $Ba_{0.6}K_{0.4}BiO_3$ is consistent with a Bardeen–Cooper–Schriefer (BCS) type superconductivity[6]. The infrared and Raman bands related to electron–phonon coupling in bismate SCs show a softening between $400cm^{-1}$ and $480cm^{-1}$, when doped by potassium[3]. At this stochiometry, Tc is about 30 K. In the superconducting range of compositions, $Ba_{0.6}K_{0.4}BiO_3$ has a cubic perovskite structure, as determined by powder X-ray diffraction[7,8].

In this paper, we present experimental infrared measurements at room temperature, and a theoretical investigation of the vibrational properties of $Ba_{0.6}K_{0.4}BiO_3$ using atomistic MD simulation. A good agreement was found between calculated and measured properties.

2. Experimental procedure

MD Simulations: The $Ba_{0.6}K_{0.4}BiO_3$ crystal lattice is conveniently described by a purely rigid ionic model[2]. All ions were considered to interact through Born–Mayer–Huggins type potentials, including Coulombic interactions,

short range core-core repulsion, and an attractive Van der Waals term. The interaction between an ion "i" and another ion "j" is modeled with a pair potential:

$$\phi_{ij}(r_{ij}) = \frac{Z_i Z_j e^2}{4\pi\varepsilon_0 r_{ij}} + A_{ij}exp\left[-\frac{r_{ij}}{\rho_{ij}}\right] - \frac{C_{ij}}{r^6_{ij}}$$

where r_{ij} is the distance between ions, Z_i is the ionic charge of ion i and C_{ij} is a Van der Waals attractive coefficient. A_{ij} and ρ_{ij} are characteristic of the size and "hardness" of the interacting ions. Ba, K, Bi, and O atoms were represented as interacting point charges; charges on the ions Ba, K and O were taken as $+2$, $+1$ and -2, respectively. The charge on the Bi was adjusted, according to the potassium composition, to balance the net charge of the lattice. Short range cation-cation repulsions: Ba-Ba, K-K, Bi-Bi, Ba-K, Ba-Bi, and K-Bi were neglected. The three parameters for the oxygen-oxygen short range interaction were taken from quantum mechanical calculations[9]. Parameters for Ba-O were variations of the parameters for the oxide BaO[10]. The Van der Waals coefficients for all cation-cation interactions were set to zero. The remaining parameters for the Bi-O and K-O bonds were determined empirically by fitting the lattice parameters and interionic distances of the models to experimental values. The best sets of parameters are shown in table 1. The $Ba_{0.6}K_{0.4}BiO_3$ systems consisted of 320 particles in a cubic simulation cell, with the substitution of 26 K ions for 64 Ba ions, randomly but uniformly distributed among the Ba sites. Periodic boundary conditions were used in the MD simulation.

Table 1. Parameters used in the rigid ion model of $Ba_{0.6}K_{0.4}BiO_3$.

Ion	Z(i)	A_{ij}^2-(eV)	ρ_{ij}^2-(Å)	C_{ij}^2-(eV Å)
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-	22764.3	0.149	20.37

Simulations were run using constant temperature and pressure molecular dynamics. The time integration step was taken as 2.68 fs. The stability of $Ba_{0.6}K_{0.4}BiO_3$ cubic bismuth compounds at room temperature within a purely ionic model was verified in simulations lasting about 54.0 ps. Lattices were stable and only vibrational processes about well defined lattice sites were observed. The lattice parameter of found using MD, 4.294 ± 0.002Å was identical with the experimental value, 4.293Å[7].

Anisotropic vibrational spectra were calculated for individual atoms. The velocities of Ba, K, Bi, and O ions from different K environments were followed during 10000 time steps at room temperature. The vibrational spectrum of a selected ion was calculated by fast Fourier transformation of the ion's normalized velocity autocorrelation function[11]. The Wiener-Khintchine theorem[12] connects the correlation function and the spectral density; if the velocity, v(t), is the normalized velocity autocorrelation function is

$$C(\tau) = \frac{<\sum^N_{i-1} v_i(\tau) \cdot v_i(0)}{<v^2_i(0)>}$$

And the Fourier transform of $C(\tau)$ is

$$S(\omega) = \int d\tau \, cos\omega\tau \, C(\tau)$$

where $S(\omega)$ is called the spectral density of random process v(t).

Vibrational state density spectra were calculated from ions located near the center of the simulation cell, to avoid artifacts due to periodic boundary conditions. The projections of the normalized spectra along the cubic directions of the simulation cell are shown in Fig. 1.

Sample preparation and IR Measurements: Samples of $BaBiO_3$ and $Ba_{0.6}K_{0.4}BiO_3$ were synthesized at Argonne National Laboratories. $BaBiO_3$ was made by a sintering technique[13], while $Ba_{0.6}K_{0.4}BiO_3$ was synthesized by a melt-processing technique[14]. The crystal structure of $Ba_{0.6}K_{0.4}BiO_3$ was checked using Bragg-Brentano X-ray diffraction with CuKα radiation. The final lattice parameter agreed fairly
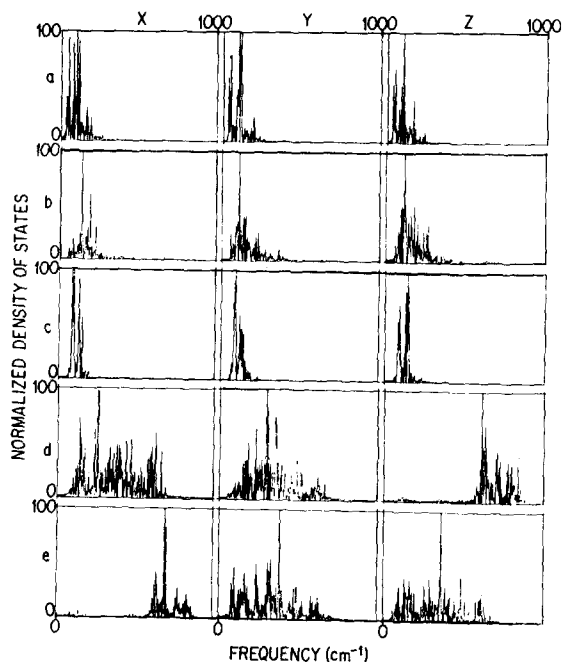
Fig. 1. Room temperature anisotropic partial vibration-
al density of states of $Ba_{0.6}K_{0.4}BiO_3$; a) Ba, b)
Bi, c) K, d) Bi–O along Z direction with K poor
environment and e) Bi–O along X direction
with K rich environment.

Fig. 2. Transmission infrared spectrum of $BaBiO_3$.

Fig. 3. Reflection infrared spectra of $Ba_{0.6}K_{0.4}BiO_3$; a)
Background substraced, b) Background subs-
traced and baseline flattened.

well with that of Hinks et al.[14], and Fleming et
al.[5].

IR sample pellets were prepared by the fol-
lowing mehods: (1) $BaBiO_3$ was ground to ca.
5μm and mixed (5% w/w) with IR grade poly-
ethylene powder. The mixed powders were
then pelletized at ca. 8 kbar for 10 min. in a 13
mm diameter evacuable pellet die. (2) $Ba_{0.6}K_{0.4}BiO_3$ was ground to ca. 5μm and spread in the
pellet die, KBr powder was put on top of the
sample, and the combination pressed at 8 kbar,
thus capturing and holding sample powder on
the surface of the pellet. KBr was used be-
cause $Ba_{0.6}K_{0.4}BiO_3$ is reported to react readily
with organic materials. The sample–side of the
pellet was cleansed using silicon carbide sand–
paper and spectral acquisition begun immedi-
ately.

Infrared spectra were obtained using a
Perkin Elmer FTIR 1800 with DTGS detec-
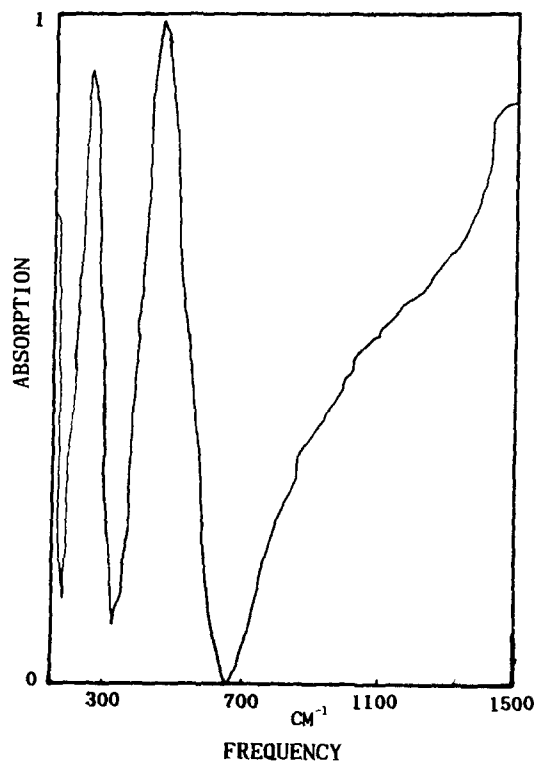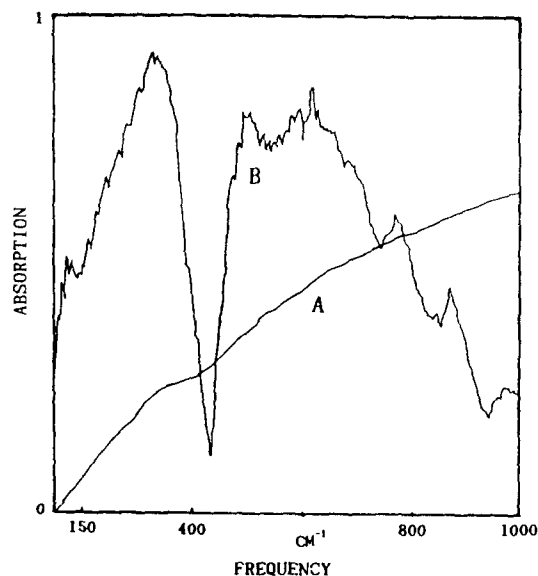tion. Spectra were the averages of 250 double-

beam scans, at $4cm^{-1}$ resolution, and are
shown in Fig. 2 and 3. IR absorbance in $BaBiO_3$

was moderated, so transmission spectra could be obtained. $Ba_{0.6}K_{0.4}BiO_3$, however, is strongly absorbing, so a reflectance technique was required. Great care was required to determine the value of the reflectance of samples. The sample beam focus and diffusely reflected light was collected with a $10 cm^{-1}$ Al mirror.

3. Results and Discussion

The low energy vibrational modes of the bismate models (below $100 cm^{-1}$) are predominately due to the cations. The calculated high density of low frequency modes of the Ba ion near 60 cm^{-1} is in very good agreement with acoustic mode dispersion curves for $BaO^{[15]}$. Oxygen vibrations are associated with the very highest energy modes; Their anisotropy is noteworthy. Oxygen ion vibrational modes in this lattice appear near at about 610 and 820 cm^{-1} when motion is parallel to the Bi-O bond but cover a wide range, 125-600 cm^{-1}, when motion is perpendicular to the Bi-O bond. The density of vibrational modes of the oxygen ion depends upon the potassium environment. Assuming that the internal modes of the BiO_6 octahedra may be separated from the internal modes of the perovskite[16]. The high frequency oxygen modes can be ascribed to a stretching mode of the BiO_6 octahedra and the lower frequency oxygen modes to a bending mode of the octahedra. This notion is in accord with absorption spectra of $BaBiO_3$ whcih exhibit bands at 265 and 440 cm^{-1} as-sociated with the bending and stretching of BiO_6 octahedra, respectively[17]. An increase in the proximity of potassium ions to the oxygen ions increases the density of states at 820 cm^{-1}, due to a tightening of the Bi-O bond upon substitution of the weaker K^--O^{2-} Coulombic attraction of the $Ba^{2+}-O^{2-}$ interaction. Because the ionic polarizability was neglected, and excessive longitudinal/transvers optical-mode splitting appeared[18].

The positions of the oxygen vibrations parallel to the Bi-O bond are at about 610, 700, and 820 cm^{-1}. The perpendicular modes to the Bi-O bond appear at about 90, 170, 240, 330, 390, 500, and 600 cm^{-1}. The total density of phonon states for the material was also calculated. At room temperature, there were three dominant features: a high density peak at 150 cm^{-1}, a broad band extending from 210 cm^{-1} to 400 cm^{-1} and a band at 600 cm^{-1}. Other bands with lower densities of states are present at 475, 700, and 820 cm^{-1}.

Fig. 2. shows the trasmission IR spectrum of $BaBiO_3$; bands are at 465, 269, and 152 cm^{-1}. The band at 465 cm^{-1} is related to the Bi-O bending mode, according to Hair et al[17]. The band at 152 cm^{-1} is related to the rotational mode of BiO_6 octahedra as reported by Sugai[19].

Because $Ba_{0.6}K_{0.4}BiO_3$ has very stong IR absorbance above ca. 600 cm^{-1}, a diffuse reflection technique was used. Fig 3a. shows the IR expanded spectrum of $Ba_{0.6}K_{0.4}BiO_3$ after subtraction of the Al mirror background. Fig 3b. shows an expansion of the same spectrum after background subtraction and baseline leveling using a long spline-fitting curve. Dispersion in refractive index was large near the absorption peaks. Absorption band maxima were assigned to the points of the spectra, at 330, 480, 640, 750, and 830 cm^{-1}. Frosting of the sample during the very long spectral acquisition times prevented collection of spectra at 100 K.

The peak at 330 cm^{-1} corresponds to a large absorption band containing Bi vibration and some contribution from oxygen vibration, according to the MD simulation. This band is similar to that of McCarty, et al[3]. The observed band of Sugai, who reported that the measured IR band of $BaPb_{1-x}Bi_xO_3$, which displays physical behavior little similar to that of $Ba_{0.6}K_{0.4}BiO_3$,was about 325 cm^{-1}[19]. The band at 480 cm^{-1} is similar to that found by McCarty, and a bond at a similar position occured in Sugai's $BaPb_{1-x}Bi_xO_3$ spectra. MD simulation results showed that the weak peaks at 640 and 830 cm^{-1} are related to anisotropic

oxygen motions, which in turn depend on the potassium ion distribution. These peaks were not shown in previous papers using neutron scattering and Raman measurements, perhaps due to their very low intensities. The new thing about our spectrum is that it shows structure that was not visible in Rosenberg's Fig 4c of $Ba_{0.6}K_{0.4}BiO_3$ due to weak reflection[20]. According to Bonn, et al.[21], and Gervais, et al.[22], the bands above $200cm^{-1}$ look our absorbance spectra due to oxygen anisotropy. A Kramers-Kroning analysis revealed no difference from fits of absorption bands.

In conclusion, the vibrational data of MD simulation and these experimental results are in fairly good agreement. Low temperature capabiliy below 30 K would have improved spectral contrast and measured superconducting energy gap. Dispersion may have caused the differences between these band position assignments and those cited from the literature.

Acknowledgement

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