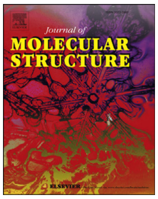
Journal of Molecular Structure 1154 (2018) 463–468

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: http://www.elsevier.com/locate/molstruc



# Lattice dynamics and force constant calculation for the Raman and infra-red wave numbers of cubic bismuth-based pyrochlore compounds

Y.M. Jana [a, *], S. Nandi [a], H.C. Gupta [b]

[a] Department of Physics, University of Kalyani, Kalyani, 741235, Nadia, W.B., India
[b] Department of Physics, Indian Institute of Technology, Hauz Khas, New Delhi, 110016, India

ARTICLE INFO

*Article history:*
Received 7 August 2017
Received in revised form
17 October 2017
Accepted 17 October 2017
Available online 1 November 2017

*Keywords:*
Bismuth pyrochlores
Raman and infra-red frequencies
Lattice dynamics
Phonons

ABSTRACT

Lattice dynamics computations utilizing a short-range electrostatic force-field model have been performed for the first time to investigate the fundamental Raman and infra-red wave numbers in some cubic bismuth-based composites, namely, BMN, BZN, BMT and BZT pyrochlores. The calculations of phonons involve three stretching and four bending force-field constants in Wilson *GF*-matrix method. The calculated phonon wave numbers agree satisfactorily with the observed spectra in the infra-red and Raman excitation zones for all these compounds. A Raman $E_g$ mode has been assigned within the wave number range of 360–375 $\mathrm{cm}^{-1}$. The significant contributions of each force constant towards the calculated Raman and IR wave numbers have also been obtained through investigating the potential energy distribution (PED). The PED mapping for these compounds shows that the lattice dynamical properties of the $\mathrm{Nb}^{5+}$-compounds, BMN and BZN, are remarkably different from the $\mathrm{Ta}^{5+}$-compounds, BMT and BZT. This difference may be attributed to the different degree of orientational dipole disorder caused by the local hopping of the disordered atoms at the *A* and O′ sites in the $A_2\mathrm{O}'$ sub-structure as well as electro-negativity of $B^{5+}$-cations in these bismuth pyrochlores.

## 1. Introduction

Cubic bismuth pyrochlores in the composite form, e.g., $(\mathrm{Bi}_{1.5}\mathrm{Zn}_{0.42})(\mathrm{Zn}_{0.5}\mathrm{Nb}_{1.5})\mathrm{O}_{6.92}$ (denoted as BZN), $(\mathrm{Bi}_{1.5}\mathrm{Zn}_{0.5})(\mathrm{Zn}_{0.5}\mathrm{Ta}_{1.5})\mathrm{O}_7$ (BZT), $(\mathrm{Bi}_{1.5}\mathrm{Mg}_{0.5})(\mathrm{Mg}_{0.5}\mathrm{Nb}_{1.5})\mathrm{O}_7$ (BMN), and $(\mathrm{Bi}_{1.5}\mathrm{Mg}_{0.5})$ $(\mathrm{Mg}_{0.5}\mathrm{Ta}_{1.5})\mathrm{O}_7$ (BMT) have been extensively investigated over the recent years as promising dielectric materials for use in capacitors and manufacturing low-fire high-frequency filter devices in microwave communications, owing to their low dielectric loss, high dielectric constant and good temperature stability [1–6]. The pyrochlore compound is one of the oxygen-polyhedron based families with general formula unit (f.u.) of $A_2B_2\mathrm{O}_7$ or $B_2\mathrm{O}_6{\cdot}A_2\mathrm{O}'$ (*A* and *B* are metals), where the bigger *A* cations (~1 Å) are eight-coordinated and the smaller *B* cations (~0.6 Å) are six-coordinated with respect to oxygen ions [7]. The ideal pyrochlore structure can be considered as an ordered defect fluorite structure with twice the lattice constant, and is usually constructed by taking one of the *A* atoms at the origin with other atoms located at the following positions: *A* at 16*d*, *B* at 16*c*, O at 48*f*, and O′ at 8*a*, and the 8*b* positions are vacant [7,8]. The atoms constitute two networks of corner-shared $B\mathrm{O}_6$ octahedra and $A_2\mathrm{O}'$ chains, in the form of corner-shared $A_4\mathrm{O}'$ tetrahedral (Fig. 1a). The O′–*A*–O′ chains are perpendicular to the puckered hexagonal rings of six 48*f* oxygens surrounding the *A* ion, and the O′ atom is tetrahedrally coordinated to four *A* cations, such that the two networks interpenetrate to make the three-dimensional structure (Fig. 1b). The 48*f* oxygen is displaced from its ideal position, specified by an oxygen *x*-parameter, to the vacant 8*b* site at the center of *B*-tetrahedron [8].

In the above bismuth-based compounds, the *A* site is mostly occupied by the larger, heavy mass $\mathrm{Bi}^{3+}$ ions (78% in BZN; 75% for BZT, BMN and BMT) for all compounds and the *B*-site mostly (75%) by the smaller $\mathrm{Nb}^{5+}$ ($r = 0.64$ Å [9]) or $\mathrm{Ta}^{5+}$ ions ($r = 0.64$ Å); while $\mathrm{Zn}^{2+}$ ($r = 0.74$ Å) in BZN and BZT or $\mathrm{Mg}^{2+}$ ($r = 0.72$ Å) [9] in BMN and BMT partially occupies both *A* and *B*-sites because of their medium ionic radius. The BZN compound is particularly interesting to study their complex structure, in which 4% of the *A* positions remain vacant and 8% of 8*b* oxygen O′-ions remain deficient. As a result, the *A*-site cations are randomly displaced from the ideal

---

* Corresponding author.
*E-mail addresses:* yatramohan@yahoo.com, ymjana@klyuniv.ac.in (Y.M. Jana).

https://doi.org/10.1016/j.molstruc.2017.10.067
0022-2860/

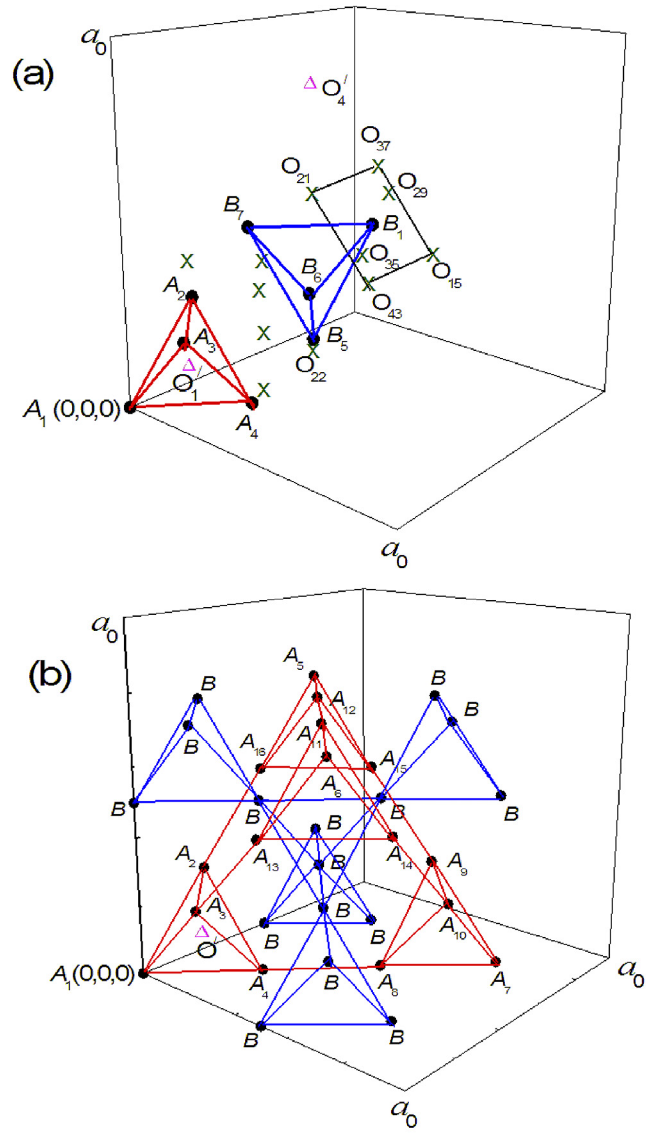


**Fig. 1.** (a) A Bravais cell within a cubic unit cell of dimension $a_0$ of the ideal cubic pyrochlore is drawn using the atomic coordinates given in Ref. [8]. The tetrahedron of 4 $A$-site ions (connected by red lines) with $A_1$ atom at the origin and $O_1'$ (Δ) at the tetrahedral center, and the tetrahedron of 4 $B$-site ions (connected by blue lines) with a vacant 8$b$ site at the center are shown. $B_1$ ion is octahedrally coordinated to six 48$f$ O oxygen ions (×), e.g., $O_{15}$, $O_{21}$, $O_{29}$, $O_{35}$, $O_{37}$, $O_{43}$. (b) Interpenetrating network of four $A$-tetrahedra (red lines) and four $B$-tetrahedra (blue lines) within the unit cell of the pyrochlore $A_2B_2O_6O'$. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

eightfold-coordinated positions along the six ⟨112⟩ directions, perpendicular to the O′–$A$–O′ chains and the O′-ions are found to be randomly displaced along the ⟨110⟩ directions [10–12].

Recently Fourier-transform infra-red (FT-IR) and Raman spectroscopies have been employed [6,10,12–18] for the polycrystalline bismuth compounds, BZN, BZT, BMN and BMT, of different compositions to investigate their complex crystal structure and the local disorder induced by the displacement of the atoms from the behavior of vibrational phonon modes. The group theoretical analysis for the ideal pyrochlore structure shows that the vibrational spectra consist of six Raman modes and seven IR modes [7]. Earlier Nino et al. [6] assigned the infra-red modes for BZN material to a bending or stretching mode. Chen et al. [13] also assigned the IR-active modes, obtained from fit to the oscillator model and Kramers-Kronig analysis of the reflectance spectra, to specific bending and stretching vibrational modes using McCauley's classification [19] for all these ceramic pyrochlore materials. Recently, Arenas et al. [14] reported Raman spectroscopy for these cubic bismuth pyrochlores and assigned the IR and Raman wave numbers by reference to the Raman spectra of many other pyrochlores, some of which include lattice-dynamical calculations [20–22] and first principles calculations [23]. In their work, Arenas et al. assumed $Fd\bar{3}m$ space group for the Bi-pyrochlores and considered displacement disorder in the $A_2O'$ network for these systems. The displacements (or local hopping) of atoms in the $A$ and O′ sites lower the local site symmetry, resulting in the relaxation of the selection rules and could make predicted optically-inactive modes to appear in both IR and Raman spectra, and IR only modes in the Raman and vice versa. Therefore, Arenas et al. [14] assigned the two Raman modes observed around 75 and 150–180 $cm^{-1}$ to IR $F_{1u}$ modes, which actually appear in the IR spectra of Bi-based pyrochlores around 80, 145 and 178 $cm^{-1}$ [13]. It is pertinent to mention that systematic changes in the IR and Raman wave numbers found in the pyrochlore systems can be attributed to the changes in the force-field constants for different substitutions at $A$ and $B$ sites [20–22]. The force field also reflects the electronic structure of the inter-atomic bond and its variations with the bond environment, thus affecting the vibrational spectra [20,24].

To the best of our knowledge, no force-field study on the experimental IR and Raman phonons to assign the vibrational modes has been made till date for these bismuth composites. Hence, in this paper an attempt is undertaken to investigate the observed fundamental Raman and IR phonons of the bismuth pyrochlores using normal coordinate analysis within the short-range force-field model. A total of seven inter-atomic electrostatic force-field constants, including three stretching and four bending constants between $A$, $B$ and O ions, are utilized for lattice dynamics computations of zone center phonons to obtain a reasonable agreement between the theoretical and experimental wave numbers. An effort is also made to assign the experimental wave numbers to their respective optical phonon modes. The potential energy distribution has also been investigated for determining the significance of contribution from each force constant toward the Raman and infra-red wave numbers of the bismuth pyrochlore composites, BZN, BZT, BMN and BMT.

## 2. Theoretical details

Ideal pyrochlore compounds crystallize in face-center cubic structure belonging to the space group $O_h^7 - Fd\bar{3}m$. The factor group analysis using the standard correlation method [25] provides the irreducible representation for vibrational modes for the Bravais unit cell at the zone center:

$$\Gamma = A_{1g} + E_g + 2F_{1g} + 4F_{2g} + 3A_{2u} + 3E_u + 8F_{1u} + 4F_{2u}. \qquad (1)$$

Out of these 26 normal modes, only seven $F_{1u}$ vibrations are active in the infra-red absorption region, but one of the eight $F_{1u}$ modes is associated with three degrees of translation of the unit cell as a whole and refers to the acoustic branch of the crystal vibrations [7]. Six modes, e.g., $\Gamma_{\mathrm{Raman}} = A_{1g} + E_g + 4F_{2g}$, are Raman active. The remaining modes ($\Gamma_{\mathrm{inactive}} = 2F_{1g} + 3A_{2u} + 3E_u + 4F_{2u}$) are optically inactive in both IR and Raman modes of vibrations in ideal cubic pyrochlores.

However, since in the bismuth pyrochlores the atoms at $A$ sites and O′ atoms are displaced from their ideal crystallographic positions (16$d$ and 8$a$, respectively) to off-center ones (96$g$ and 96$g$, respectively) [10–12], the factor group analysis for the disordered systems yields the following phonon modes at the center of the