Structure and lattice dynamics of Jahn-Teller crystal BiMnO$_3$: ab initio calculation

D Nazipov[1*], A Nikiforov[1] and L Gonchar[1,2]

[1]Ural Federal University, 19 Mira St., Ekaterinburg, Russia
[2]Ural State University of Railway Transport, 66 Kolmogorov St., Ekaterinburg, Russia

*E-mail: qwear0@gmail.com

Abstract. In this work, ab initio study of crystal structure and phonon spectra of BiMnO$_3$ has been performed using density functional theory (DFT) with hybrid DFT/Hartree-Fock functionals in CRYSTAL14 code. Crystal structure parameters, infrared and Raman spectra of BiMnO$_3$ have been calculated for magnetic ordered monoclinic C2/c phase. Results are compared with existing experimental data. Our results are in agreement with last x-ray diffraction and optical experiments. Using isotopic substitution method ions involved in vibrations are determined. Calculated charge density maps show the antiferroelectric ordering of dipole moments of Bi^{3+}.

1. Introduction

Crystal compounds of BiMO$_3$ (M – transition metal ion or Al, Ga, In) range are under investigation because of various physical properties which could be used in electronics [1]. The Jahn-Teller crystal BiMnO$_3$ (BMO) is a bismuth-based distorted perovskite oxide like BiFeO$_3$. The trivalent bismuth ion possesses of 6s^2 lone-pair electrons [2,3,4,5], which make this ion polarized. The transition-metal ions (Mn^{3+} or Fe^{3+}) are magnetic. The dipole moments of Bi^{3+} sublattice and the magnetic moment of transition metal sublattice are ordered at low temperatures [1-5,6,7]. This coincidence leads to widely discussed multiferroic properties of these compounds [1-7]. The sublattice of orbitally degenerated Mn^{3+} ions adds new properties to the correlation between polarization and magnetic subsystem. Thus, the BiFeO$_3$ is an antiferromagnetic crystal with ferroelectric (FE) ordering [5]. The BiMnO$_3$ is ferromagnetic (FM) and has no spontaneous polarization in the bulk samples [3, 4]. The FM ordering of BiMnO$_3$ is caused by orbital ordering of manganese sublattice due to Jahn-Teller effect [8,9]. Under Curie temperature, the centrosymmetric group C2/c of crystal structure leads to absence of ferroelectricity due to symmetry considerations [2, 3, 9]. An inversion symmetry operation causes an impossibility of FM+FE ordering in this crystal. The temperature and external pressure change the crystal structure to monoclinic and orthorhombic symmetry [3, 4, 10], but they cause no changes of spontaneous polarization in the bulk crystal. The experiments using Raman and infrared spectroscopy confirm these considerations [11]. But the phonon spectra are still not investigated in detail due to problems related to very low symmetry of the crystal in magnetic ordered phase. The Bi^{3+} dipole moments ordering is studied only in cases FM+FE ordering. The authors have studied the thin films [7] or considered magnetic symmetry breaking [12,13]. The presence of dipole moments is not yet studied neither theoretically nor experimentally.

The current investigation is devoted to *ab initio* calculations of $BiMnO_3$ crystal structure and optical spectra. We perform a detailed investigation of phonon spectra for the first time and describe the experimental data [11].

2. Computational Details

Calculations have been performed in program package CRYSTAL14 [14], within the framework of density functional theory (DFT) using linear combination of atomic orbitals (LCAO) approximation. Hybrid DFT/HF functional WC1LYP has been used with 16% of Hartree-Fock exchange energy. In this functional, the DFT-exchange part is calculated using Wu-Cohen method in generalized gradient approximation (GGA). It should be noted that this functional developed without the fitting parameters. The correlations are taken into account by the functional LYP. All-electron Gauss-type basis sets are used for description of Mn^{3+} and O^{2-} ions, 86-411d41G and 8-411d1, correspondingly [15]. Heavy Bi^{3+} ion is described by Hay-Wadt effective small-core pseudopotential that is taken from a source [16]. External $6s^2$ orbital of Bi^{3+} ion plays an important role in the formation of the distortion of the crystal lattice, so it is taken into account directly and was not included in the core. All calculations performed in spin-polarized mode in high-spin state S=2 for Mn^{3+}. The accuracy of calculations is determined by a set of tolerances for the overlap of wave functions, above which the Coulomb and exchange integrals are calculated. In this paper, the tolerance is selected to be 10^{-10} for Coulomb and 10^{-20} for the exchange integrals. The integration in reciprocal space is made with 4 x 4 x 4 grid using Monkhrost-Pack scheme. The energy per unit cell is calculated with an accuracy of 10^{-8} Hartree.

Phonon frequencies are calculated in the center of first Brillouin zone in harmonic approximation.

3. Results and Discussion

3.1. *Crystal structure*

The calculation of crystal structure parameters of $BiMnO_3$ has been made for monoclinic phase, C2/c space group, in ferromagnetic arrangement of spins. According to x-ray diffraction experiment, that performed for $BiMnO_3$ single crystal in magnetic ordered state, at T $<T_c$ there is a center of symmetry and monoclinic C2/c structure is realized, instead of the C2, as previously assumed [17]. The results of our calculation (table 1) are in a good agreement with the experiment [18] (the difference is less than 1%).

Table 1. Calculated and experimental [18] (in brackets) crystal structure parameters of $BiMnO_3$

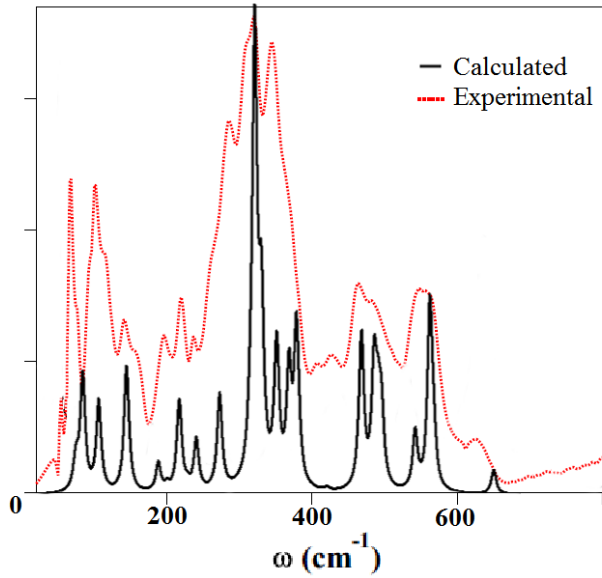| Lattice constant		a	b	c	β
Value, Å		9.484(9.569)	5.589(5.602)	9.799(9.879)	110.96(111.02)
Atom coordinates in cell					
Atom	Wyckoff symbol	x/a	y/b	z/c	
Bi	8f	0.1351(0.1365)	-0.230(-0.217)	0.1181(0.1269)	
Mn1	4e	0	0.2014(0.2113)	0.25	
Mn2	4c	0.25	0.25	0	
O1	8f	0.0993(0.0991)	0.1666(0.1776)	0.0794(0.0815)	
O2	8f	0.3510(0.3524)	0.4496(0.4567)	0.1662(0.1646)	
O3	8f	0.1447(0.1443)	0.4161(0.4342)	0.3782(0.3639)	
Bond lengths, Å					
Mn1-O1	2.20(2.20)		Mn2-O1	1.91(1.93)	
Mn1-O2	1.91(1.90)		Mn2-O2	2.24(2.23)	
Mn1-O3	1.95(1.97)		Mn2-O3	1.92(1.95)	

3.2. *Phonon spectra*

The set of fundamental vibrations in gamma point of $BiMnO_3$, in monoclinic C2/c phase, looks as follows:

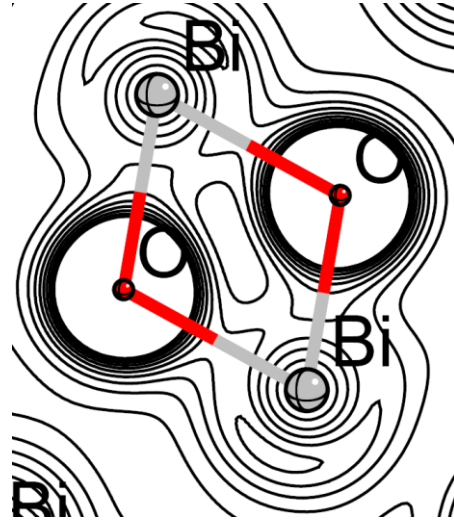$$\Gamma = (13A_g + 14B_g)^{Ram} + (14A_u + 16B_u)^{IR} + (A_u + 2B_u)^{Acoust} \tag{1}$$

Table 2. Irreducible representations, frequencies of IR and Raman modes in cm^{-1} and calculated intensities in IR spectrum in a.u.

Infrared					Raman			
№	Repr.	Calc.	Exp. [11]	Calc. Intens.	№	Repr.	Calc.	Exp. [11]
5	A_u	74	68	16	4	A_g	53	50
6	B_u	76	75	59	7	B_g	81	75
8	B_u	85	92	255	10	B_g	93	84
9	A_u	88	101	0.5	11	B_g	102	93
12	A_u	107	115	200	13	A_g	108	99
16	B_u	145	143	282	14	A_g	113	
17	A_u	189	159	64	15	B_g	137	133
19	B_u	201	196	14	18	A_g	196	180
20	B_u	218	219	200	21	B_g	223	
22	A_u	229		11	23	B_g	232	
24	B_u	241	237	112	26	A_g	262	242
25	A_u	244		2	28	A_g	287	278
27	B_u	273	261	213	29	B_g	287	
30	A_u	291		1	34	B_g	346	
31	B_u	316	284	66	36	A_g	358	347
32	B_u	321	308	1000	37	A_g	360	
33	A_u	331	321	374	39	B_g	373	
35	A_u	351	345	312	42	B_g	395	
38	B_u	368	369	249	44	A_g	422	400
40	B_u	379		335	45	A_g	450	424
41	A_u	381	407	34	46	B_g	456	440
43	A_u	421	426	7	47	A_g	462	
48	B_u	468	463	341	49	B_g	482	
50	A_u	485	486	261	53	A_g	523	
51	A_u	490		141	54	B_g	533	530
52	B_u	495	508	159	58	B_g	646	635
55	B_u	542	541	128	60	A_g	652	
56	B_u	562	561	401				
57	A_u	567	604	87				
59	A_u	649	628	54				

Among 60 modes, 27 even modes are active in Raman spectrum, 30 odd are active in infrared (IR) spectrum and 3 odd modes are acoustic. Our calculation predicts all the modes, their irreducible representations, a comparison of results with the experiment [11] is presented in table 2. The comparison with experimental data is complicated because not all the lines are identified in the experimental spectra. There are 25 lines in infrared spectrum, which are taken at T=10K, and 15 Raman lines, which are taken at room temperature in backscattering geometry. Both of the experimental spectra are obtained in the unpolarized configuration, so we compare with the results calculated for the powder sample. Also it should be noted that missing lines in experimental IR spectrum are low intensity lines or narrow doublets.

Figure 1. Calculated and experimental (T=10K) infrared spectrum

Figure 2. Charge density map in plane of two Bi^{3+} ions

In CRYSTAL package, the intensity of the modes I_p in infrared spectrum is computed according to

$$I_p = \frac{\pi}{3}\frac{N_A}{c^2}d_p\left|\vec{Z}_p\right|^2,\tag{2}$$

where N_A is the Avogadro's number, c is the speed of light, d_p is the degeneracy of the mode, $\vec{Z}_p$ is the mass-weighted effective mode Born charge vector. Calculated I_p for the IR-active modes for $BiMnO_3$ are presented in table 2.

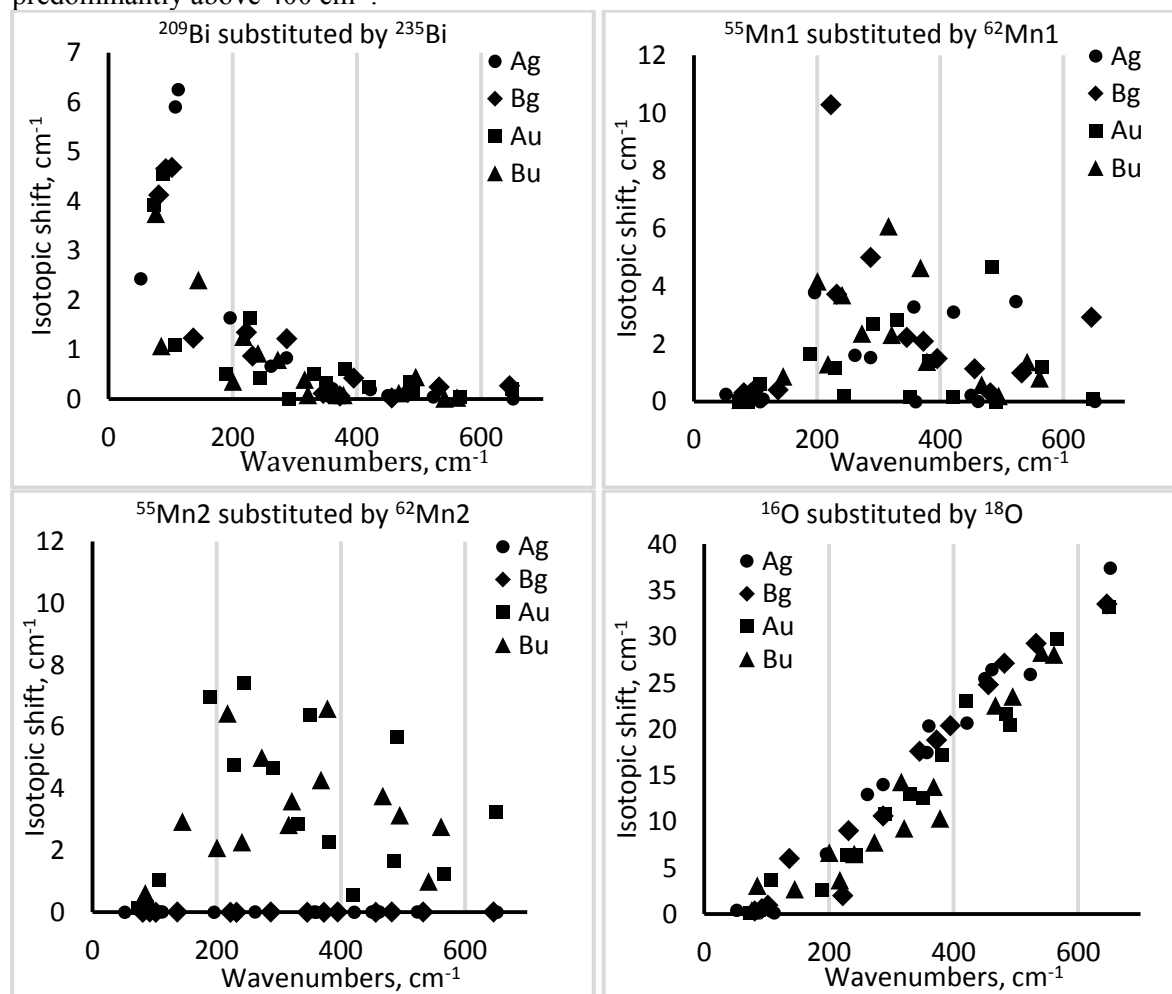The infrared absorbance spectrum $A(\omega)$, which is shown in figure 1, is calculated using following model:

$$A(\omega) = \sum_p \frac{I_p}{\pi}\frac{\gamma_p/2}{\left(\omega-\omega_p\right)^2+\gamma_p^2/4},\tag{3}$$

where ω_p is TO frequency, γ_p is the damping factor (γ_p=8 cm^{-1}), and I_p is integrated intensity computed as described above.

The phonon frequencies and a IR spectrum which have been obtained in this work are in a good agreement with the existing experimental data [11]. Thereby our results confirm that $BiMnO_3$ single crystal has centrosymmetric C2/c space group at low temperature.

3.2.1. Dipole moments. Using *ab initio* calculations, it is possible to draw a map of charge density in specific plane. Figure 2 shows a charge density around bismuth ions. There is a localization of negative charge near Bi^{3+} ion and formation of dipole moment.

3.2.2. Isotopic substitution. To determine the ions that take part in vibrations, the isotopic substitution method has been used. The phonon spectrum was recalculated with a changed mass of each symmetrically nonequivalent ion. Obtained frequencies were compared with the initial spectrum and frequency shifts have been determined. In figure 3, results of isotopic substitution are presented. Heavy Bi^{3+} ions are involved in vibrations with frequencies below 200 cm^{-1} approximately. Both positions of manganese ions take part in vibrations in a region of frequencies 200 to 400 cm^{-1}, but Mn2 sublattice is not involved in Raman-active even modes. Oxygen ions take part in all vibrations, predominantly above 400 cm^{-1}.

Figure 3. Isotopic substitution data for $BiMnO_3$

4. Conclusion

In this paper, crystal structure parameters of monoclinic centrosymmetric phase of $BiMnO_3$ were calculated from first principles. The phonon spectra were calculated and full set of fundamental vibrations, their frequencies and irreducible representations were obtained. Intensities in infrared spectrum were calculated. Despite that the symmetry of the investigated crystal is very low the results obtained are in a good agreement with existing experimental data. The phonon spectra are investigated

using isotopic substitution method. Presence of dipole moments in bismuth sublattice is reproduced in calculations.

References

[1]   Khomskii D 2006 *J. Magn. Magn. Mat.* **306** 1

[2]   Pyatakov A and Zvezdin A 2012 *Phys. Usp.* **55** 557 (Russian text published in 2012 *Usp. Phys. Nauk* **182** 593)

[3]   Kozlenko D, Belik A, Kichanov S, Mirebeau I, Sheptyakov D, Strässle Th, Makarova O, Belushkin A, Savenko B and Takayama-Muromachi E 2010 *Phys. Rev B* **82** 014401

[4]   Kozlenko D, Dang N, Jabarov S, Belik A, Kichanov S, Lukin E, Lathe C, Dubrovinsky L, Kazimirov V, Smirnov M, Savenko B, Mammadov A, Takayama-Muromachi E and Khiem L 2014 *J. of Alloys and Compounds* **585** 741

[5]   Kozlenko D, Belik A, Belushkin A, Lukin E, Marshall W, Savenko B and Takayama-Muromachi E 2011 *Phys. Rev B* **84** 094108

[6]   Grizalez M, Martinez E, Caicedo J, Heiras J and Prieto P 2008 *Microelectronics Journ.* **39** 1308

[7]   Moreira dos Santos A, Parashar S, Raju A, Zhao Y, Cheetham A and Rao C 2002 *Solid State Commun.* **122** 49

[8]   Gonchar L, Nikitina T and Nikiforov A 2013 *JETP* **116** 812 (Russian Text published in 2013 *Zhurnal Eksperimental'noi i Teoreticheskoi Fiziki* **143** 935)

[9]   Gonchar L and Nikiforov A, 2013 *Phys. Rev. B* **88** 094401

[10]   Calestani G, Orlandi F, Mezzadri F, Righi L, Merlini M and Gilioli E 2014 *Inorg. Chem.* **53** 8749

[11]   Mohamed W, Nucara A, Calestani G, Mezzadri F, Gilioli E, Capitani F, Postorino P and Calvani P 2015 Phys Rev. B **92** 054306

[12]   Solovyev I and Pchelkina Z 2010 *Phys. Rev B* **82** 094425

[13]   Solovyev I and Nikolaev S 2014 *Phys. Rev. B* **90** 184425

[14]   URL: http://www.crystal.unito.it/

[15]   URL: http://www.crystal.unito.it/basis-sets.php

[16]   URL: http://www.tc.uni-koeln.de/PP/clickpse.en.html

[17]   Moreira dos Santos A, Cheetham A, Atou T, Syono Y, Yamaguchi Y, Ohoyama K, Chiba H and Rao C 2002 *Phys. Rev. B* **66** 064425

[18]   Toulemonde P, Bordet P, Bouvier P and Kreisel J 2014 *Phys. Rev.* B **89** 224107