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Lattice dynamics and phase transitions in a crystal Ba_2ZnTeO_6

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The lattice dynamics of Ba_2ZnTeO_6 double perovskite in three phases has been studied. Vibrational spectra and dynamic charges are calculated. In the rhomobohedral phase $R\bar{3}m$, soft modes were found; after their condensation, the $C2/m$ phase was obtained, which agrees with the experiment. An assessment was made of the dependence of the enthalpy of different phases on pressure; it showed that the monoclinic phase is more favorable at 0 pressure, but as the pressure increases to 2.9 GPa, the cubic phase $Fm\bar{3}m$ becomes advantageous.

Keywords: Lattice dynamics, phase transitions, double perovskites.

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1. Introduction

Double perovskites with the general formula $A_2BB'O_6$ are being studied for several decades due to their structural phase transitions and diversity of physical properties, which depend both on chemical composition of A, B and B' cations and on different types and degree of cation ordering in the structure [1]. Most of these compounds in the highly symmetrical cubic phase (with the space group of symmetry $Fm\bar{3}m$) have the elpasolite structure where octahedra BO_6 and $B'O_6$ are linked by oxygen at the octahedron vertexes. Most double perovskites with the elpasolite structure (with few exceptions), regardless of the degree of cation ordering in the cubic phase, have instabilities related to lattice vibration modes either in the center or at the grating boundary point X of the Brillouin zone in a face-centered cubic lattice, the eigen vectors of these „soft" modes correspond to „turns" of BO_6octahedron. In rarer cases, with a large ionic radius of the A cations, double perovskites can have other structure types, in particular, with hexagonal or a rhombohedral symmetry [2–4]. The BO_6 and $B'O_6$ octahedra in such structures have common vertexes, edges and faces. Such double perovskites with common edges and faces of BO_6 and $B'O_6$ octahedra are less well understood both from the viewpoint of their physical properties and structure instability.

Double perovskite Ba_2ZnTeO_6 has rhombohedral symmetry with space group $R\bar{3}m$ and with two molecules in the unit cell.

The results of the study of Raman and IR spectra of Ba_2ZnTeO_6 were published in [5,6]. The authors of these papers have found a structural phase transition ($R\bar{3}m \rightarrow C2/m$) at 140 K, which is related to the „soft" vibration mode. The authors have also found the crystal lattice vibration frequencies and classified them. The authors of [7] studied the behavior of Ba_2ZnTeO_6 under hydrostatic pressure and found that at higher pressures Ba_2ZnTeO_6 has the elpasolite structure with symmetry $Fm\bar{3}m$.

The aim of the present paper is to calculate the lattice vibration frequencies and to study the phase transitions in the Ba_2ZnTeO_6 compound using the ab initio calculation methods implemented in the Crystal software package [8,9].

2. Structural characteristics and calculation method

The crystal structure of the Ba_2ZnTeO_6 compound is shown in Fig. 1. Several types of octahedra can be distinguished in the structure. The first type is TeO_6 octahedra located in layers in plane ab and linked to ZnO_6 octahedra by oxygen at the octahedron vertexes. The second type is TeO_6 octahedra located in columns along axis c and linked by faces with ZnO_6 octahedra. The third type is ZnO_6 octahedra located in columns along axis c; on one side they have a common face with a TeO_6 octahedron of the second type, on the other side their vertexes are linked to TeO_6 octahedra of the first type. A shift of axis c of the Zn atom from the octahedron center should also be noted.

The calculations in the present paper were performed using the CRYSTAL package. The hybrid B3LYP method was used in the DFT calculations [10]. The chosen bases are (HAYWSC-31(2df)G) for the barium atom, (Zn_pob_TZVP_rev2) for the zinc atom, (Te_POB_TZVP_2018) for the tellurium atom and (O_8-411d11G_valenzano_2006) for the oxygen atom [11].

3. Results

We have calculated the equilibrium lattice parameters and the coordinates of atoms in the structure with the symmetry group $R\bar{3}m$, which are given in Table 1 together

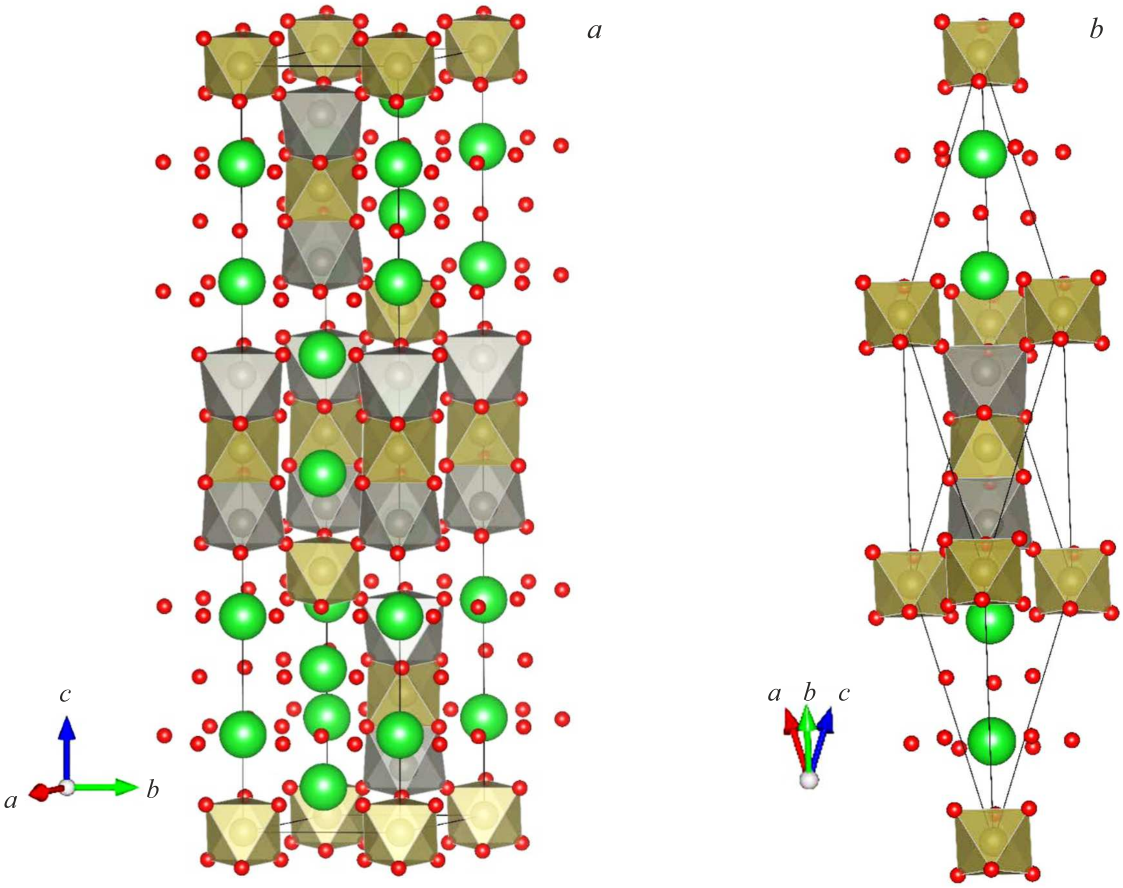

Figure 1. Crystal structure of the Ba_2ZnTeO_6 compound in the rhombohedral phase with the space group $R\bar{3}m$: *a* — unit cell and *b* — primitive cell.

with the experimental data. An expansion of a vibrational representation at the Brillouin zone center in indecomposable representations of point group D_{3d} has the form $\Gamma = 7A_{1g} + 2A_{2g} + 9E_g + 2A_{1u} + 9A_{2u} + 11E_u$. The calculated vibration frequencies of atoms at the Brillouin zone center are given in Table 2 together with the experimental data [5,6]). The values of dynamic ion charges are given in Table 3.

It can be seen from Table 2 that the calculated vibration frequencies mainly agree well with the experimental values, but there are some discrepancies both between the experimental and calculated values of vibration frequencies and between the experimental data. In particular, both experimental spectra have a high-frequency vibration E_g with the frequency of $767\,\mathrm{cm}^{-1}$, but vibrations with this frequency are not presented in the calculated spectrum.

Two soft vibration modes are present in the calculated vibration frequencies of the BZTO compound in the structure with symmetry group $R\bar{3}m$. One doubly degenerate mode E_g with the frequency of $-67\,\mathrm{cm}^{-1}$ and non-degenerate mode A_{2g} with the frequency of $-53\,\mathrm{cm}^{-1}$. The observed structural phase transition $R\bar{3}m \rightarrow C2/m$ is related to the unstable mode E_g.

Table 1. Calculated and experimental (*) [7] lattice parameters and coordinates of atoms of the Ba_2ZnTeO_6 compound in the rhombohedral phase with space group $R\bar{3}m$

Lattice parameters, Å	a		c
	5.920 (5.825*)		29.13 (28.69*)
Atom	x	y	z
Ba_1	0	0	0.6274
Ba_2	0	0	0.7815
Zn	0	0	−0.0963
Te_1	0	0	0.5
Te_2	0	0	0
O_1	0.8199	0.1800	0.2931
O_2	0.1783	0.8216	0.1272

Let us consider atomic displacements in the eigen vector of the imaginary vibration mode E_g, which are shown by arrows in Fig. 2, *a*. It can be seen from this figure that displacements of oxygen ions at the vertexes of the TeO_6

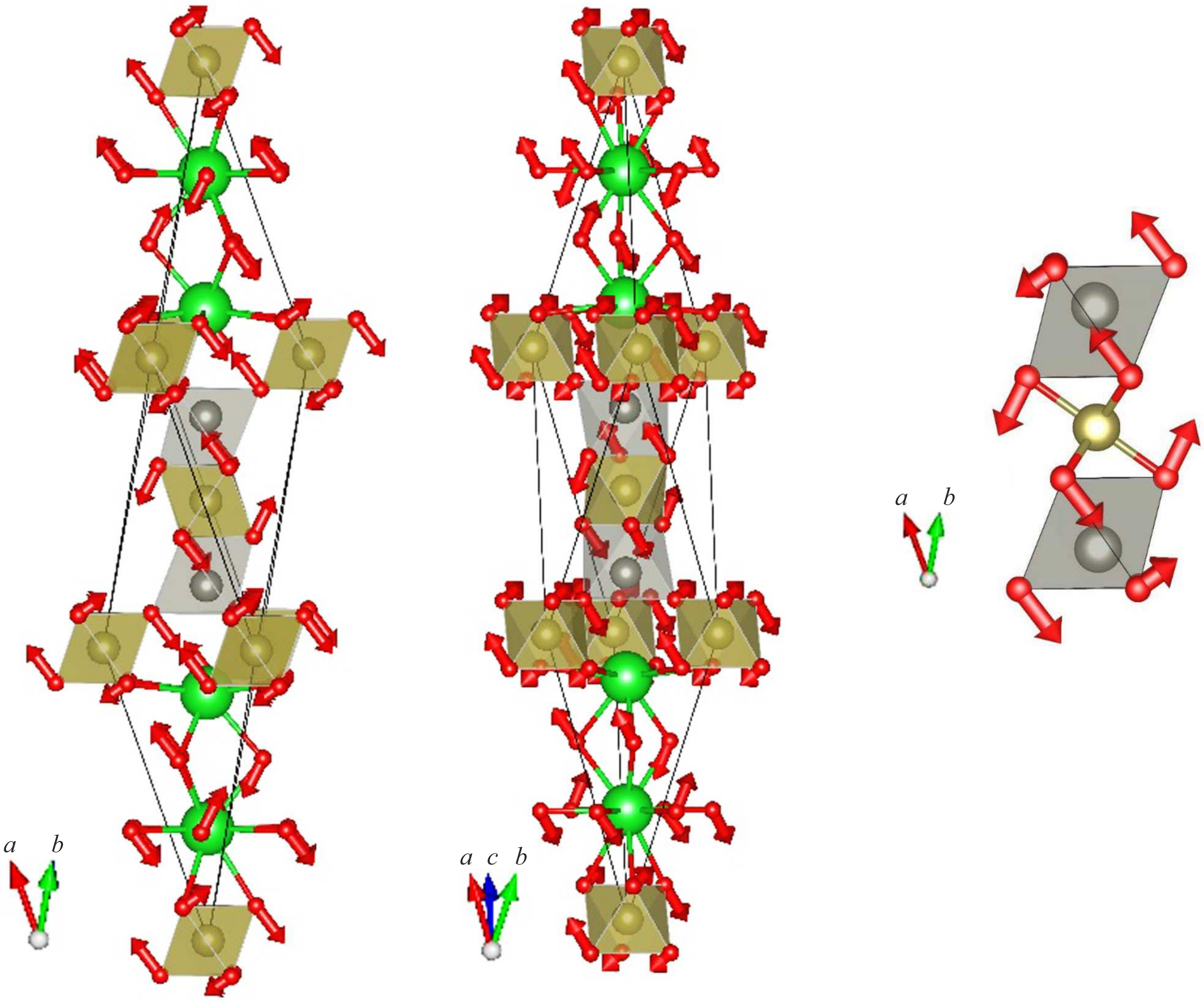

Figure 2. Eigen vector of one component of the dual mode E_g for Ba_2ZnTeO_6 compound in the rhombohedral phase with space group $R3m$.

octahedra both of the first and the second type correspond to a „turn“ of this octahedra, as in double perovskites with the elpasolite structure where the octahedra are linked by the vertexes. However, ZnO_6 octahedra, as distinct from the elpasolite structure, are distorted in thiscase.

A distortion of the structure of the highly symmetrical phase $R\bar{3}m$ along the eigen vectors of duel mode E_g causes the formation of a structure with symmetry group $C2/m$. It should be noted that a distortion of the structure along one component or along two equal components of the eigen vector of mode E_g causes the formation of the same structure (An expansion of the thermodynamic potential in the order parameter, which is converted by the presentation E_g, contains a single quartic invariant). The total crystal energy vs. the amplitude of atomic displacement along one component of the eigen vector is shown in Fig. 3.

The optimized lattice parameters and coordinates of atoms of the structure with group $C2/m$ are given in Table 4. The experimental data is also given there. It should be noted that there is a disagreement with the experimental data on the lattice parameter, namely parameter a — the difference between the calculated and the experimental value is $\approx 10\%$.

The calculated vibration frequencies at the center of the Brillouin zone of the distorted structure are given in Table 5. An expansion in indecomposable representations at the center of the Brillouin zone for symmetry group $C2/m$ is $\Gamma = 16A_g + 11B_g + 13A_u + 20B_u$. The experimental frequencies are also given there. Good agreement with the experiment can be seen. A soft vibration mode B_g with the frequency of $-57.3\,\mathrm{cm}^{-1}$ is present in the calculated vibration frequencies of the BZTO compound in the structure with symmetry group $C2/m$. The symmetry

Table 2. Calculated and experimental [5*, 6**] vibration frequencies (cm^{-1}) of the Ba_2ZnTeO_6 compound in the rhombohedral phase with space group $R\bar{3}m$

E_g			A_{1g}			A_{2g}		
Calc.	Exp.*	Exp.**	Calc.	Exp.*	Exp.**	Calc.	Exp.*	Exp.**
−67.2	28.8	31	84.5	86.0	87.0	−53.7		
79.3	121.4	103	116.2	104.3	110.0	130.9	185	185.0
95.6	382.7	120	219.1	109.7	405.0			
122.7	395.5	153	392.3	142.5	470.0			
205.0	406.2	382	440.9	153.7	689.0			
365.3	572.0	394	665.3	471.3	736.0			
384.2	616.0	573	760.0	756.1				
555.5	690.8	616						
629.2	767.7	766						

E_g		A_{1g}		A_{2g}	
Calc.	Exp.*	Calc.	Exp.*	Calc.	Exp.*
0.0	67.1	200.8	231.0	0.0	99
52.9	109.6	233.3	331.5	101.3	141.6
116.9	124.5			106.3	182.2
122.3	135.2			173.1	192.1
208.2	259.5			220.2	200.6
234.8	312.1			357.0	437.5
282.4	361.2			438.4	475.4
345.4	388.4			650.7	755.3
367.0	619.2			756.9	
595.1	660.4				
664.6					

Table 3. Calculated dynamic charges of the Ba_2ZnTeO_6 compound in the rhombohedral phase with space group $R\bar{3}m$

Atom	Z_{xx}	Z_{yy}	Z_{zz}
Ba_1	2.8	2.8	2.7
Ba_2	2.8	2.8	2.7
Ba_3	2.9	2.9	2.71
Ba_4	2.9	2.9	2.71
Zn_1	2.37	2.37	2.71
Zn_2	2.37	2.37	2.71
Te_1	5.05	5.05	4.92
Te_1	4.29	4.29	5.23
O_1	−2.63	−1.79	−1.98
O_2	−2.63	−1.79	−1.98
O_3	−2.63	−1.98	−1.79
O_4	−2.63	−1.98	−1.79
O_5	−2.63	−1.79	−1.98
O_6	−2.63	−1.79	−1.98
O_7	−3.14	−1.73	−1.67
O_8	−3.14	−1.73	−1.67
O_9	−3.14	−1.67	−1.73
O_{10}	−3.14	−1.67	−1.73
O_{11}	−3.14	−1.73	−1.67
O_{12}	−3.14	−1.73	−1.67

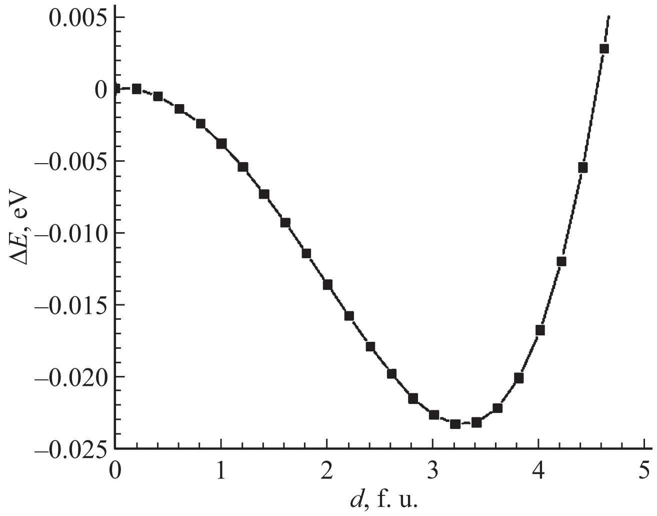

Figure 3. Total energy of BZTO crystal in the monoclinic phase vs. shift amplitude.

decreases to group $P\bar{1}$ in case of a crystal structure distortion along the eigen vector of the given vibration. As per the literature data, such a transition is not observed in the BZTO crystal, but there is experimental data [12]

Table 4. Calculated and experimental [10] lattice parameters and coordinates of atoms of the Ba_2ZnTeO_6 compound in the monoclinic phase with space group $C2/m$

	a	b	c
Lattice parameters, Å	10.185 9.0228*	5.9186 5.8236*	10.289 10.086*
	90	109.08 109.36*	90
Atom	x	y	z
Ba_1	0.1258	0	0.3853
Ba_2	0.2870	0	0.8453
Zn	0.3975	0	0.2102
Te_1	0	0	0
Te_2	0	0.5	0.5
O_1	0.3815	0.2303	0.3821
O_2	0.6081	0	0.3741
O_3	0.5587	0.2658	0.8956
O_4	0.8154	0	0.8610

that the isomorphic Ba_2CuTeO_6 compound undergoes a $C2/m \rightarrow P\bar{1}$ transition at 290 K.

The values of dynamic ion charges in phase $C2/m$ are given in Table 6.

As already stated in the introduction, the authors of [7] found a phase transition to the elpasolite structure with space symmetry $Fm\bar{3}m$ in the BZTO crystal under hydrostatic pressure. We optimized the BZTO structure in terms of lattice parameters and atom coordinates in phase $Fm\bar{3}m$. The results are given in Table 7. The vibration frequencies at the center of the Brillouin zone and dynamic Born charges were calculated for this optimized structure. The results are given in Table 7, 8. It should be emphasized that the BZTO crystal in the elpasolite structure has no unstable vibration modes, i.e. this structure remains stable at all temperatures.

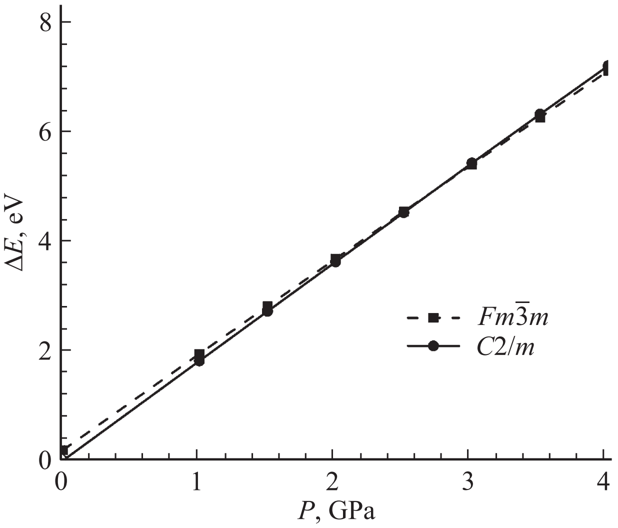

Figure 4. Enthalpy ΔH of the BZTO compound in $C2/m$ and $Fm\bar{3}m$ phases vs. applied pressure.

Enthalpy $\Delta H = E_{\text{full}} - PV$ of the BZTO compound in phases $C2/m$ and $Fm\bar{3}m$ vs. applied pressure is shown in Fig. 4. The zero is the energy at 0 pressure of the structure with symmetry group $C2/m$, all energies were standardized to the formula unit. Enthalpy vs. pressure is not given for the phase with structure $R3m$, because this

Table 5. Calculated and experimental [5] vibration frequencies ω, cm^{-1} of the Ba_2ZnTeO_6 compound in the monoclinic phase with space group$C2/m$

Calc.	IR			Calc.	Calc.	Raman			Calc.
A_u	A_u	$A_u + B_u$	B_u	B_u	A_g	A_g	$A_g + B_g$	B_g	B_g
38.4		63		68.3	72.8		37.3		−57.3
119.6		71.7		90.6	77.2		50.7		47.8
135.1		105		99.1	96.9	92.6	119.1		89.2
184.4		109.6	100.4	122.1	103.5	99.4	125.9		113.9
209.3		122	143	135.8	124.6	108.7	379.2		126.9
224.9		128.2	183.7	179.7	153.0	140.6	382.2		144.6
235.1		133.7	193.4	208.0	206.3	166	397.9	184.8	195.9
291.5		139.2	201	220.4	232.1		399.9		358.4
344.5	331.5	251		279.6	367.8		404.6		380.9
369.5		266		300.8	384.2		406.6		551.6
593.2		310		343.8	414.6		574.2		609.2
647.5		314.5		362.6	450.8	469.8	577.6		
		358.9		367.3	555.5		615.9		
		386.9	438.5	449.1	609.3		621.8		
		613	476	589.9	660.7		693.6		
		621.3		640.8	737.8	756.1	695.7		
		660		647.8			770.9		
		664.3	761.5	734.2		773.3			

Table 6. Calculated dynamic charges of the Ba_2ZnTeO_6 compound in the monoclinic phase with space group $C2/m$

Atom	Z_{xx}	Z_{yy}	Z_{zz}
Ba_1	2.89	2.61	2.76
Ba_2	2.89	2.61	2.76
Ba_3	2.73	2.92	2.95
Ba_4	2.73	2.92	2.95
Zn_1	2.74	2.37	2.37
Zn_2	2.74	2.37	2.37
Te_1	4.94	4.94	5.18
Te_2	4.31	5.19	4.27
O_1	−2.57	−1.79	−2.01
O_2	−2.57	−1.79	−2.01
O_3	−2.68	−1.95	−1.79
O_4	−2.68	−1.95	−1.79
O_5	−2.57	−1.79	−2.01
O_6	−2.57	−1.79	−2.01
O_7	−3.16	−1.73	−1.64
O_8	−3.16	−1.73	−1.64
O_9	−3.01	−1.77	−1.74
O_{10}	−3.01	−1.77	−1.74
O_{11}	−3.16	−1.73	−1.64
O_{12}	−3.16	−1.73	−1.64

Table 7. Calculated and experimental [7] lattice parameters and coordinates of atoms of the Ba_2ZnTeO_6 compound in the cubic phase with space group $Fm\bar{3}m$

Lattice parameter, Å	a		
	8.2518 (8.1479*)		
Atom	x	y	z
Ba	0.25	0.25	0.25
Zn	0	0	0
Te	0.5	0.5	0.5
O	0.2636 0.2520*	0	0

Table 8. Calculated vibration frequencies of the Ba_2ZnTeO_6 crystal in the cubic phase with structure $Fm\bar{3}m$

Sim.	ω, cm^{-1}
F_{1u}	0
F_{1g}	55.6
F_{2g}	120.5
F_{1u}	121.2
F_{1u}	158.5
F_{2u}	236
F_{1u}	332.8
F_{2g}	372.6
E_g	446.6
F_{1u}	555.4
A_g	648.9

Table 9. Calculated dynamic charges of the Ba_2ZnTeO_6 crystal in the cubic phase with structure $Fm\bar{3}m$

Atom	Z_{xx}	Z_{yy}	Z_{zz}
Ba_1	2.73	2.73	2.73
Ba_2	2.73	2.73	2.73
Zn	2.96	2.96	2.96
Te	4.76	4.76	4.76
O_1	−1.69	−3.19	−1.69
O_2	−1.69	−1.69	−3.19
O_3	−1.69	−1.69	−3.19
O_4	−3.19	−1.69	−1.69
O_5	−1.69	−3.19	−1.69
O_6	−3.19	−1.69	−1.69

phase does not become more favorable than the others at all the studied pressure values (calculations are performed at zero temperature). As seen in Fig. 4, the phase with structure $Fm\bar{3}m$ becomes more favorable than the phase with structure $C2/m$ at 2.9 GPa. The obtained data agrees with the experiment [7], where this phase transition was found at the pressure of 4.0 GPa.

4. Conclusion

In the present paper we have calculated the vibration frequencies at the center of the Brillouin zone of the Ba_2ZnTeO_6 compound in the rhombohedral, monoclinic and cubic phases. Imaginary vibration modes were obtained in the spectrum of the calculated frequencies for the rhombohedral phase: doubly degenerate mode E_g with the frequency of $-67\,\mathrm{cm}^{-1}$ and non-degenerate mode A_{2g} with the frequency of $-53\,\mathrm{cm}^{-1}$. The structural phase transition $R\bar{3}m \to C2/m$ is related to the unstable mode E_g. An experimentally observed monoclinic phase of BZTO was obtained after distortion along one component of mode E_g. A soft vibration mode Bg with the frequency of $-57.3\,\mathrm{cm}^{-1}$ was found in the spectrum of the calculated frequencies of the monoclinic phase. After its condensation, a structure with symmetry group $P\bar{1}$ was obtained.

The enthalpy of the different phases vs. pressure was estimated. It was found that the cubic phase with structure $Fm\bar{3}m$ becomes more favorable than the monoclinic phase with structure $C2/m$ at 2.9 GPa. The obtained data agrees with the experiment [7], where this phase transition was found at the pressure of 4.0 GPa.

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Conflict of interest

The authors declare that they have no conflict of interest.

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