



A lattice dynamical investigation of the Raman and infrared wavenumbers of Ba₂MgTeO₆ double-perovskite oxide

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Abstract. The Raman and infrared phonons in the tetragonal structure of double-perovskite Ba₂MgTeO₆ with space group I4/m have been studied using a short-range force constant model. This study used six stretching and two bending force constants to calculate zone centre phonons theoretically using the normal coordinate analysis. Some optical vibrational modes have been reported for the first time for Ba₂MgTeO₆ compounds in the I4/m phase using Wilson's GF-Matrix method. The rest of the phonon modes calculated in this work have been compared with the available experimentally observed frequencies in the literature. The significance of interatomic force constant in the calculated Raman and infrared phonons has also been investigated in the potential energy distributions for the double-perovskite compound Ba₂MgTeO₆.

Keywords. Raman and infrared wavenumber; double perovskite; phonon.

1. Introduction

The general formula of double-perovskites A₂B'B''O₆ is observed from the perovskites ABO₃, where the B sites are replaced by the two cations B' and B''. These compounds are classified as ordered or disordered, depending on the degree of long-range order of B' and B'' cations [1]. Compounds having the formula A₂B'B''O₆ with a double-perovskite structure have been intensively researched in recent years. This is because of the attractive electrical and magnetic properties in several compounds in this class that could be useful in technological applications and scientific significance [2]. The double-perovskite structure is a three-dimensional network of alternating B'O₆ and B''O₆ octahedra, with A atoms occupying the interstitial spaces. This structure is simple but sometimes difficult to determine the real crystal structure due to the relative B-cation disorder, and due to pseudo-cubic symmetry which is present in many compounds of double perovskite [3,4].

The crystallographic properties and physical properties such as dielectric, magnetic and electrical properties of the double-perovskite A₂B'B''O₆ have been studied. These Perovskites can have electronic structures that range from insulating to metallic. Also they can even be half-metallic with spin-polarized electrical conductivity along with a variety of fundamentally remarkable chemical and physical characteristics [5]. The double perovskites have a

fascinating application in area of superconductivity, ferroelectricity, magnetoelectricity, ferromagnetism and magnetic ordering from antiferromagnetic to ferrimagnetic. These materials have ionic conductivity, high magnetoresistance as well as properties like multiferroicity [6–8].

Now a days, tellurium (Te)-based double-perovskite oxides like Ba₂MgTeO₆ are extensively studied due to their structural features and dielectric resonator properties.

To study the origin of any property, it becomes necessary to have a detailed microstructure analysis of the compound. Hence, an attempt is made to study the double perovskite, Ba₂MgTeO₆, by analysing the bonds' impact in the vibrational spectrum. Vibrational spectroscopy is non-destructive optical crystallography that can be used for information regarding crystalline phases, chemical identity, local chemical environment, and so on, covering a large number of complex systems just by exploring the characteristic vibrational modes of the related property under study. In other words, the vibrational modes can explain the complete microstructure of the complexes, thereby revealing information about the properties that can originate from such chemical environments. When the light interacts with the vibrational compound (phonons), several interactions are observed. Raman spectroscopy shows the difference in energy in terms of wavenumber between the incident and scattered photons, explaining the shift in vibrations due to polarization observed by the molecule during the

interaction, making it a good method for chemical analysis. It depends upon the masses of the constituent atoms and the strength of their bond. On the other hand, infrared (IR) spectroscopy helps to find the wavenumber at which the vibrational mode is observed instead of the shift in vibration. IR spectroscopy reveals information about the changes in the dipole moment or charge distribution during the interaction, again helping us to study the chemical environment. Raman and IR wavenumbers are the characteristic property of a specific compound that is vibrating as a whole. Wavenumber in vibrational spectra often have multiple bonds involved, so, it becomes necessary to study in the complex compound in detail to understand its crystal structure completely.

Dias *et al* [9] have experimentally reported some Raman and IR wavenumbers for the $\text{Ba}_2\text{MgTeO}_6$ compound. But to the best of our literature survey, no theoretical calculations for optical phonon modes for $\text{Ba}_2\text{MgTeO}_6$ have been found. As a result, we used normal coordinate analysis to investigate the lattice dynamics of double-perovskite $\text{Ba}_2\text{MgTeO}_6$ compounds. In order to find the impact of interatomic forces on the vibrational modes, the potential energy distribution (PED) for tellurium-based compound $\text{Ba}_2\text{MgTeO}_6$ has also been investigated in this study.

2. Structure

Dias *et al* [9] have studied the microstructure, vibrational modes and microwave dielectric properties of tellurium-based $\text{Ba}_2\text{MgTeO}_6$ double-perovskite compound using the X-ray diffraction, Raman scattering and IR reflectivity spectra. The tellurium ion (Te^{6+}) is p-block element that can be intensely stabilized in the B-site of perovskite structure. The perovskites of general formula $\text{A}_2\text{B}'\text{B}''\text{O}_6$ type compounds are expected to be found in $\text{Fm}\bar{3}\text{m}$ cubic symmetry (No. 225). But according to the investigation of Dias *et al* [9], for $\text{Ba}_2\text{MgTeO}_6$ compound, $\text{Fm}\bar{3}\text{m}$ cubic symmetry is not suitable because of the splitting of (400) and (620) peaks. So lower symmetry is more believable for these materials. According to this investigation they have reported that this Te-based $\text{Ba}_2\text{MgTeO}_6$ compound belongs to the tetragonal I4/m space group [9].

The tetragonal structure of the compound $\text{Ba}_2\text{MgTeO}_6$ with space group I4/m (No. 87-C_{4h}^5) is shown in figure 1, obtained by using diamond software [10]. In this structure, barium (Ba) occupies the 4d (0.00,0.50,0.25), oxygen O_1 and oxygen O_2 atoms occupy the 4e (0,0, z), 8h (x, y, 0) Wyckoff sites, whereas tellurium (Te) and magnesium (Mg) atoms occupy the octahedral sites 2b (0,0,0.5) and 2a (0,0,0) respectively. The lattice parameters of the tetragonal $\text{Ba}_2\text{MgTeO}_6$ are $a = 5.6195$ (Å), $b = 5.6195$ (Å) and $c = 7.9530$ (Å) [11]. The atomic positions, Wyckoff positions and the contribution in phonons for the $\text{Ba}_2\text{MgTeO}_6$ compound at the Γ point are given in table 1 [11].

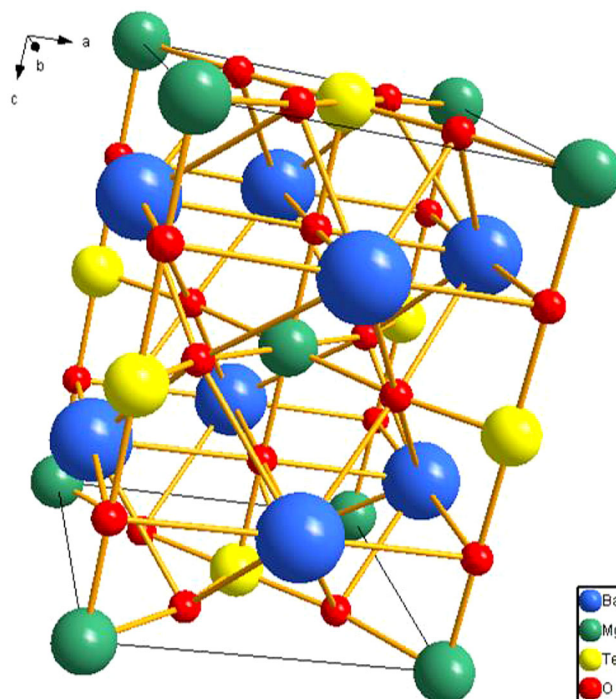


Figure 1. Structure of compound $\text{Ba}_2\text{MgTeO}_6$.

The irreducible representation of $\text{Ba}_2\text{MgTeO}_6$ compound with the space group I4/m is

$$\Gamma_{\text{total}} = 3A_g + 3B_g + 6E_g + 5A_u + 1B_u + 12E_u$$

Out of these 30 modes, $1A_u + 2E_u$ are acoustical modes and the rest 27 modes are the optical active modes, which are represented by equation as given below

$$\Gamma_{\text{optical}} = 3A_g + 3B_g + 6E_g + 4A_u + 1B_u + 10E_u$$

Here, the Raman modes are $3A_g$, $3B_g$ and $6E_g$, while $4A_u$, $1B_u$ and $10E_u$ are the IR modes. A_g and B_g are non-degenerate and E_g are double degenerate modes.

3. Theory

It is necessary to calculate the Eigenvalue equation using Wilson's GF matrix approach to get the normal vibrations' frequency, which involves the kinetic and potential energy of the system [12]. The equation of the system is given as

$$|FG - E\lambda| = 0,$$

where F is represented by H_i and K_i force constants (the bending and stretching, respectively) associated with the potential energies of vibrations, E is the unit matrix, G the kinetic energy matrix that involves the masses and λ gives the frequency ν into the equation by the relation

$$\lambda = 4\pi^2 c^2 \nu^2$$

Here c is velocity of light and ν the wavenumber [13,14].

Table 1. Wyckoff sites, atomic coordinate and the phonon contribution for $\text{Ba}_2\text{MgTeO}_6$ in $I4/m$ phase [11].

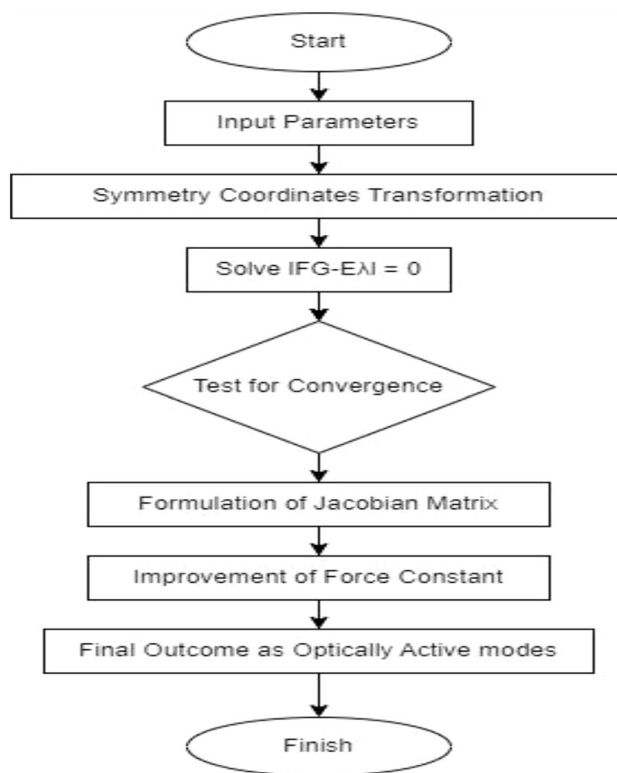
Atoms	Sites	x	y	z	Phonon contribution at Γ point
Ba	4d	0.000	0.500	0.250	$B_g + E_g + A_u + E_u$
Mg	2a	0.000	0.000	0.000	$A_u + E_u$
Te	2b	0.000	0.000	0.500	$A_u + E_u$
O1	4e	0.000	0.000	0.247	$A_g + E_g + A_u + E_u$
O2	8h	0.237	0.302	0.000	$2A_g + 2B_g + E_g + A_u + B_u + 2E_u$

The matrix F was constructed using SRFCM (short-range force constant model). This short-range force acts up to certain neighbors only. The Hook law are obeyed by the stretching vibrational forces between the various atoms. The main role plays due to the stretching forces along with the bending vibrational forces to calculate the transverse vibrations in the lattice. A comparison of the triangle in equilibrium position and the projection of the distorted triangle into the equilibrium plane can be used to compute the change in angle of a triangle.

The potential energy includes short-range stretching forces between Te-O_1 , Te-O_2 , Mg-O_1 , Mg-O_2 , Ba-O_1 , Ba-O_2 atoms, and bending forces between $\text{O}_1\text{-Ba-O}_2$ atoms. The input variables are the lattice parameters, atomic masses, and the symmetry coordinates are used for the measurement. The short-range stretching and bending force constants are optimized to give the nearly match between the experimental and the calculated Raman and IR wavenumber. The flowchart of the optimization is given in figure 2 [15]. Table 2 contains the calculated normalized symmetry coordinates for the Raman and the IR vibrational modes at the zone centre. The interatomic force constant values with coordination for the compounds of double-perovskite oxides $\text{Ba}_2\text{MgTeO}_6$ with the space group $I4/m$ are presented in table 3.

4. Results and discussion

With the help of the force constants, listed in table 3, the Raman and IR phonon modes have been obtained in this study. The present theoretically calculated results of Raman and IR wavenumber have been compared with the available experimentally observed vibrational mode frequencies by Dias *et al* [9], which have been reported in table 4. As per our literature survey, no other experimental and theoretical data was available for $\text{Ba}_2\text{MgTeO}_6$ with space group $I4/m$ for better comparison. PED has also been reported here for each vibrational mode to determine the contribution of various force constants to various frequencies. The interpretation inferred from the PED is mentioned below.

**Figure 2.** Flowchart for a computational program.

It has been obtained from the PED that the vibrations of BaO_6 octahedra are responsible for these higher frequencies, i.e., 800.5 cm^{-1} of A_g , 772.4 cm^{-1} of A_u , 662.5 cm^{-1} of B_g and 697.9 cm^{-1} of E_u mode. The stretching force constant Te-O_1 is the dominant factor in the frequencies 505.0 cm^{-1} of A_g and 403.1 cm^{-1} of A_u . The bending force constant $\text{O}_1\text{-Ba-O}_2$ also contributes to the frequencies 373.5 cm^{-1} of E_u , 363.7 cm^{-1} of E_g and 287.4 cm^{-1} of B_g , 212.6 cm^{-1} of B_u . The stretching force constant Ba-O_2 and Te-O_2 dominate in the wavenumber 177.6 cm^{-1} of E_g , 164.4 cm^{-1} of E_u and 175.6 cm^{-1} of A_u . The force constant Ba-O_1 plays an important role in the frequencies 199.0 cm^{-1} of A_g , 135.1 cm^{-1} of B_g , 95.8 cm^{-1} of E_g , and 91.5 cm^{-1} of A_u and 68.1 cm^{-1} of E_u . In the frequency 68.1 cm^{-1} of E_u , the value of stretching force constant

Table 2. Symmetry coordinates for Ba₂MgTeO₆ in I4/m structure.

Species	Symmetry coordinates
A _g	2O1 _{1x} - 2O1 _{2x} - 2O1 _{3y} + 2O1 _{4y}
	2O1 _{1y} - 2O1 _{2y} + 2O1 _{3x} - 2O1 _{4x}
	4(O2 _{1z} - O2 _{2z})
B _g	2(O1 _{1x} - O1 _{2x} + O1 _{3y} - O1 _{4y})
	2(O1 _{1y} - O1 _{2y} - O1 _{3x} + O1 _{4x})
	4(Ba _{1z} - Ba _{2z})
E _g	4(Ba _{1x} - Ba _{2x})
	4(Ba _{1y} - Ba _{2y})
	4(O1 _{1z} - O1 _{2z})
	4(O1 _{3z} - O1 _{4z})
	4(O2 _{1x} - O2 _{2x})
	4(O2 _{1y} - O2 _{2y})
	4(O2 _{1z} - O2 _{2z})
A _u	4(Ba _{1z} + Ba _{2z})
	8Mg _{1z}
	8Te _{1z}
	2(O1 _{1z} + O1 _{2z} + O1 _{3z} + O1 _{4z})
	4(O2 _{1z} + O2 _{2z})
B _u	2(O1 _{1z} + O1 _{2z} - O1 _{3z} - O1 _{4z})
	4(Ba _{1x} + Ba _{2x})
E _u	4(Ba _{1y} + Ba _{2y})
	8Mg _{1x}
	8Mg _{1y}
	8Te _{1x}
	8Te _{1y}
	4(O1 _{1x} + O1 _{2x})
	4(O1 _{1y} + O1 _{2y})
	4(O1 _{3x} + O1 _{4x})
	4(O1 _{3y} + O1 _{4y})
	4(O2 _{1x} + O2 _{2x})
	4(O2 _{1y} + O2 _{2y})

Table 3. For the compound Ba₂MgTeO₆, interatomic force constant (in N cm⁻¹) values with coordination number in tetragonal structure with space group I4/m.

Force constant	Between atoms	Coordination number	Distt./ angle Å/(°)	Force constants values
K ₁	Te-O ₁	4	1.8499	2.169
K ₂	Mg-O ₂	2	1.9644	1.523
K ₃	Te-O ₂	2	2.0121	0.474
K ₄	Mg-O ₁	4	2.1573	0.470
K ₅	Ba-O ₁	8	2.6391	0.163
K ₆	Ba-O ₂	8	2.8099	0.160
H ₁	O ₁ -Ba-O ₂	8	120.732	0.005
H ₂	O ₁ -Ba-O ₂	8	114.531	0.900

Ba-O₂ are very small but cannot be ignored because this stretching force constant K₅ plays a significant role.

Table 4. Present calculations of Raman and IR zone center vibration modes and the experimentally available modes (in cm⁻¹) for the Ba₂MgTeO₆ compound [9].

Species	Observed wavenumber by Dias <i>et al</i> [9]	Presently calculated wavenumber	Two dominant contributions
A _{g1}	794.4	800.5	H ₂ - 65%, K ₂ - 14%
A _{g2}	544.5	505	K ₁ - 56%, K ₂ - 23%
A _{g3}	149.3	199	K ₅ - 35%, K ₂ - 23%
B _{g1}	724.2, 737.2	662.5	H ₂ - 45%, K ₁ - 45%
B _{g2}	—	287.4	H ₂ - 52%, K ₁ - 41%
B _{g3}	127.9	135.1	K ₅ - 89%, K ₄ - 08%
E _{g1}	412.9	363.7	H ₂ - 84%, K ₆ - 12%
E _{g2}	131.8	177.6	K ₆ - 60%, K ₅ - 37%
E _{g3}	100	95.8	K ₅ - 56%, K ₆ - 26%
A _{u1}	718.4	772.4	K ₂ - 49% H ₂ - 43%,
A _{u2}	475.4, 489.4	403.1	K ₂ - 49%, H ₂ - 45%
A _{u3}	180.1	175.6	K ₃ - 57%, K ₅ - 40%
A _{u4}	—	91.5	K ₅ - 56%, K ₃ - 34%
B _u	333.3	212.6	H ₂ - 56%, K ₅ - 43%
E _{u1}	632.6, 652.4	697.9	K ₁ - 47%, H ₂ - 41%
E _{u2}	433.8	373.5	H ₂ - 46%, K ₁ - 36%
E _{u3}	285	258.3	K ₄ - 83%, K ₁ - 13%
E _{u4}	—	164.4	K ₆ - 61%, K ₅ - 31%
E _{u5}	—	68.1	K ₅ - 60%, K ₆ - 23%

5. Conclusion

To calculate the Raman and IR phonons of the double-perovskite oxide, Ba₂MgTeO₆, the short-range force constant model has been used with six stretching and two bending force constants. As per our literature survey, a few experimental studies and no theoretical calculations on Raman and IR wavenumbers are available for Ba₂MgTeO₆ oxides in tetragonal I4/m phase. Also, some of the phonon modes for Ba₂MgTeO₆ compounds in I4/m phase are not reported in the literature. So, we have tried to provide all the vibrational phonon modes of the Ba₂MgTeO₆ compound with mode assignments with the help of normal coordinate analysis method in this study. The PED has also been studied in order to find the impact of interatomic forces on the calculated Raman and IR phonons.

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