

Optical-active phonons in $A_3Fe_2B''O_9$ ($A=Ca, Sr$; $B''=Te, W$) double perovskites

E. N. Silva,^{1,a)} I. Guedes,² A. P. Ayala,² C. A. López,³ M. S. Augsburger,³ M. del C. Viola,³ and J. C. Pedregosa³

¹Departamento de Física, Universidade Federal do Maranhão, 65085-580, São Luis-MA-Brazil

²Departamento de Física, Universidade Federal do Ceará, Caixa Postal 6030, 60475-970, Fortaleza, Ceará, Brazil

³Área de Química General e Inorgánica "Dr. G. F. Puelles," Departamento de Química, Facultad de Química, Bioquímica y Farmacia, Universidad Nacional de San Luis, San Luis, Argentina

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Raman scattering and infrared transmittance techniques are used to investigate the phonons of the $Sr_3Fe_2TeO_9$ (SFTO), $Sr_3Fe_2WO_9$ (SFWO), and $Ca_3Fe_2WO_9$ (CFWO) double perovskites at 300 K. While SFTO and SFWO crystallize in a tetragonal structure belonging to the $I4/m$ space with two formulas per unit cell ($Z=2$), CFWO crystallizes in a monoclinic structure belonging to the space group $P2_1/n$ with $Z=2$. The observed spectra are very similar to that of the prototype cubic ($Fm\bar{3}m$) double perovskite, indicating that both the tetragonal and monoclinic structures result from small distortions of the cubic cell. The assignment of the optical phonons follows that given for the prototype $Fm\bar{3}m$ double perovskites. © 2010 American Institute of Physics.

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I. INTRODUCTION

Ideal ABO_3 perovskites crystallize in the cubic $Pm\bar{3}m$ structure, exhibiting no active first-order Raman phonons. By doping the B symmetry sites the new stoichiometry reads $AB'_{1-x}B''_xX_3$. If either the charge or the size of the B' and B'' cations are sufficiently different, an ordering at B symmetry sites may occur and the compound is commonly described as a double perovskite, whose stoichiometry is now properly written as $A_2B'B''X_6$. This structure can be described as a regular arrangement of corner-sharing $B'O_6$ and $B''O_6$ alternating along the three crystallographic directions of the compound.

Both the ordered or disordered double perovskites exhibit interesting physical properties such as: superconductivity, magnetoresistivity, ferroelectricity, piezoelectricity, electron-phonon interactions, etc.¹⁻⁹ Recently, the x-ray absorption and synchrotron radiation diffraction techniques were used to investigate the degree of disorder in polycrystalline Sr_2FeMoO_6 samples.¹⁰ It was observed, a very high degree of short range ordering even for samples presenting highly reduced long range chemical ordering.

The 1:1 ordering at B-site is the most common ordering arrangement. Recently, Howard *et al.*¹¹ used the group theory method to enumerate the 12 different $A_2B'B''X_6$ structures which are compatible with all the possible octahedral tiltings.

The highest symmetry phase is cubic belonging to the $Fm\bar{3}m$ space group, whose optical-active phonon distribution is $A_{1g}+E_g+2F_{2g}+4F_{1u}$. Small changes in the tilting of the BO_6 octahedra lead to either a tetragonal or monoclinic distortion, as observed for $Sr_2[Co]^{2a}[Mo]^{2b}O_6$ (Ref. 12) and $Ca_2[Co]^{2c}[Te]^{2d}O_6$,¹³ respectively.

Besides the 1:1 ordering at the B-sites, other orderings are also possible. For instance, the 2:1 ordering leads to the stoichiometry $A_3B'B''X_9$. This is the case for $A_3CaRu_2O_9$ ($A=Sr$ and Ba)^{14,15} and $Ba_3ZnTa_2O_9$,¹⁶ whose crystal structures are described by a trigonal system belonging to the $P\bar{3}m1$ space group, where the B' and B'' cations are located at the Wyckoff's 1b and 2d positions, respectively. In this case, there is no occupational disorder at the octahedral symmetry sites.

However, some $A_3B_2B''X_9$ perovskites exhibit a 1:1 ordering at B'' -sites. In this case, an intrinsic occupational disorder is observed and the stoichiometry is better described as $A_2B'(B'_{1/3}B''_{2/3})O_6$. If the B' -sites are also disorderly occupied the stoichiometry reads $A_2(B'_{1-x}B''_x)(B'_{1/3+x}B''_{2/3-x})O_6$.

Raman and infrared spectroscopy provide valuable insight into order-disorder phenomena and are very sensitive to sample composition and structural variations, making it suitable for studying the effects of atomic substitutions in complex perovskites.¹⁷⁻²¹

There has been an increasing interest in the study of $A_3Fe_2B''O_9$ ($A=Ca, Sr$; $B''=Te, W$) double perovskites, which exhibit exciting ferromagnetic properties at room temperature.²⁻⁷ The $Sr_3Fe_2WO_9$ (SFWO) and $Ca_3Fe_2WO_9$ (CFWO) compounds have been investigated by neutron powder diffraction by Ivanov *et al.*,^{2,3} who determined that SFWO crystallizes at 300 K in a tetragonal structure belonging to the space group $I4/m$, while CFWO crystallizes in a monoclinic structure belonging to the space group $P2_1/n$. Identical results have been obtained for CFWO by Retuerto *et al.*²² These compounds exhibit a partially ordered double perovskite structures, in which the Fe and W cations are orderly distributed at the B' - and B'' -symmetry sites of the perovskite lattice. For SFWO (CFWO), the occupation of the 2a-site is $0.79Fe(1)^{3+}+0.21W(1)^{6+}$ [$0.73Fe(1)^{3+}$

^{a)}Electronic mail: silvaen@gmail.com. Tel.: 2109-8204. FAX: 2109-8204.

+0.21W(1)⁶⁺], while the occupation of the 2*b*-sites is 0.54Fe(2)³⁺+0.46W(2)⁶⁺ (0.60Fe(2)³⁺+0.40W(2)⁶⁺). So, it is more convenient to rewrite the stoichiometry of these compounds as Sr₂[Fe_{0.79}W_{0.21}]^{2a}[Fe_{0.54}W_{0.46}]^{2b}O₆ and Ca₂[Fe_{0.73}W_{0.27}]^{2a}[Fe_{0.60}W_{0.40}]^{2b}O₆ for SFWO and CFWO, respectively, where the superscripts stand for the Wyckoff's site symmetries.^{2,3} According to Augsburg *et al.*⁵ and Viola⁶ the Te-based compound, Sr₃Fe₂TeO₉ (SFTO), also exhibits a tetragonal structure belonging to the space group *I4/m*. In this case, the stoichiometry reads Sr₂[Fe_{0.57}Te_{0.43}]^{2a}[Fe_{0.90}Te_{0.10}]^{2b}O₆. On the other hand Ivanov *et al.*⁴ observed a minor cationic ordering with formula Sr₂[Fe_{0.72}Te_{0.28}]^{2a}[Fe_{0.61}Te_{0.39}]^{2b}O₆.

In order to understand the degree of disorder of A₃Fe₂B''O₉ (A=Ca, Sr; B''=Te, W) compounds here we use the Raman scattering and infrared (IR) transmittance techniques to record their room-temperature vibration spectra. The assignment proposed is based on that given for double perovskites with *Fm* $\bar{3}$ *m* symmetry.

II. EXPERIMENTAL

Samples of SFWO, SFTO, and CFWO were prepared as polycrystalline powders by solid state reaction following the procedure described elsewhere.²⁻⁶ The phase identification and characterization of the samples were carried out by x-ray powder diffraction (XRPD) (Cu *K* α =1.5418 Å) using a Rigaku D-MAX-IIIC diffractometer. Minor traces (<1%) of parasitic phases were found. It was verified that the samples exhibit lower symmetry crystalline space groups derived from the prototype *Fm* $\bar{3}$ *m* double perovskite structure. The good agreement between the observed and calculated XRPD patterns is shown in Fig. 1. This superstructure is associated with the doubling of the lattice parameter due to the 1:1

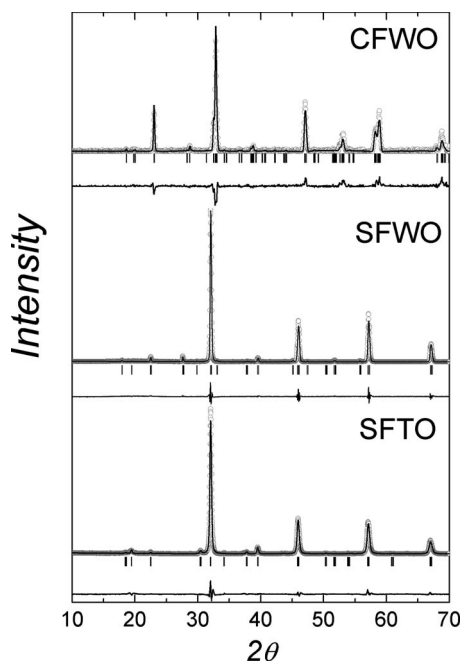


FIG. 1. Room-temperature XRPD patterns of the A₃Fe₂WO₉ (A=Sr, Ca) and SFTO double perovskites. Observed (circles), calculated (full line), and difference (bottom) profiles after refinement.

TABLE I. Crystallographic data of SFTO, SFWO, and CFWO. The 2a (000) and 2b (001/2) [2a (1/201/2) and 2b (1/200)] subscripts refer to Wyckoff's site symmetries for tetragonal [monoclinic] structures, while *eq* and *ap* subscripts refer to equatorial and apical oxygen atoms, respectively.

	SFTO (<i>I4/m</i>) ^a	SFWO (<i>I4/m</i>) ^b	CFWO (<i>P2₁/n</i>) ^c
a(Å)	5.5590	5.5784	5.4171
b(Å)	5.5590	5.5784	5.5084
c(Å)	7.8850	7.8659	7.7002
β (deg)	90.000	90.000	90.029
ϕ [001](°)	4.5	5	13
ψ [110](°)	0	0	13
V(Å ³)	246	245	230
$\langle A-O \rangle_{eq}$ (Å)	2.786	2.788	2.764
$\langle A-O \rangle_{ap}$ (Å)	2.780	2.789	2.755
$\langle (Fe/B'')_{2a-O} \rangle_{eq}$ (Å)	1.983	1.988	2.000
$\langle (Fe/B'')_{2a-O} \rangle_{ap}$ (Å)	1.908	1.927	1.984
$\Delta d_{2a} (\times 10^{-5})$	37	24	2.25
$\langle (Fe/B'')_{2b-O} \rangle_{eq}$ (Å)	1.960	1.972	1.974
$\langle (Fe/B'')_{2b-O} \rangle_{ap}$ (Å)	2.034	2.006	1.970
$\Delta d_{2b} (\times 10^{-5})$	35	7.21	1.28

^aReference 11.

^bReference 9.

^cReference 15.

order of the B cations. The crystallographic data are shown in Table I. The monoclinic space group *P2₁/n* requires that the Fe(1)/W(1) and Fe(2)/W(2) octahedra have different tilt angles due to the difference in the size and distortion of each polyhedron. ϕ and ψ denotes the rotation around the [001] and [110] axes, respectively. The octahedron was quantified using the distortion index²³

$$\Delta d = \frac{1}{6} \sum_{n=1}^6 \left(\frac{d_n}{\bar{d}} - 1 \right)^2, \quad (1)$$

where, d_n and \bar{d} are the individual and average B''-O bond distances, respectively.

The IR transmission spectra were recorded between 2000 and 250 cm⁻¹ with a Nicolet Protège 460 Fourier transform infrared (FTIR) spectrometer with 32 scans, using the KBr pellet technique. The spectral resolution was ± 4 cm⁻¹. All measurements were performed at room temperature.

The Raman spectra were recorded on a Jobin-Yvon T64000 triple-spectrometer instrument equipped with a N₂-cooled charge coupled device. The spectra were taken in the backscattering configuration using a microscope equipped with a long working distance objective (20 \times , 20 mm) and the 514.5 nm emission line of an Ar⁺ laser (Innova 70, Coherent Inc.). The laser power on the sample surface was less than 50 mW. The spectral slit widths were set for yielding a spectral resolution of 2 cm⁻¹. All measurements were performed at room temperature.

III. RESULTS AND DISCUSSION

According to the crystallographic data both SFWO and SFTO belong to the tetragonal *I4/m* (*Z*=2) space group, whereas CFWO belongs to the monoclinic *P2₁/n* (*Z*=2) space group. The tetragonal *I4/m* structure is derived from

the prototype $Fm\bar{3}m$ cubic structure by an antiphase tilt of the FeO_6 and $\text{B}''\text{O}_6$ octahedra in the basal plane along the $[001]$ direction of the cubic cell. This corresponds to the $a^0a^0c^-$ Glazer's notation as derived by Woodward.²⁴ The monoclinic $P2_1/n$ structure results from an in-phase and antiphase tilts of the FeO_6 and $\text{B}''\text{O}_6$ octahedra along the $[001]$ direction and in the basal plane of the pseudocubic cell, respectively. This corresponds to the $a^-a^-c^+$ Glazer's notation.

As it is reported in Ref. 20, due to the 1:1 order characteristics of the $\text{A}_2\text{B}'^{2+}\text{B}''^{6+}\text{O}_6$ double perovskites, which intercalates strongly $\text{B}''^{6+}\text{O}_6$ and weakly $\text{B}'^{2+}\text{O}_6$ bonded octahedra, only the internal modes of the $\text{B}''^{6+}\text{O}_6$ octahedron have to be considered from a vibrational point of view. This is a very interesting structural arrangement because it allows the investigation of the internal modes of the $\text{B}''^{6+}\text{O}_6$, which in simple and disordered perovskites form a network of corner sharing octahedra. In the case of disordered occupation of the B'' octahedral symmetry sites for two different cations, a strong vibrational coupling between the two different octahedra may occur. Also, their B–O bonds are stronger than those belonging to the 12-coordinated $\text{A}^{2+}\text{–O}$ units. Based on this simple argument, we assume that the octahedra placed at B'' symmetry sites behave approximately as “isolated” groups. In the case of occupational disorder at the B''^{6+} sites, vibrations originating from both octahedra (two-phonon-like behavior^{21,25}) are possible to be observed.

The method of factor group analysis allows us to determine the distribution of the zone-center phonons in the terms of the respective optical-active irreducible representations of C_{2h} and C_{4h} point groups. By considering the internal modes of the $\text{B}''^{6+}\text{O}_6$ octahedron, the following distributions are obtained:²⁰

$$\begin{aligned} \Gamma(I4/m) = & 6T(2A_u + B_g + E_g + 2E_u) + 2L(A_g + E_g) \\ & + \nu_1(A_g) + 2\nu_2(A_g + B_g) + 2\nu_3(A_u + E_u) \\ & + 2\nu_4(A_u + E_u) + 2\nu_5(B_g + E_g) + \nu_6(E_u), \quad (2) \end{aligned}$$

$$\begin{aligned} \Gamma(P2_1/n) = & 21T(3A_g + 8A_u + 3B_g + 7B_u) + 6L(3A_g \\ & + 3B_g) + 2\nu_1(A_g + B_g) + 4\nu_2(2A_g + 2B_g) \\ & + 6\nu_3(3A_u + 3B_u) + 6\nu_4(3A_u + 3B_u) \\ & + 6\nu_5(3A_g + 3B_g) + 6\nu_6(3A_u + 3B_u). \quad (3) \end{aligned}$$

In Eqs. (2) and (3), ν_1 , ν_2 , and ν_3 , are related to the $\text{B}''^{6+}\text{–O}$ stretching modes, and ν_4 , ν_5 , and ν_6 correspond to the $\text{O–B}''^{6+}\text{–O}$ bending modes. T and L are translational and librational lattice modes, respectively. The wavenumber of most of the vibrations was determined for several authors. Liegeois-Ducykaerts and Tarte²⁶ determined that for cubic compounds, the vibrations T , ν_4 , ν_5 , ν_2 , ν_3 , and ν_1 , appear in the following wavenumber ranges, respectively, <350 , $305\text{–}417$, $348\text{–}446$, $470\text{–}608$, $580\text{–}715$, and $716\text{–}847$ cm^{-1} . Lavat and Baran²⁷ determined that for orthorhombic, tetragonal (pseudocubic) and cubic compounds, the vibrations ν_4 and ν_3 , appear in the $265\text{–}454$ and $534\text{–}674$ cm^{-1} wavenumber range, respectively. Ayala *et al.*²⁰ reported that for

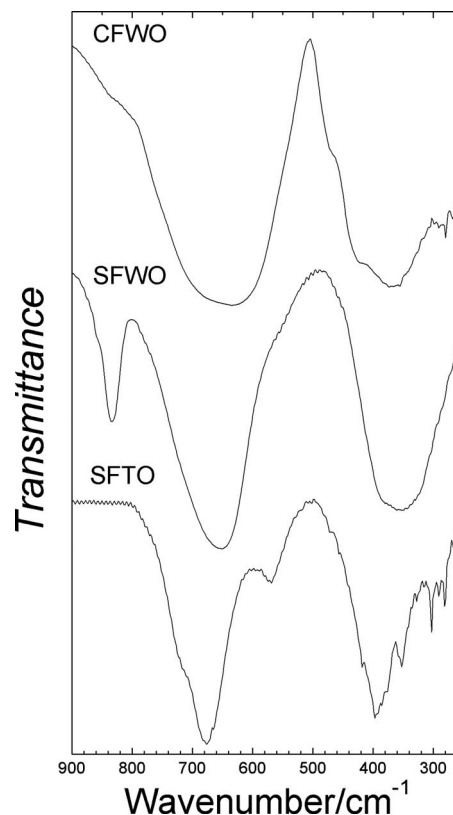


FIG. 2. Room-temperature FTIR spectra of the $\text{A}_3\text{Fe}_2\text{WO}_9$ ($\text{A}=\text{Sr}, \text{Ca}$) and SFTO double perovskites.

monoclinic and tetragonal compounds, the Raman-active librational modes are in the wavenumber range $190\text{–}310$ cm^{-1} .

Figure 2 shows, from bottom to top the IR transmittance spectra of SFTO, SFWO and CFWO, respectively. They are very similar to those exhibited by cubic $Fm\bar{3}m$ perovskites. This is due to the fact that the tetragonal and monoclinic distortions are very small as shown in Table I.

In Ref. 21, we obtained the IR spectra of the cubic $\text{Ba}_3\text{In}_2\text{UO}_9$ (BIUO) and $\text{Ba}_3\text{In}_2\text{WO}_9$ (BIWO) perovskites. They consist of three strong IR bands at 293, 371, and 603 cm^{-1} for BIUO and at 299, 360, and 653 cm^{-1} for BIWO. Following the assignment given in Ref. 21, the bands at 293 (299), 371(360), and 603(653) cm^{-1} for BIUO (BIWO) were assigned to the translational, ν_4 and ν_3 modes of the $\text{B}''^{6+}\text{O}_6$ octahedron. Here, we observe two strong absorption bands between $300\text{–}400$ cm^{-1} and $600\text{–}700$ cm^{-1} corresponding to the ν_4 and ν_3 modes, respectively.

For SFTO, these bands split at least in two narrower components ($2\nu_4$ and $2\nu_3$). This is in agreement with the group theory analysis for the tetragonal $I4/m$ space group [see Eq. (2)]. The reason why we do not observe similar splitting for SFWO can be related to the degree of octahedral distortion given by Eq. (1). From Table I, we observe that the SFTO exhibits the largest octahedral distortion (Δd). The band appearing at 565 cm^{-1} may result from either combination ($280+290$ cm^{-1}) or overtones ($\sim 2 \times 280$ and $\sim 2 \times 290$ cm^{-1}) of the condensed lattice modes.

In the IR spectra of SFWO and CFWO an additional band around 830 cm^{-1} is observed. This band is probably

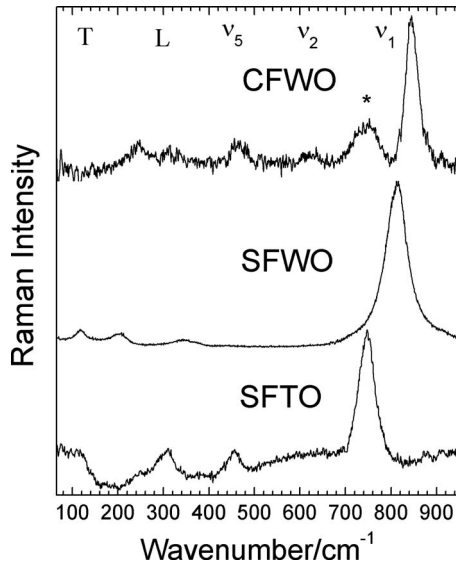


FIG. 3. Room-temperature Raman spectra of the $A_3Fe_2WO_9$ ($A=Sr, Ca$) and SFTO double perovskites. The asterisk shows $Fe(III)O_6$ stretching induced by the occupational disorder.

due to the WO_6 symmetric stretching (ν_1) mode which is very intense in the Raman spectrum, as can be seen in Fig. 3. The appearance of these unexpected bands is likely to be related with a disordered-induced local symmetry lowering, which gives rise to a local loss of the inversion center and allows the ν_1 Raman-active mode to become IR-active.

Figure 3 shows, from bottom to top, the unpolarized Raman spectra of SFTO, SFWO, and CFWO, respectively. They are also very similar to those exhibited by the cubic $Fm\bar{3}m$ perovskites. The Raman-active phonons of cubic $Fm\bar{3}m$ perovskites are $A_{1g}(\nu_1)+E_g(\nu_2)+2F_{2g}(T, \nu_5)$. The

highest wavenumber appearing in the Raman spectrum ($\nu > 700 \text{ cm}^{-1}$) is assigned to ν_1 , that appearing in the range of $470\text{--}650 \text{ cm}^{-1}$ is assigned to ν_2 , that appearing in the range of $350\text{--}450 \text{ cm}^{-1}$ is assigned to ν_5 , and that appearing in the range of $100\text{--}150 \text{ cm}^{-1}$ is assigned to T . However, the ν_2 mode is missing in most of cubic double perovskites studied in Ref. 20. In Ref. 20 we obtained the Raman spectra of tetragonal and monoclinic $A_2B''^{6+}B''^{6+}O_6$ double perovskites. They also resemble those of cubic $Fm\bar{3}m$ perovskites. This evidences that the tetragonal, orthorhombic, and even monoclinic structures result from very small distortions of the cubic cell. Taking into account the discussion presented in Refs. 20, 21, 26, and 27, we list in Table II the Raman and IR wavenumbers as well as their tentative assignment.

The Raman spectrum for monoclinic CFWO presents a band at around 760 cm^{-1} . Since the CFWO exhibits an intrinsic occupational disorder at $2b$ symmetry sites ($Ca_2[Fe_{0.73}W_{0.27}]^{2a}[Fe_{0.60}W_{0.40}]^{2b}O_6$), this band is likely to be related to the ν_1 vibration of the FeO_6 octahedron, evidencing a two-phonon-like behavior.^{21,25} The $\nu_1(FeO_6)$ vibration has been observed at around 710 cm^{-1} for $CaFeO_3$ and $La_{0.33}Sr_{0.67}FeO_3$ compounds, as reported by Ghosh *et al.*²⁸

We observe that the difference between the ν_1 vibration of SFWO and SFTO is approximately 65 cm^{-1} . Such a difference is related to the chemical nature of hexavalent Te or W cations. While the Te^{6+} cation has a fully occupied d^{10} orbital configuration, the W^{6+} cation has a d^0 orbital configuration. So, the increase in the wavenumber of the ν_1 vibration is correlated with increase of the force constant of the $B''^{6+}\text{--}O$ bond due to the overlapping of t_{2g} orbitals of W^{6+} cation.^{20,26}

TABLE II. Optical phonons (in cm^{-1}) of SFTO, CFWO, and SFWO.

SFTO ($I4/m$)		SFWO ($I4/m$)		CFWO ($P2_1/n$)		Assign.
Raman	IR	Raman	IR	Raman	IR	
746		815		844		ν_1
	720		651		632	ν_3
	676s					ν_3
...		...		620		ν_2
454		...		465		ν_5
	397s		352		460	ν_4
	352				421	ν_4
					372s	ν_4
		370				Lattice
		344				Lattice
				320		Lattice
309						Lattice
	300					Lattice
	290					Lattice
	280			274	279	Lattice
					267	Lattice
254			255		254	Lattice
			238	245	242	Lattice
		205				Lattice
...		117		...		Lattice

IV. CONCLUSIONS

In this investigation, the IR and Raman spectra of a series of complex double perovskites of the type $A_3Fe_2B''O_9$ have been recorded and analyzed. Typical internal modes are observed, two (ν_3 and ν_4) IR and three (ν_1 , ν_2 , and ν_5) Raman modes. Observation of fewer modes than formally predicted by Eqs. (2) and (3) evidences the fact that both the tetragonal and monoclinic structures result from small distortion of the prototype $Fm\bar{3}m$ cubic structure. The presence of a ν_1 -like vibration of the FeO_6 octahedron reflects the occurrence of a two-phonon-like behavior due to the intrinsic occupational disorder at octahedral symmetry sites.

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