

Lattice Dynamical Calculations for $\text{Li}_{1+x}\text{Ti}_{2-x}\text{O}_4$ ($x = 0.33$) and $\text{Li}_{1-y}\text{Mg}_y\text{Ti}_2\text{O}_4$ ($y = 0.1, 0.3$)

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Zone-centre Raman and infrared phonon frequencies for the spinel phases of oxides $\text{Li}_{1+x}\text{Ti}_{2-x}\text{O}_4$ ($x = 0.33$) and $\text{Li}_{1-y}\text{Mg}_y\text{Ti}_2\text{O}_4$ ($y = 0.1, 0.3$) of space group $Fd3m$ have been calculated using a proposed short-range force constant model. In this model, the lattice potential energy is expanded using Taylor's expansion in the harmonic approximation. The calculated zone-centre phonon frequencies are in good agreement with the available experimental and previously calculated results.

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1. Introduction

Among large number of solids, spinel structure compounds AB_2C_4 are of technological and geological interest due to presence of large number of vacancies in this structure. Among large number of spinels, only few spinels shows superconductivity behavior, such as LiTi_2O_4 , show superconducting behavior with a transition temperature $T_c = 13$ K [1]. On insertion of Li in LiTi_2O_4 the compound $\text{Li}_{1+x}\text{Ti}_{2-x}\text{O}_4$ shows a homogeneity range for $0 \leq x \leq 1.5$. The superconducting properties disappear and the compound shows insulating behavior at $x = 0.33$ [2, 3].

In recent years many studies have been done to study the zone-centre phonon frequencies for $\text{Li}_{1+x}\text{Ti}_{2-x}\text{O}_4$ ($x = 0, 0.33$) and $\text{Li}_{1-y}\text{Mg}_y\text{Ti}_2\text{O}_4$ ($y = 0, 0.1, 0.3$) [4–7]. Gupta and Ashdhir [4] have calculated the zone-centre phonon frequencies for LiTi_2O_4 and Sinha and Gupta [5] have calculated zone-centre phonon frequencies for $\text{Li}_{1+x}\text{Ti}_{2-x}\text{O}_4$ ($x = 0, 0.33$) and $\text{Li}_{1-y}\text{Mg}_y\text{Ti}_2\text{O}_4$ ($y = 0, 0.1, 0.3$) using de-Launay type short-range force constant model. In this model they have calculated only three bond-stretching force constants for the above said compounds and using these three bond-stretching force constants, zone-centre phonon frequencies are calculated. Recently, Buletsa et al. [6] have calculated the zone-centre phonon frequencies for $\text{Li}_{1+x}\text{Ti}_{2-x}\text{O}_4$ system, by superspace symmetry approach using a short-range force constants model. Very recently, Kushwaha [7] has calculated the zone-centre phonon frequencies for LiTi_2O_4 using six parameter bond-bending force constant model. In this model they have used three bond-stretching and three bond-bending force constants.

In the present paper, we are using a bond-bending force constant model proposed by Kushwaha [7]. Three-bond stretching and three bond-bending force constants are calculated for the compounds $\text{Li}_{1+x}\text{Ti}_{2-x}\text{O}_4$ ($x = 0,$

0.33) and $\text{Li}_{1-y}\text{Mg}_y\text{Ti}_2\text{O}_4$ ($y = 0.1, 0.3$) and then the calculated force constants are used to calculate the zone-centre Raman and infrared phonon frequencies for above compounds.

2. Theory

The crystal of AB_2C_4 classified as HI_1 space group O_h^7 ($Fd3m$) is cubic and consists of a slightly distorted cubic close-packed arrangement of C-ions with the A and B ions occupying 1/8 of the tetrahedral and 1/2 of the octahedral interstices, respectively [8]. There are eight formula units in a unit cell. The C anions are at the 32 sites. The A cations fill the tetrahedral 8a sites and B ions occupy the octahedral 16d sites.

Only two formula units are present in the primitive unit cell. The group theoretical treatment of the optical zone-centre $\Gamma(k=0)$ phonon modes for the spinel structure yields [9–11]:

$$\Gamma(k=0) = A_{1g}(R) + E_g(R) + 2E_u + 2A_{2u} + F_{1g} + 3F_{2g}(R) + 4F_{1u}(IR) + 2F_{2u}, \quad (1)$$

where R and IR correspond to the Raman and infrared-active modes, respectively. Five modes A_{1g} , E_g , $3F_{2g}$ are Raman active and four modes $4F_{1u}$ are infrared active. Rest are Raman inactive F_{1g} and infrared inactive $2A_{2u}$, $2E_u$, and $2F_{2u}$ modes.

In the present paper, the potential energy ϕ of the superconducting spinels can be expanded by using Taylor's series and can be written as

$$\phi = \sum_{lmn} \left\{ \frac{1}{r} \left(\frac{d\phi}{dr} \right) \Big|_{r=|r_k|} \left[r_{lmn}^0 (S_{lmn} - S_0) + \frac{1}{2} |S_{lmn} - S_0|^2 \right] + \frac{1}{2} \left[\frac{1}{r} \frac{d}{dr} \left(\frac{1}{r} \frac{d\phi}{dr} \right) \right] \Big|_{r=|r_k|} \times [r_{lmn}^0 (S_{lmn} - S_0)]^2 \right\}, \quad (2)$$

where S_0 and S_{lmn} are the displacements of the central ion and its first neighbor ions from their equilibrium position r_{lmn}^0 represent the position coordinates of neighboring ions in equilibrium. l, m, n represent the direction

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cosines of the line joining the central ion and nearest neighbor ions. $|r_k|$ is the nearest neighbor distance.

Let A_k be the bond-stretching force constant defined by the second derivative of the potential energy ϕ :

$$\frac{e^2}{V} A_k = \frac{d^2 \phi}{dr^2} \Big|_{|r|=|r_k|} \quad (3)$$

The bond-bending force constant B_k is expressed as the first derivative of the potential energy ϕ :

$$\frac{e^2}{V} B_k = \frac{1}{r} \frac{d\phi}{dr} \Big|_{|r|=|r_k|} \quad (4)$$

Here $k = 1, 2, 3$ for first, second, and third neighbors.

3. Results and discussion

In the present paper, let $A_1, A_2,$ and A_3 be the bond-stretching and $B_1, B_2,$ and B_3 be the bond-bending interactions between Li-O (tetrahedral), Ti-O (octahedral) and O-O ions, respectively. The bond-stretching and bond-bending force constants for LiTi_2O_4 are taken from the literature [7]. Taking the values of force constants for LiTi_2O_4 from [7] and the force constants for the compounds $\text{Li}_{1+x}\text{Ti}_{2-x}\text{O}_4$ ($x = 0.33$) and

$\text{Li}_{1-y}\text{Mg}_y\text{Ti}_2\text{O}_4$ ($y = 0.1, 0.3$) are calculated with the assumption that the linear variation of mass with composition x :

$$\begin{aligned} m^\circ(\text{Li}_{1+x}\text{Ti}_{2-x}\text{O}_4) &= (1-x)m^\circ(\text{LiTi}_2\text{O}_4) \\ &+ xm^\circ(\text{Li}_3\text{O}_4) \quad \text{for } x = 0.33, \\ m^t(\text{Li}_{1-x}\text{Mg}_x\text{Ti}_2\text{O}_4) &= (1-x)m^t(\text{LiTi}_2\text{O}_4) \\ &+ xm^t(\text{MgTi}_2\text{O}_4) \quad \text{for } x = 0.1, 0.3, \end{aligned}$$

where m° and m^t are the masses of atoms of corresponding systems in octahedral and tetrahedral sites.

The calculated values of three bond-stretching ($A_1, A_2,$ and A_3) and three bond-bending ($B_1, B_2,$ and B_3) force constants for $\text{Li}_{1+x}\text{Ti}_{2-x}\text{O}_4$ ($x = 0.33$) and $\text{Li}_{1-y}\text{Mg}_y\text{Ti}_2\text{O}_4$ ($y = 0.1, 0.3$) are listed in Table I along with the force constants for LiTi_2O_4 [7].

Using above force constants, we have calculated the zone-centre phonon frequencies of $\text{Li}_{1+x}\text{Ti}_{2-x}\text{O}_4$ ($x = 0.33$) and $\text{Li}_{1-y}\text{Mg}_y\text{Ti}_2\text{O}_4$ ($y = 0.1, 0.3$) and these are listed in Tables II and III, respectively, along with the experimental results [12, 13] and theoretical results [5, 6] available in the literature.

TABLE I

The values of force constants (kdynes/cm) for $\text{Li}_{1+x}\text{Ti}_{2-x}\text{O}_4$ ($x = 0.33$) and $\text{Li}_{1-y}\text{Mg}_y\text{Ti}_2\text{O}_4$ ($y = 0.1, 0.3$) along with the force constants for LiTi_2O_4 [7].

Force constant	Internal coordinates	LiTi ₂ O ₄ [7]	Present calculation		
			Li _{1.33} Ti _{1.67} O ₄	Li _{0.9} Mg _{0.1} Ti _{2-x} O ₄	Li _{0.7} Mg _{0.3} Ti _{2-x} O ₄
A_1	Li-O	76.50	73.25	89.78	115.38
B_1	Li-O	8.25	5.38	7.32	10.78
A_2	Ti-O	121.95	119.85	122.35	131.81
B_2	Ti-O	12.95	10.28	11.32	13.25
A_3	Ti-Ti (O-O)	18.25	17.9	18.30	9.38
B_3	Ti-Ti (O-O)	1.32	1.49	1.78	0.95

TABLE II

Observed [12] and calculated [7] zone-centre phonon frequencies for LiTi_2O_4 along with the previous results [4-6, 13].

Species	Frequencies [cm^{-1}]				
	Observed	Calculated	Oda et al.	Sinha et al.	Buletsa et al.
A_{1g}	628	628.0	584.1	628.0	628.4
E_g	429	428.6	337.2	429.0	429.3
$F_{2g}(1)$		596.8	687.3	680.5	652.5
$F_{2g}(2)$	494	343.2	516.4	535.4	542.3
$F_{2g}(3)$	339	196.8	288.5	348.4	344.2
$F_{1u}(1)$		695.1	696.3	694.7	668.3
$F_{1u}(2)$		515.3	506.4	513.6	508.5
$F_{1u}(3)$		412.7	389.2	435.2	424.9
$F_{1u}(4)$		247.2	289.0	201.3	210.2
$A_{2u}(1)$		659.2	650.0	665.3	664.5
$A_{2u}(2)$		397.6	459.9	316.8	323.7
$E_u(1)$		581.0	565.0	597.2	603.1
$E_u(2)$		275.3	286.4	229.4	236.7
F_{1g}		413.0	397.9		429.3
$F_{2u}(1)$		493.6	461.0	542.5	542.4
$F_{2u}(2)$		141.2	128.4	159.3	165.0

TABLE III

Calculated zone-centre phonon frequencies for $\text{Li}_{1.33}\text{Ti}_{1.67}\text{O}_4$, $\text{Li}_{0.9}\text{Ti}_{0.1}\text{O}_4$ and $\text{Li}_{0.7}\text{Mg}_{0.3}\text{Ti}_2\text{O}_4$ along with the results of Sinha et al. [12].

Species	Frequencies [cm^{-1}]					
	$\text{Li}_{1.33}\text{Ti}_{1.67}\text{O}_4$		$\text{Li}_{0.9}\text{Ti}_{0.1}\text{O}_4$		$\text{Li}_{0.7}\text{Mg}_{0.3}\text{Ti}_2\text{O}_4$	
	Calculated	Sinha et al.	Calculated	Sinha et al.	Calculated	Sinha et al.
A_{1g}	628.0	628.0	628.0	628.0	628.0	628.0
E_g	429.0	429.0	429.0	429.0	429.0	429.0
$F_{2g}(1)$	618.6	623.0	682.3	683.7	691.2	688.5
$F_{2g}(2)$	530.8	535.5	519.8	521.8	501.2	498.8
$F_{2g}(3)$	320.9	317.5	336.2	334.5	310.8	311.0
$F_{1u}(1)$	659.8	662.3	692.8	700.3	710.4	708.9
$F_{1u}(2)$	545.2	548.2	520.3	518.3	526.9	527.3
$F_{1u}(3)$	432.9	429.6	336.2	334.5	413.8	413.2
$F_{1u}(4)$	232.4	228.9	184.1	185.9	155.0	157.6
$A_{2u}(1)$	693.5	689.3	670.5	667.2	672.2	670.3
$A_{2u}(2)$	375.3	379.8	305.4	307.1	291.8	290.2
$E_u(1)$	635.6	629.1	582.1	589.7	579.5	578.4
$E_u(2)$	277.1	275.7	219.3	217.6	218.2	193.0
$F_{2u}(1)$	580.3	576.2	539.9	543.5	544.0	545.5
$F_{2u}(2)$	201.1	188.7	149.2	150.3	129.8	132.1

The present calculation shows that the inclusion of bond bending force constants gives better results in comparison to the other calculations available in the literature. The present calculation also shows that the potential energy of spinel structure compounds $\text{Li}_{1+x}\text{Ti}_{2-x}\text{O}_4$ ($x = 0.33$) and $\text{Li}_{1-y}\text{Mg}_y\text{Ti}_2\text{O}_4$ ($y = 0.1, 0.3$) are mainly controlled by Ti–O and Li (Mg)–O stretching and bending force constants both and O–O repulsive stretching force constants.

It is also concluded that in the case of compounds $\text{Li}_{1+x}\text{Ti}_{2-x}\text{O}_4$ ($x = 0.33$) and $\text{Li}_{1-y}\text{Mg}_y\text{Ti}_2\text{O}_4$ ($y = 0.1, 0.3$) the second neighbour interaction; dominates over the first neighbour interaction this means that the octahedral bonding is stronger than the tetrahedral bonding.

The interatomic interactions for LiTi_2O_4 and $\text{Li}_{1.33}\text{Ti}_{1.67}\text{O}_4$ (Table I) show that the interatomic interactions decrease as the concentration of Li-ion increases. The reason for this is that the ionic radii of Li-ion is less comparable with the ionic radii of O-ion in comparison to the ionic radii of Ti-ions, and in the case of $\text{Li}_{0.9}\text{Mg}_{0.1}\text{Ti}_2\text{O}_4$ and $\text{Li}_{0.7}\text{Mg}_{0.3}\text{Ti}_2\text{O}_4$, the interatomic interactions increase with the concentration of Mg-ions, the reason being that the ionic radii of Mg-ion are more comparable with the ionic radii of O-ion in comparison to the ionic radii of Li-ions, since the interatomic interaction between the ions of comparable radii is more than that of having different ionic radii. The ionic radii of Li, Mg, Ti, and O are 0.71, 0.66, 0.85, and 1.35, respectively.

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