J. Mater. Environ. Sci. 3 (1) (2012)58-65
ISSN : 2028-2508
CODEN: JMESCN

Vibrational spectra and force field studies of $K_{1,125}Rb_{1,875}La(VO_4)_2$ vanadate

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Received in 8 May 2011, Revised 4 Nov 2011, Accepted 4 Nov 2011.

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Abstract

This work is focused on the vibrational study of $K_{1,125}Rb_{1,875}La(VO_4)_2$ vanadate (space group $P2_1/m$). The infrared and Raman spectra have been interpreted in molecular group (T_d) according to previous works. A previously X-rays diffraction study shows that this compound presents two non homologous VO_4 in the unit cell. The vibrationnal spectra can not permit to distinguish between the vibrations of each kind of vanadate. So a force-field calculation has been made in order to make a separation between the vibrations of the two different VO_4 and to complete the interpretation in the factor group (C_{2h}).

*Key words :*Vanadate, Vibration, Raman spectrum, Infrared spectrum, Force-field

1. Introduction

The compounds $M_3Ln(XO_4)_2$ and $M_2M'Ln(XO_4)_2$ (M, M' = Na, K, Rb ; Ln = rare earth and X = P, As, V) have been studied in our laboratory by X-ray diffraction and vibrational spectroscopy [1-12]. It's well known that, when the rare earth and XO_4 anions are present in the unit cell, the compounds show very interesting optical properties [13].

The crystals with $K_{1,125}Rb_{1,875}La(VO_4)_2$ formula were synthesized by the flux method using a mixture of K_2CO_3, Rb_2CO_3,La_2O_3 and V_2O_5 corresponding to 1 mol of $K_{1,125}Rb_{1,875}La(VO_4)_2$ and 1 mol of Rb_3VO_4 [11]. The aim of this work is to study this vanadate by vibrational spectroscopy and to calculate its force field in order to give a separation between the different vibrations of the two kinds of vanadate group.

2. Vibration spectroscopy study

2-1. Theory

The $K_{1,125}Rb_{1,875}La(VO_4)_2$ vanadate crystallizes in the monoclinic system, space group $P2_1/m$ with Z=2 [11]. There is two independents VO_4 tetrahedra in the unit cell, noted V(1) and V(2) and having the same site group symmetry (Cs) but they present different environment (table 1) [11].

The free VO_4^{3-} anions have T_d symmetry group. Their fundamentals vibrations are subdivided as follows [14]:

$\Gamma_{vib}{}^{Td}$ (VO_4^{3-}) = A_1(Raman activity) + E(Raman activity) + $2T_2$(IR, Raman activity).

Table 1: V-O distances (Å) in $K_{1,125}Rb_{1,875}La(VO_4)_2$

V(1)-O(3)= 1,6744	V(2)-O(4)= 1,6813
V(1)-O(1)= 1,7168	V(2)-O(5)= 1,7071
V(1)-O(2)= 1,7213	V(2)-O(6)= 1,7141
V(1)-O(2)= 1,7213	V(2)-O(6)= 1,7141

Table 2-a: Correlation scheme for the internal modes of each type of VO_4^{3-} in $K_{1,125}Rb_{1,875}La(VO_4)_2$

Normal modes	G.M. = T_d	→	G.S. = C_s	→	G.F. = C_{2h}
ν_1	(1)A_1	→	A’	→	$A_g + B_u$
ν_2	(1)E	→	A’ + A’’	→	$A_g + B_u + B_g + A_u$
ν_3, ν_4	(2)T_2	→	(2)(2A’ + A’’)	→	$(2)(2A_g + 2B_u + B_g + A_u)$

G.M.: molecular group, G.S.: site group, G.F.: factor group

Table 2-b : Correlation scheme for the internal modes of VO_4^{3-}, K^+, Rb^+ and La^{3+} in $K_{1,125}Rb_{1,875}La(VO_4)_2$

	rotation	translation	C_s	C_{2h}	rotation	translation
XO_4^{3-}	1	2	A’	A_g	1x2	2x2
				B_u	1x2	2x2
	2	1	A’’	B_g	2x2	1x2
				A_u	2x2	1x2
K^+, $Rb^+$and Eu^{3+}		2	A’	A_g		2x4
				B_u		2x4
		1	A’’	B_g		1x4
				A_u		1x4

In the crystal, the internal modes of the VO_4^{3-} ions and the external modes of the VO_4^{3-}, K^+, Rb^+ and La^{3+} are presented in the correlation schemes given in tables 2-a and 2-b respectively. Factor group analyses using Halford method [15] predict the distribution of the internal and external modes of the ions to be as follows:

$\Gamma_{interne}$ $(VO_4^{3-}) = 12A_g + 6A_u + 6B_g + 12B_u$

$\Gamma_{rotation}$ $(VO_4^{3-}) = 2A_g + 2B_u + 4B_g + 4A_u$

$\Gamma_{translation}{}^{total} = 12A_g + 10B_u + 6B_g + 5A_u$ with $\Gamma_{acoustic}=A_u+2B_u$

The A_g and B_g species are Raman active, while the A_u and B_u species are infrared active.

2.2 Experimental

The Raman spectrum were measured on a Dilor RT30 spectrometer using the 647.1 nm line of a Kr^+ ion laser for excitation (600 mw power).

The infrared spectrum were recorded at ambient temperature using the KBr pellets technique at 1% proportion and under 10 t/cm^2 pressure. Two different spectrometers were used:

- Perkin Elmer 1600 FTIR spectrometer with 4 cm^{-1} resolution
- Brucker I.F.S. 113 spectrometer with 2 cm^{-1} resolution.

3. Results and discussion

The Raman and infrared spectra of $K_{1,125}Rb_{1,875}La(VO_4)_2$ vanadate are shown in figures 1 and 2 respectively. According to other vibrational studies on $M_3Ln(VO_4)_2$ and $K_2CsLa(VO_4)_2$ vanadates [1,6,7], the band assignments are given in table 3.

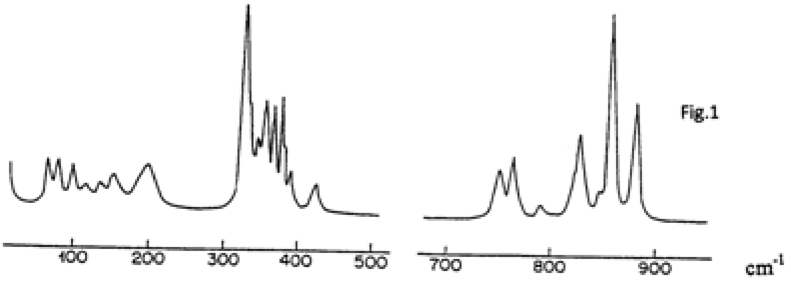
Fig.1

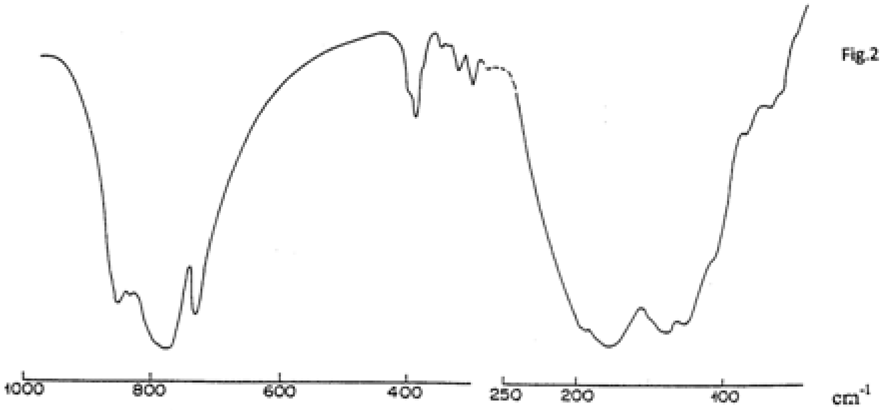
Fig.2

Figure 1: Raman spectrum of $K_{1,125}Rb_{1,875}La(VO_4)_2$ vanadate

Figure 2: Infrared spectrum of $K_{1,125}Rb_{1,875}La(VO_4)_2$ vanadate

In vanadates, the symmetric stretching modes of VO_4^{3-} anions give rise to strong bands in the Raman spectra [1,6,7]. Consequently, the symmetric stretching vibration $\nu_1(VO_4)$ is attributed to the Raman intense bands at 853 and 823 cm^{-1}. The corresponding infrared bands are situated at 870 and 810 cm^{-1}. The lines observed at 875, 844, 815, 784, 759 and 745 cm^{-1} in the Raman spectrum (fig.1) are assigned to the antisymmetric $\nu_3(VO_4)$ mode. While, the infrared spectrum shows only three bands at 850, 790 and 745 cm^{-1} corresponding to this mode.

In the Raman and the infrared spectra, the bands lying between 420 and 295 cm^{-1} are assigned to the VOV symmetric (ν_2) and antisymmetric (ν_4) deformation modes. As in our previous works [1,6,7], the separation between these two modes is not clear on the vibrational spectra.

In the 230-50 cm^{-1} range, we find the bands attributed to the lattice vibrations. They are dues to the VO_4^{3-} rotation and to the VO_4^{3-}, K^+, Rb^+ and La^{3+} translation modes.

Force field calculation

The bands observed on Raman and infrared spectra (internal mode) are assigned to the two tetrahedral groupings movements and the spectra obtained in this zone are consequently the superposition of the vibrations of the two types of VO_4. Separation between the vibrations of each type of VO_4 is not possible.

In order to make a separation between the two VO_4 vibrations and to suggest a force field for the title compound, we carry out a normal coordinate analysis using the more general force field established by T. Shimanouchi [16] and modified by D. Dohy [17].

Table 3 : Vibrational frequencies (cm^{-1}) of $K_{1,125}Rb_{1,875}La(VO_4)_2$ vanadate

Raman	Infrared	Assignments
875	-	$\nu_3(T_2)$
853	870	$\nu_1(A_1)$
844	850	$\nu_3(T_2)$
823	810	$\nu_1(A_1)$
815	790	$\nu_3(T_2)$
784	-	$\nu_3(T_2)$
759	745	$\nu_3(T_2)$
745	-	$\nu_3(T_2)$
419	415	$\nu_4(T_2)$ and $\nu_2(E)$
-	405	
385	395	
375	-	
371	365	
362	355	
350	335	
338	-	
326	320	
324	295	
-	228	Lattice vibrations
-	203	
188	182	
176	-	
147	149	
131	135	
-	117	
109	95	
92	78	
73	71	
58	59	

A knowledge of the crystal structure enabled us to take into account the environment of each atom within a distance of 3,5 Å. Cartesian coordinates were deduced from the crystal structure. In addition to the internal coordinates of the VO_4 tetrahedra, the following interactions are considered: lanthanum-oxygen, potassium-oxygen, rubidium-oxygen, oxygen-oxygen bond between two VO_4. A total of 58 different atoms have been introduced (those in the unit cell and their closest neighbours) to build the 114 internal coordinates.

Using a generalized force field, we can consider 69 force constants, divided up as follows: force constants for V-O bonds and O-V-O angles, force constants for the La-O, Rb-O and K- O interactions, force constants for bond-bond and angle-angle interactions and finally force constants reflecting the interactions between homologous VO_4 groups. Each interatomic distance is described by a force constant, which is allowed to vary as a function of the bond length. Within a given tetrahedral environment, we considered two types of bond- angle interactions, according to whether the bond is part of the angle or not, and also two types of angle-angle interactions, those with a side in common and those in a vertically opposite position. Table 4 gives the average values of the force constants and their characterization. The main force constants of the initial field was chosen from previous studies [1,6,9,18,19].

The force constants values were introduced in stages: first the stretching, then the bending, then the stretching-stretching interactions and the angle-angle interactions, then the bond-angle interactions and finally the V-O/V-O and O-V-O/O-V-O interactions between two homologous VO_4.

Table 4 : Values and characterization of force constants

Force constant (mdyn/Å)	Characterization	Interatomic distance (Å)
4,655	Stretching V-O (f_V)	1,7025
0,957	Angle O-V-O(f_α)	-
0,5813	Stretching-Stretching interaction (f_{VV})	-
0,1841	Potassium-oxygen interaction (f_K)	2,986
0,178	Rubidium-oxygen interaction (f_{Rb})	3,1486
0,3596	Lanthanum-oxygen interaction (f_{La})	2,5256
0,055	Angle-angle interaction (side in common) ($f_{\alpha\alpha}$)	-
-0,125	Angle-angle interaction (opposites) ($f_{\alpha\beta}$)	-
0,1225	Bond-angle interaction (bond is part of angle) ($f_{r\alpha}$)	-
0,1025	Bond-angle interaction (independent) ($f_{r\beta}$)	-
-0,0025	V-O/V-O interaction between two homologous VO_4(frr’)	-
0,0338	O-V-O/O-V-O interaction between two homologous VO_4 ($f_{\alpha\alpha'}$)	-

The tables 5 and 6 present the potential energy distribution (%) for active species in the Raman and the infrared spectroscopy and the comparison between observed and calculated frequencies (cm^{-1}) of the $K_{1,125}Rb_{1,875}La(VO_4)_2$ vanadate. Only the greater contributions more than 10% are presented. Simulation of vibrational spectra by force field calculation can be considered as satisfying since the average deviation between the calculated and observed frequencies is about 1.5%.

All the vibrations bands located between 875 and 745 cm^{-1} are mainly due to the V-O bonds vibrations with a participation of bonding interactions in the same tetrahedron. Between 420 and 295 cm^{-1}, the vibrations are mainly due to the VOV symmetric (ν_2) and antisymmetric (ν_4) deformation with a contribution of angle-angle, potassium-oxygen, rubidium-oxygen and lanthanum-oxygen interactions.

In the lattice vibrations range (ν<230 cm^{-1}), the potential energy distribution (P.E.D.) does not permit to distinguish between VO_4 vibrations (rotations and translations) and cations (K^+, Rb^+ and La^{3+}) translations. In fact different internal coordinates involved in the P.E.D. and the separation between the librations and translations appears difficult.

The force field calculation permits us to separate between the two independent VO_4 vibrations. In Tables III-a and IV-a, the indices 1 and 2 denote the force constants related respectively to tetrahedral $V(1)O_4$ and $V(2)O_4$.

Table 5-a: Calculated and observed frequencies (cm^{-1}) in Raman diffusion and potential energy distribution term (internal modes)

$\nu_{cal.}$	$\nu_{obs.}$	Species	ΣP.E.D. (%)
877	875	A_g	$80\ f_{v1}$
856	853	A_g	$70\ f_{v2} + 27\ f_{rr}$
840	844	B_g	$95\ f_{v1}$
819	823	A_g	$96\ f_{v1}$
819	815	B_g	$101\ f_{v2} - 10\ f_{rr}$
784	784	A_g	$109\ f_{v2} - 15\ f_{rr}$
759	759	A_g	$116\ f_{v2} - 24\ f_{rr}$
748	745	A_g	$116\ f_{v1} - 26\ f_{rr}$
429	419	A_g	$55\ f_{\alpha 2} + 16\ f_{La}$
407	-	A_g	$59\ f_{\alpha 2} + 11\ f_{La}$
384	385	B_g	$90\ f_{\alpha 1}$
383	375	A_g	$82\ f_{\alpha 1}$
370	371	B_g	$84\ f_{\alpha 2}$
366	362	A_g	$77\ f_{\alpha 1}$
348	350	A_g	$80\ f_{\alpha 1}$
343	338	B_g	$77\ f_{\alpha 1} - 10\ f_{\alpha\alpha}$
326	326	B_g	$72\ f_{\alpha 2} + 21\ f_{Rb}$
321	324	A_g	$72\ f_{\alpha 2} - 18\ f_{\alpha\beta}$

P.E.D.: Potential Energy Distribution

Table 5-b: Calculated and observed frequencies (cm^{-1}) in Raman diffusion and potential energy distribution term (external modes)

$\nu_{cal.}$	$\nu_{obs.}$	Species	ΣP.E.D. (%)
232	-	A_g	$43f_{Rb} + 42\ f_{La}$
198	-	A_g	$85\ f_K$
189	188	B_g	$60\ f_{La} + 21\ f_{Rb}$
177	-	B_g	$45\ f_{Rb} + 40\ f_K$
176	176	A_g	$70\ f_K + 14\ f_{La}$
167	-	B_g	$47\ f_K + 36\ f_{Rb} + 10\ f_{La}$
165	-	A_g	$46\ f_{Rb} + 31\ f_{La}$
150	147	B_g	$87\ f_K$
145	-	A_g	$52\ f_K + 29\ f_{La}$
136	131	A_g	$51\ f_{La} + 30\ f_K$
126	-	B_g	$80\ f_K$
113	109	A_g	$51\ f_K + 34\ f_{La}$
99	-	A_g	$43\ f_{La} + 25\ f_K + 18f_{Rb}$
99	-	B_g	$55f_K + 25\ f_{La}$
94	92	B_g	$50\ f_{Rb} + 25\ f_K$
90	-	A_g	$55\ f_K + 21f_{La} + 14\ f_{Rb}$
83	-	A_g	$43f_K + 28f_{Rb} + 19f_{La}$
76	71	A_g	$33f_{Rb} + 31f_K + 30f_{La}$
67	-	A_g	$48f_K + 26f_{La}$
62	58	B_g	$45f_K + 25f_{La} + 17f_{Rb}$
60	-	A_g	$30f_K + 26f_{Rb} + 22f_{La}$
43	-	B_g	$73f_K + 10f_{Rb}$
34	-	A_g	$61f_K + 26f_{Rb} + 22f_{La}$
28	-	B_g	$50f_K + 41f_{Rb}$

Table 6-a: Calculated and observed frequencies (cm^{-1}) in infrared and potential energy distribution term (internal modes)

$\nu_{cal.}$	$\nu_{obs.}$	Species	ΣP.E.D. (%)
871	870	B_u	80 f_{v1}
863	-	B_u	71 f_{v2} + 24 f_{rr}
848	852	A_u	93 f_{v1}
814	810	B_u	97 f_{v1}
808	-	A_u	103 f_{v2} – 10 f_{rr}
793	790	B_u	106 f_{v2} – 14 f_{rr}
753	750	B_u	116 f_{v2} – 22 f_{rr}
747	-	B_u	118 f_{v1} – 28 f_{rr}
422	415	B_u	57 $f_{\alpha2}$ + 18 f_{La} + 12 f_{Rb}
401	405	B_u	62 $f_{\alpha2}$ + 16 $f_{\alpha\beta}$ + 11 f_{La}
395	395	A_u	85 $f_{\alpha1}$
389	-	B_u	80 $f_{\alpha1}$
360	365	A_u	88 $f_{\alpha2}$
354	355	B_u	84 $f_{\alpha1}$
331	-	B_u	88 $f_{\alpha1}$ + 20 f_K
337	335	A_u	81 $f_{\alpha1}$ + 24 f_K
319	320	A_u	76 $f_{\alpha2}$ + 21 f_{Rb}
295	295	B_u	85 $f_{\alpha2}$ - 20 $f_{\alpha\beta}$

Table 6-b: Calculated and observed frequencies (cm^{-1}) in infrared and potential energy distribution term (external modes)

$\nu_{cal.}$	$\nu_{obs.}$	Species	ΣP.E.D. (%)
226	228	B_u	47f_{Rb} + 37 f_{La}
198	203	B_u	84 f_K + 13 fRb
193	-	A_u	41 f_{La} + 33 f_K
184	182	A_u	50 f_K+23 f_{La}+17 f_{Rb}
178	-	B_u	74 f_K
173	-	B_u	48 f_{Rb} + 26 f_{La}
172	-	A_u	70 f_{Rb} + 25 f_K
155	-	B_u	70 f_{Rb} + 25 f_K
153	149	A_u	75 f_K + 21 f_{La}
129	135	A_u	71 f_K +14 f_{Rb}+13 f_{La}
125	-	B_u	46 fLa +27 f_K +14 f_{Rb}
115	117	B_u	52 f_K+23 f_{La}+18 f_{Rb}
104	-	B_u	41 f_{La}+34 f_K+15f_{Rb}
92	95	B_u	64f_K+14 f_{La}+11 f_{Rb}
91	-	A_u	45 f_{Rb}+23 f_K+10 f_{La}
85	-	B_u	41 f_{Rb} + 34 f_{La}
74	78	B_u	77f_K
72	71	B_u	43f_{La}+28f_K+20f_{Rb}
71	-	A_u	63 f_K + 18 f_{La}
61	59	A_u	45f_K+25f_{La}+17f_{Rb}
47	-	A_u	66f_K + 24f_{Rb}

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