

IR, Raman, and X-Ray Photoelectron Spectroscopy Investigations of the Ordered Cubic Perovskite La_2LiVO_6

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The ordered cubic perovskite La_2LiVO_6 has been prepared under 60 kbar oxygen pressure at 900°C. The double perovskite unit cell has a parameter of $7.746 \pm 0.003 \text{ \AA}$. An ionic radius of pentavalent vanadium has been estimated for CN6. The assignment of the IR absorption and Raman scattering bands seems to confirm the cubic symmetry of the VO_6 octahedra in the lattice. According to the XPS study the binding energy of the $\text{V}_{2p_{3/2}}$ orbital electron in La_2LiVO_6 is estimated as 516.8 eV, which is quite consistent with that of V_2O_5 . Some examples of vanadium oxides, where vanadium has an environment close to octahedral are also discussed. © 1988 Academic Press, Inc.

Introduction

We have recently reported the preparation of a La_2LiVO_6 perovskite under 60 kbar oxygen pressure and also discussed the lattice contraction due to high effective charge of vanadium (V).

The stabilization of the 3d elements with oxidation state (V) in a perovskite lattice seems to be more difficult than that of the 4d and 5d elements. Therefore, the only La_2LiMO_6 oxides which have been prepared contain either vanadium (1) or iron (2). As 4d or 5d elements such as Nb, Mo, Ru, Ta, Re, Os, and Ir have lower ionization potentials, they are easier to stabilize in a perovskite lattice (3, 4).

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Although some studies of IR absorption and Raman spectra of MO_6 groups ($M = 4d$ or $5d$ element) have already been achieved for such materials, no investigation has been reported for the corresponding 3d transition metals.

In the present paper bonds of a chemical nature and site symmetry of the VO_6 octahedra in La_2LiVO_6 are discussed with vibrational and XPS spectra and compared to results of the X-ray diffraction study.

Experimental

The La_2LiVO_6 phase have been prepared in three steps. The first is a calcination at 700°C of a mixture of lanthanum and lithium nitrates (the last one with 30% excess) and vanadium oxide taken in stoichiometric

proportions with La_2O_3 . The second step is a thermal treatment at 750°C for 5 hr under O_2 stream. The last step is a 15-min heating at 900°C under oxygen pressure of 60 kbar. High pressure favors CN6 for vanadium (V), presence of oxygen being required for stabilizing this high oxidation in the temperature range necessary for the synthesis of perovskite-type phases. KClO_3 was added to the reaction product of the second step for setting up the oxygen pressure. After temperature quenching the remaining KCl was quickly leached out with water. The color of the obtained phase is yellow-orange. Samples were checked by X-ray powder diffraction analysis. IR absorption spectra were recorded on a JASCO DS-701G grating spectrometer by KBr method. Raman spectra were obtained on a Spectra Physics 700 Raman spectrometer using an argon laser. All of these measurements were performed at room temperature. X-ray photoelectron spectra using an $\text{MgK}\alpha$ -X-radiation were recorded on an Perkin-Elmer electron spectrometer. The spectra were calibrated with C_{1s} (B.E. = 285.0 eV) peak.

Results and Discussion

The X-ray powder diffraction pattern of a La_2LiVO_6 leads to an indexation on the basis of a cubic perovskite unit cell ($Fm\bar{3}m$, $a_0 = 3.873 \pm 0.002\text{ \AA}$). But, due to the presence of a few weak superstructure lines resulting from a 1:1 three-dimensional ordering between Li and V, it can be indexed in a more correct way with a double unit cell using a lattice parameter of $a = 2a_0 = 7.746\text{ \AA}$, which is in good agreement with the size and the charge difference of Li and V.

For the ABO_3 perovskites structure Poix (5) has established a relation between the A-O and B-O distances:

$$a = \frac{(A-O)^{\text{XII}} + (B-O)^{\text{VI}}}{1.207}$$

On the basis of the values given in the corresponding tables ($d(\text{La(III)}-\text{O})^{\text{XII}} = 2.71\text{ \AA}$, $d(\text{Li(I)}-\text{O})^{\text{VI}} = 2.14\text{ \AA}$, $d(\text{V(V)}-\text{O})^{\text{VI}} = 1.77\text{ \AA}$) and assuming $d(\text{B-O})^{\text{VI}} = \frac{1}{2}[d(\text{Li(I)}-\text{O}) + d(\text{V(V)}-\text{O})]$ the simple cubic cell constant can be calculated as $a_0 = 3.87\text{ \AA}$, a value close to that observed experimentally ($a_0 = 3.873\text{ \AA}$).

Group theoretical considerations for the MO_6 octahedron lead to 15 normal modes: $A_{1g} + E_g + 2T_{1u} + T_{2g} + T_{2u}$. From this representation we can deduce the following list of normal modes grouped according to the activities of the fundamental vibrations: infrared-active, $2T_{1u}$; Raman-active, A_{1g} , E_g , T_{2g} , and inactive, T_{2u} .

Each of the two T_{1u} modes involves a combination of bond stretching and angle deformation, the A_{1g} and E_g modes only bond stretching, and the T_{2g} and T_{2u} modes only angle deformations. As we have only one MO_6 octahedron per primitive unit cell, we may expect three bands in the Raman and two in the IR absorption spectra.

The IR and Raman spectra of La_2LiVO_6 are given in Fig. 1. As shown in IR spec-

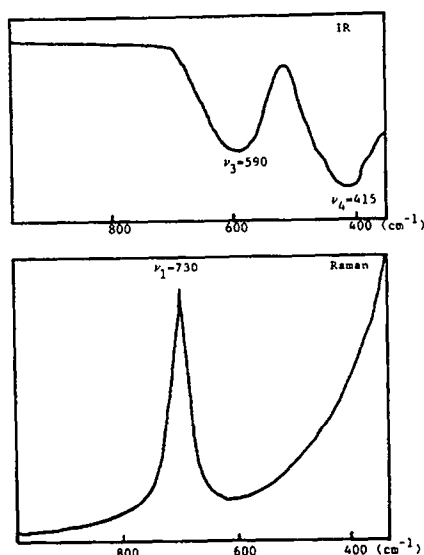


Fig. 1. IR absorption and Raman spectra of La_2LiVO_6 .

trum two strong absorption bands were observed as expected at about 590 and 415 cm^{-1} . The Raman spectrum contains only one band at about 730 cm^{-1} , the intensity of which is rather strong. Since the color of La_2LiVO_6 crystals is yellow–orange, the laser beam used was partly absorbed particularly below 500 cm^{-1} . Therefore the expected bands could not be observed in the region 200–500 cm^{-1} .

Assuming that the binding forces in the VO_6 octahedron are large compared to the other ones within the crystal, the frequencies of the vibrations of this group must be close to the frequencies of the free-ion modes, and the internal and external modes should be completely separated (6). An approach for the interpretation of the vibrational spectra of the perovskites of La_2LiMO_6 type was recently carried out by Hayashi *et al.* (7), but for the 4d and 5d elements. For La_2LiVO_6 , the IR absorption bands can be assigned as two T_{1u} vibrational modes (ν_3 and ν_4) and the strong Raman band as a A_{1g} vibrational mode (ν_1).

The ν_1 , ν_3 , and ν_4 modes of the La_2LiMO_6 oxides ($M = \text{V}, \text{Nb},$ and Ta) are compared in Fig. 2. For the T_{1u} modes, there is almost no difference for ν_3 in the three cases, but a relatively large shift of ν_4 toward higher wave numbers is observed for La_2LiVO_6 with respect to $\text{La}_2\text{LiNbO}_6$ and $\text{La}_2\text{LiTaO}_6$. In the Raman spectrum, however, an appreciable dependence on the cation has not been detected. Similar phenomena have been observed for $(\text{Nb}^{\text{V}}\text{Cl}_6)$ and $(\text{Ta}^{\text{V}}\text{Cl}_6)$ as well as for $(\text{Ti}^{\text{IV}}\text{Cl}_6)$, $(\text{Zr}^{\text{IV}}\text{Cl}_6)$, and $(\text{Hf}^{\text{IV}}\text{Cl}_6)$ (8).

For V^{V} , Nb^{V} , and Ta^{V} which have high effective nuclear charges (11.80, 13.25, and 15.35, respectively) and low-lying empty t_{2g} - d orbitals, strong π bonding may be expected. The increased frequency of the asymmetric ν_4 vibration may result from the enhancement of the π bonding between vanadium and oxygen compared to that of

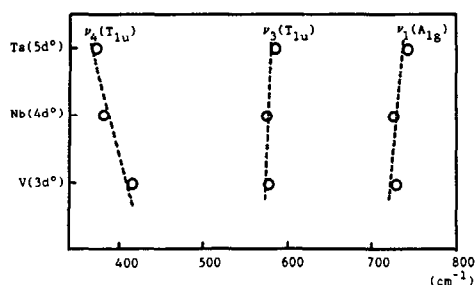


FIG. 2. Comparison of the IR absorption ($2T_{1u}$) and Raman (A_{1g}) modes in La_2LiMO_6 [$M = \text{V}$ ($3d^0$), Nb ($4d^0$), and Ta ($5d^0$)].

the Nb–O or Ta–O bonds because of the decrease of the M –O distances ($\text{V–O} = 1.77 \text{ \AA}$, $\text{Nb–O} = 2.06 \text{ \AA}$, and $\text{Ta–O} = 2.05 \text{ \AA}$).

As the formal ionic radius of $\text{V}(\text{V})$ (0.54 \AA) is smaller than that of $\text{Nb}(\text{V})$ (0.64 \AA) or $\text{Ta}(\text{V})$ (0.64 \AA) (9), the magnitude of the Goldschmidt factor (t is defined by $R_A + R_O = t \sqrt{2}[(R_B + R_B')/2 + R_O]$, where R represents corresponding ionic radii in $A_2BB'O_6$ perovskite) of La_2LiVO_6 is 0.961, which is much larger than the value calculated for $\text{La}_2\text{LiNbO}_6$ or $\text{La}_2\text{LiTaO}_6$ (0.938) and therefore the size of vanadium (V) fits geometrically better than that of niobium (V) or tantalum (V) to set up the perovskite structure with regular MO_6 octahedra. A Jahn–Teller effect is indeed excluded for the $\text{V}(\text{V})$, $\text{Nb}(\text{V})$, or $\text{Ta}(\text{V})$ with d^0 electronic configurations.

The fact that the value of the band half-width (110 cm^{-1}) of the T_{1u} vibrational band (ν_3) is much smaller than those of NbO_6 or TaO_6 shows that there can be little lowering of the site symmetry (7). Nevertheless a small shoulder is observed in the IR bands of the VO_6 octahedral group. Thus it can be concluded that the structure of La_2LiVO_6 should be slightly different from that of $\text{La}_2\text{LiNbO}_6$ or $\text{La}_2\text{LiTaO}_6$, the lattice of which is, respectively, orthorhombic or monoclinic with a small deviation from the pure cubic symmetry.

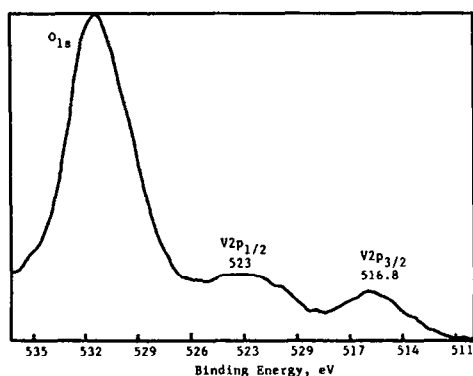


FIG. 3. XPS spectrum of La_2LiVO_6 .

Therefore in La_2LiVO_6 we may expect the VO_6 octahedra to be regular, i.e., of O_h symmetry in agreement with the X-ray data.

To confirm the oxidation state V of vanadium in La_2LiVO_6 XPS measurements have been performed as shown in Fig. 3. The binding energies of the V_{2p} orbital electrons are found at 523 eV for $\text{V}_{2p_{1/2}}$ and 516.8 eV for $\text{V}_{2p_{3/2}}$. In Fig. 4 the binding energies

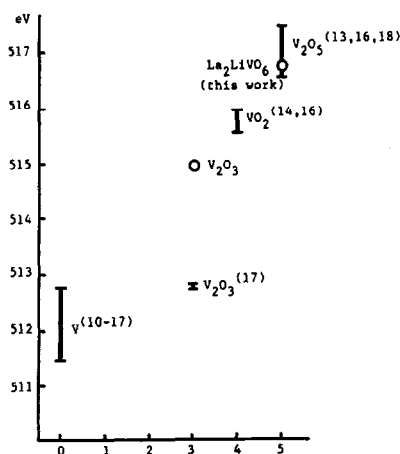


FIG. 4. Variation of the binding energy for the $\text{V}_{2p_{3/2}}$ orbital electrons in some vanadium oxides and vanadium metal with respect to their oxidation states. See Refs. for V (10-17), V_2O_3 (17), VO_2 (14, 16), and V_2O_5 (13, 16, 18). The binding energy data with the open circles are obtained in the present work.

($\text{V}_{2p_{3/2}}$) of various vanadium oxides and vanadium metals published in previous papers are plotted against the respective oxidation state of vanadium. It was found that the binding energy of $\text{V}_{2p_{3/2}}$ for La_2LiVO_6 , 516.8 eV, is close to those previously determined for V_2O_5 (516.6-517.3 eV). For all materials considered, a linear variation of the binding energy vs oxidation state of vanadium has been detected, except for V_2O_3 , where $2p_{3/2}$ electron binding energy was reported to be 512.8 eV. Therefore, we have attempted to check this value. Commercial V_2O_3 with a 99.999% purity was used for the XPS measurements. As shown in Fig. 5, the $\text{V}_{2p_{3/2}}$, $\text{V}_{2p_{1/2}}$, and O_{1s} electron binding energies have been detected at 515.0, 522.5, and 529.7 eV, using the same standard. The value obtained for La_2LiVO_6 confirms the linear variation shown in binding energy vs oxidation state for the same anionic surrounding (Fig. 4).

Table I allows us to compare the oxidation states of vanadium and the average V-O bond lengths of the various oxides as well as the binding data.

It is well known that in the oxides intermediate between V_2O_3 and VO_2 the coordination of vanadium is octahedral with strong distortions, but in the oxides between VO_2 and V_2O_5 the distortion of some octahedron is so keen that the coordination

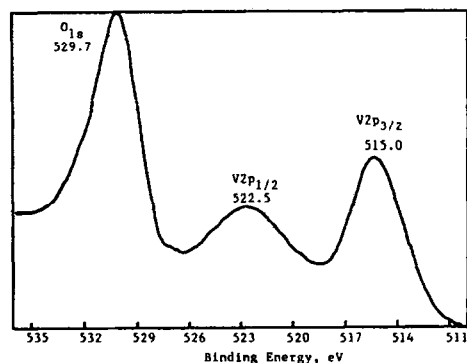


FIG. 5. XPS spectrum of V_2O_3 .

TABLE I
V-O BOND LENGTH OF SOME VANADATES

Compound	Oxidation number of vanadium ion	Average V-O bond length (Å)
V_2O_3	3	2.01
VO_2	4	1.94
V_2O_5	5	1.83
La_2LiVO_6	5	1.77

is better described as trigonal bipyramidal (19). But the higher the oxidation state of vanadium is the shorter the V-O bond length becomes. If we compare, however, V_2O_5 and La_2LiVO_6 , we find that the V-O bond length in La_2LiVO_6 is shorter than the average value in V_2O_5 despite similar oxidation states. This observation confirms the fact that La_2LiVO_6 has a smaller unit cell than that expected from the variation of the parameter with ionic radius (I) and that the covalency of the V-O bonds in La_2LiVO_6 is higher than that observed for V_2O_5 due to bond competition in the perovskite oxide.

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