phys. stat. sol. (a) 117, K189 (1990)
Subject classification: 61.70 and 78.30; S10.1

Department of Chemistry, Technical University of Dresden[1])

Identification of LiO Bands in the Infrared Spectra of the Insertion Compound δ-LiV_2O_5

By
E. PIGORSCH and W.E. STEGER

Introduction Vanadium pentoxide, V_2O_5, is known for its ability to form $Li_xV_2O_5$ compounds by inserting Li^+ ions. This insertion process can be performed by chemical /1, 2/ or electrochemical /3/ techniques at room temperature.

According to X-ray studies /1, 2/ the three phases α-, ε-, and δ-$Li_xV_2O_5$ with composition ($0 < x \leq 0.1$), ($0.35 \leq x \leq 0.5$), and ($0.9 \leq x \leq 1.0$), respectively, were considered to contain the basic V_2O_5 structure nearly unaltered save for slight expansion. A study into δ-LiV_2O_5 proceeding by way of stepwise structure refinements by neutron and X-ray diffraction data /4/ has shown that an alternative shifting of V_2O_5 sheets occurs in order to accomodate the Li^+ ions in rather regular tetraedric coordination.

Before these results were available, nothing about the Li^+ positions in ambient temperature $Li_xV_2O_5$ compounds was known positively, and some conclusions were drawn from the infrared spectra of α-, ε-, and δ-$Li_xV_2O_5$ /7/. The tetrahedral coordination of Li^+ by two O atoms in V-O-V bridges and two atoms from V=O was proposed, just as it is established now. But this was deduced from changes in V-O vibrations only, since so far the Li-O vibrations had not been identified. To this end experiments with ^6Li were done. It is known /9 to 11/ that Li-O vibration bands lie in the range of 500 to 350 cm^{-1} for tetrahedral coordinated Li^+ and lower at 300 cm^{-1} for octahedral coordinated Li^+. Therefore we prepared δ-LiV_2O_5 with natural lithium which is practically ^7Li (92.6%) and with ^6Li (90.6%) in order to compare their infrared spectra especially in the range of 450 to 200 cm^{-1} to identify Li-O bands.

Experimental The δ-LiV_2O_5 samples were obtained by reduction of solid V_2O_5 with lithium iodide in acetonitrile as described by Murphy et al. /1/. ^6LiI was prepared by dissolving metallic ^6Li (90.6%) in water and neutralizing with HI solution. The salt was dried in vacuo at 150 °C.

Electrochemical formation of δ-LiV_2O_5 was achieved in galvanic cells of the structure Li/PC, $LiClO_4/V_2O_5$.

Infrared spectra were obtained by means of a FTIR spectrometer IRF 180 in the range of 450 to 200 cm^{-1} using TlBr pressed disks.

---

[1] Mommsenstr. 13, DDR-8027 Dresden, GDR.

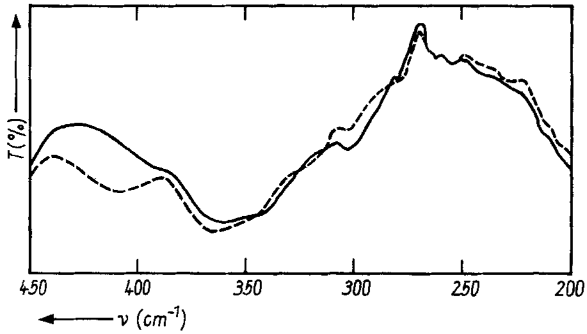

Fig. 1. Infrared spectra between 450 to 200 cm^{-1} of $^{7}LiV_2O_5$ (—) and $^{6}LiV_2O_5$ (---)

Results Fig. 1 shows the infrared spectra of samples of chemically prepared $^{6}LiV_2O_5$ and $^{7}LiV_2O_5$ compounds. In comparison to V_2O_5 /12, 13/ the spectra exhibit one main band near 360 cm^{-1} which does not show any significant difference in both compounds. Therefore it has to be assigned to new V-O vibrations resulting from changes in the V_2O_5 lattice in the course of lithium insertion /8/. At 390 cm^{-1} there is a shoulder on the flank of the V-O band for $^{7}LiV_2O_5$. For $^{6}LiV_2O_5$ this shoulder is shifted to 408 cm^{-1} and appears as a resolved band. We can assign this band to a Li-O vibration for a tetrahedral or more generally fourfold coordinated Li^+ ion. The isotopic shift of about 18 cm^{-1} agrees well with the value reported by Tarte /9/.

Spectra of $Li_xV_2O_5$ samples with $x = 0.8$ and 0.9 also show the Li-O bands but with lower intensity.

Electrochemically prepared $Li_xV_2O_5$ compounds give the same infrared spectra as chemically prepared samples.

The intensity of the Li-O band is rather low, because of the small polarity of the Li-O bonds. Apparently the change in electric dipole moment is much higher in V-O vibrations.

Conclusion From the isotopic shift of a band near 400 cm^{-1} in the infrared spectra we may conclude that in the structure of δ-LiV_2O_5 the Li^+ ions occupy fourfold coordinated sites. But without the results reported by Cava et al. /4/ infrared spectroscopy as an indirect method of structure elucidation could not arrive at the correct Li positions. The former assertion of an unchanged V_2O_5 lattice for δ-LiV_2O_5 /1, 2/ led to a not very probable structure with alternative twofold occupied and empty vacancies /7/.

We are confident that our further investigations of the $Li_xV_2O_5$ $(0 < x \leq 1)$ insertion compounds by infrared and NMR spectroscopy are better supported now.

References

/1/ D.W. MURPHY, P.A. CHRISTIAN, F.J. DI SALVO, and J.V. WASCZAK, Inorg. Chem. 18, 2800 (1979).

/2/ G.G. DICKENS, S.J. FRENCH, A.T. HIGHT, and M.F. PYE, Mater. Res. Bull. 14, 1295 (1979).

/3/ M.S. WITTINGHAM, J. Electrochem. Soc. 123, 315 (1976).

/4/ R.J. CAVA, A. SANTORO, D.W. MURPHY, S.M. ZAHURAK, R.M. FLEMING, P. MARSH, and R.S. ROTH, J. Solid State Chem. 65, 63 (1986).

/5/ K. WIESENER, K. SCHNEIDER, D. ILIC, E. STEGER, K.H. HALLMEIER, and E. BRACKMANN, J. Power Sources 20, 157 (1987).

/6/ S. EGGEBRECHT, Diploma Project, TU Dresden, 1987.

/7/ W.E. STEGER, Progress in Molecular Spectroscopy, Teubner-Texte zur Physik, Vol. 20, Leipzig 1988 (p. 164).

/8/ E. PIGORSCH, unpublished.

/9/ P. TARTE, Spectrochim. Acta 20, 238 (1964).

/10/ Y. HASE, Spectrochim. Acta A 35, 377 (1979).

/11/ L.N. KURILENKO, Izv. Akad. Nauk SSSR, Ser. khim. 5, 966 (1988).

/12/ P. CLAUWS, J. BROECKX, and J. VENNIK, phys. stat. sol. (b) 131, 459 (1985).

/13/ L. ABELLO, E. HUSSON, Y. REPLIN, and G. LUCAZEAU, Spectrochim. Acta A 39, 641 (1983).

(Received December 28, 1989)