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Epitactic Ion-Exchange Reactions into Vanadyl(IV) Arsenate

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The synthesis, structural characterization, thermal stability, and spectroscopic (IR, UV–vis–diffuse reflectance) properties of three vanadyl arsenates are described. Vanadyl(IV) bis(dihydrogenarsenate), $[VO(H_2AsO_4)_2]$ (**I**), lithium vanadyl arsenate, $[(Li_4VO(AsO_4)_2 \cdot 0.5H_2O]$ (**II**), and nickel(II) and lithium vanadyl arsenate, $[(Li_{2.4}Ni_{0.8}VO(AsO_4)_2 \cdot 4H_2O]$ (**III**), have been prepared. (**I**) Tetragonal (a = 9.128 Å; c = 8.128 Å) is prepared by reduction with isobutanol or ethanol from vanadyl(V) arsenate. (**II**) Cubic (a = 9.024 Å) is obtained from (**I**) by lithium ion-exchange, and (**III**) tetragonal (a = 9.106 Å; c = 8.454 Å) is made from (**II**) by Ni^{2+} ion-exchange. These exchange reactions are epitactic and the overall result is a topotactic transformation. © 1991 Academic Press, Inc.

Introduction

The phosphates and arsenates of vanadium, niobium, and molybdenum oxocations constitute a series of compounds which have very similar structural chemistry (*1*) that at present provoke a high interest due to catalytic properties (*2*) and a rich and varied intercalation chemistry (*3–5*).

Of all the solids mentioned, the vanadyl phosphates and arsenates are the ones which have received greater attention from researchers. $VOPO_4 \cdot 2H_2O$ is considered the precursor of the catalyst in the all-important synthesis of the maleic anhydride starting from butane and air. The active catalytic phases in this reaction is $VOHPO_4 \cdot 0.5H_2O$ and the results of its heating $(VO)_2P_2O_7$ (*6*).

Although the structure and intercalation chemistry of $VOPO_4$ and $VOAsO_4$ are very similar (*1*) we show here that the reaction of the vanadyl arsenate (V) with reducers such as isobutanol or ethanol leads to different stoichiometry products and structures from those produced by phosphate.

Experimental

$VOAsO_4 \cdot 3H_2O$ was synthesized following the method of Chernorukov (*7*), modified as described in a previous paper (*3*).

$VO(H_2AsO_4)_2$ (HVAs) was prepared in two ways: (i) 10 g of $VOAsO_4 \cdot 3H_2O$ was refluxed with isobutanol (~50 ml) for 20 hr. The blue suspension was centrifuged, then the solid was washed with isobutanol and finally with ethanol. The solid was vacuum dried at 100°C; (ii) 9 g of V_2O_5 was suspended in a mixture of 47.5 ml of H_3AsO_4 (75% w/w) and 100 ml of ethanol and then refluxed for 2 days. The solution was evaporated to 100 ml and then the blue-greyish suspension was centrifuged. The solid was

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washed with ethanol and dried at 60°C for 10 hr.

For $Li_4VO(AsO_4)_2 \cdot 0.5H_2O$ (LiVAs), 1 g of $VO(H_2AsO_4)_2$ was suspended in a mixture of $LiOH \cdot H_2O$ (0.6 g), acetone (40 ml), and absolute ethanol (20 ml). The suspension was stirred for 7 days at room temperature. The product was filtered off, washed with acetone and ethanol, and air dried.

The Li/Ni exchange was carried out by suspending 1 g of $Li_4VO(AsO_4)_2 \cdot 0.5H_2O$ in a solution of 1 g $NiCl_2 \cdot 6H_2O$ in absolute ethanol for 1 day. The suspension was centrifuged and then resuspended with a fresh solution of Ni^{2+}. The process was repeated three times. Finally, the solid was washed with absolute ethanol and air dried. The chemical composition of the final product is $Li_{2.4}Ni_{0.8}VO(AsO_4)_2 \cdot 4H_2O$ (LiNiVAs).

The solids were dissolved in diluted H_2SO_4 for chemical analysis. Li, V, Ni, and As were determined by atomic absorption spectrophotometry. V and As were checked by redox potentiometry. The water content was determined thermogravimetrically. The stoichiometries have been proposed on the basis of the analytical results.

Calculated for $VO(H_2AsO_4)_2$: V, 14.6%; As, 42.96%. Found: V, 14.6; As, 42.8%.

Calculated for $Li_4VO(AsO_4)_2 \cdot 0.5H_2O$: V, 13.35%; As, 39.27%; Li, 7.28%; H_2O, 2.36%. Found: V, 13.44%; As, 39.1%; Li, 7.11%; H_2O, 2.12%.

Calculated for $Li_{2.4}Ni_{0.8}VO(AsO_4)_2 \cdot 4H_2O$: V, 10.6%; As, 31.19%; Li, 3.47%; Ni, 9.78%; H_2O, 14.99%. Found: V, 10.6%; As, 31.4%; Li, 3.33%; Ni, 9.67%; H_2O, 14.0%.

Thermal analysis (TGA and DTA) was carried out in air on a Rigaku Thermoflex apparatus at a heating rate of 10 $K \cdot min^{-1}$ with calcined Al_2O_3 as the standard reference. X-ray powder diffraction patterns were obtained with a Siemens D-501 automated diffractometer using graphite-monochromated Cu$K\alpha$ radiation. Infrared spectra were recorded on a Perkin–Elmer 883 spectrometer into a spectral range of 4000–200 cm^{-1} using dry KBr pellet containing 2% of the sample. The diffuse reflectance spectra (UV–vis–near IR) were obtained on a Shimadzu UV-3100 spectrophotometer using an integrating sphere and with $BaSO_4$ as the reference blank.

Results and Discussion

$VO(H_2AsO_4)_2$ (HVAs)

The similarity in the chemical reactivity and other properties shown by $VOPO_4 \cdot 2H_2O$ and $VOAsO_4 \cdot 3H_2O$ led us to believe that the reduction with isobutanol or ethanol of the last compound would lead to $VOH AsO_4 \cdot xH_2O$. Nevertheless, this stoichiometry has not been found in the several attempts we have carried out. The vanadyl arsenate (IV) obtained in these media is $VO (H_2AsO_4)_2$; the V and As dissolved in the reaction medium (isobutanol or ethanol) are found in a V/As ratio of 2.0, whereas the final solid product has a V/As ratio of 0.5, as expected from the equimolar reaction of the starting compound. This seems to indicate that the vanadyl bis-dihydrogenarsenate is the most stable or insoluble solid chemical species. It is quite possible that such a compact structure as shown by $VOH PO_4 \cdot 0.5H_2O$ (6) cannot be obtained when P is substituted by As, due to the As–O distance and the cohesion role that the water molecules had on the phosphate.

If the hypothetical $VOHAsO_4 \cdot 0.5H_2O$ were isostructural with the phosphate, it would have a more open structure that would allow the presence of more water molecules per formula and which therefore could no longer represent the reticular agglutinant function they have in $VOHPO_4$ $0.5H_2O$ (6).

The $VO(H_2AsO_4)_2$ obtained in the reduction of the $VOAsO_4 \cdot 3H_2O$ with isobutanol is quite crystalline and shows an X-ray diffractogram (Fig. 1) that can be indexed in a tetragonal system with cell constants a =

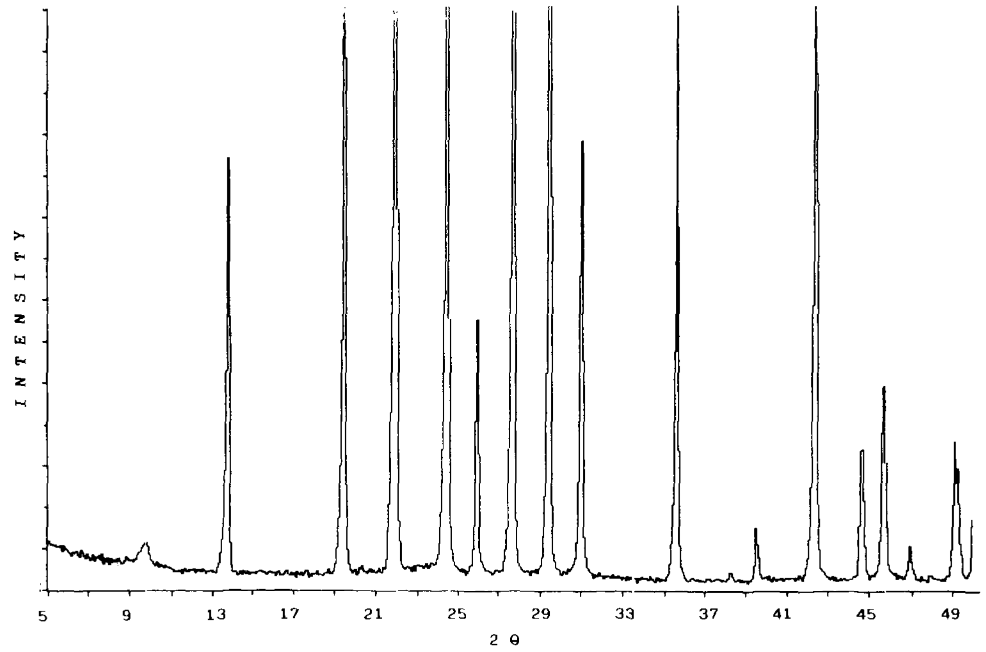


FIG. 1. X-ray diffraction pattern of $VO(H_2AsO_4)_2$.

b = 9.128 Å and c = 8.128 Å, with a figure of merit M_{20} = 92 as seen in Table I. The TG-DTA curves, the infrared spectrum and the X-ray data agree with those obtained by Chernorukov (*8*) from VO_2 and H_3AsO_4.

The diffuse reflectance spectrum in the UV-vis range shows four bands situated at 796, 587, 375, and 254 nm. The latter, of great intensity, falls into the range of the bands of charge transference and it partially overlaps the 375-nm band which appears as a differentiated shoulder (Fig. 2).

The three bands situated in the zone of the visible correspond to a six-coordinated environment with a C_{4v} symmetry of VO^{2+}; the lower energy band (796 nm, $^2B_2 \rightarrow {}^2E$) has the greatest intensity, as it corresponds to a lesser prohibition grade, since the electronic dipole selection rules in C_{4v} symmetry allowing a transition $xz, yz \rightarrow xy$ (*9, 10*); the other two bands are assigned to the forbidden transitions $^2B_2 \rightarrow {}^2B_1$ (587 nm) and $^2B_2 \rightarrow {}^2A_1$ (375 nm).

$Li_4VO(AsO_4)_2 \cdot 0.5H_2O$ (LiVAs)

The substitution of all the protons of HVAs by Li takes place in a neutralization reaction with lithium hydroxide. The reaction must be carried out in acetone/ethanol

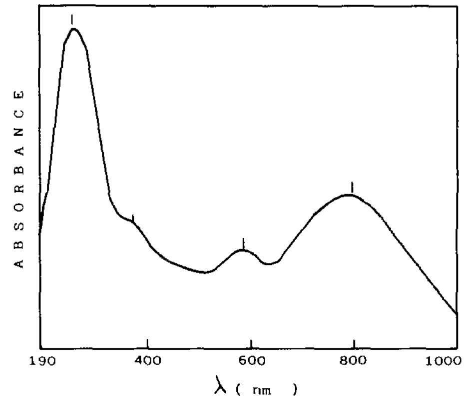


FIG. 2. Diffuse reflectance spectrum of VO $(H_2AsO_4)_2$.

TABLE I

Experimental and Calculated Lattice Spacings and Intensities of $VO(H_2AsO_4)_2$ [Tetragonal, $a = b = 9.1281(2)$ Å; $c = 8.1284(3)$ Å; $V = 677.28$ Å^3] $M_{20} = 92$

d_{obs} (Å)	d_{cal} (Å)	I/I_0	Assignment
6.4537	6.4543	40	110
4.5639	4.5641	58	200
4.0640	4.0642	100	002
3.6483	3.6480	82	211
3.4390	3.4393	22	112
3.2274	3.2273	98	220
3.0352	3.0353	70	202
2.8860	2.8865	40	310
2.5274	2.5273	50	222
2.3534	2.3528	2	312
2.2821	2.2819	6	400
2.1363	2.1361	74	411
2.0320	2.0321	14	004
1.9899	1.9898	19	402
1.9384	1.9383	4	114
1.8563	1.8564	14	204
1.8242	1.8240	6	422
1.7899	1.7902	4	510
1.7812	1.7813	8	501
1.7146	1.7144	27	413
1.6137	1.6136	11	440
1.5654	1.5655	11	530
1.5140	1.5140	9	503
1.4757	1.4757	20	611
1.4609	1.4608	13	532

due to the solubility of the products in water. The reaction can be reversed in the presence of arsenic acid.

The IR spectrum of the Li derivative, together with the starting hydrogenated compound can be seen in Fig. 3 (spectra a and b). The vibration bands associated with the existence of H linked to the AsO_4 groups, present in the dihydrogenarsenate, disappear or are drastically reduced in the lithium compound. Thus, the stretching vibration band $\nu_{sym}AsO_2(OH)_2$ at 745 cm^{-1} (mode ν_1 that becomes active in the IR due to the falling of T_d symmetry of the AsO_4 group, which is presumably a C_{2v} symmetry here) diminishes 90% in its intensity in the lithium compound. The intense band assignable to the bending As–O–H near 1045 cm^{-1} present in the starting compound disappears in the lithium derivative.

On the other hand, it is known (*11*) that an asymmetry in the AsO_4 environment provokes a splitting of the ν_3 vibration, showing both a ν_{sym} and ν_{asym} stretching. The latter is present in the dihydrogenarsenate at 880 cm^{-1} and it is assignable to $\nu_{asym}AsO_2(OH)_2$; in the lithium derivative it changes drastically toward 830 cm^{-1} [$\nu_{asym}AsO_2(OLi)_2$] as was expected, when the covalence of the environment of oxygens diminishes. The symmetric stretching $\nu_{sym}AsO_2$ does not vary in position in the two compounds and is situated toward 905 cm^{-1} like a shoulder.

TABLE II

Experimental and Calculated Lattice Spacings and Intensities of $Li_4VO(AsO_4)_2 \cdot 0.5H_2O$ [Cubic, $a = b = c = 9.0246(11)$ Å; $V = 735.01$ Å^3] $M_{20} = 45$

d_{obs} (Å)	d_{cal} (Å)	I/I_0	Assignment
6.3780	6.3815	9	110
4.5200	4.5124	81	200
4.0360	4.0354	5	120
3.6870	3.6844	100	211
3.1920	3.1907	73	220
3.0090	3.0082	4	300
2.8540	2.8538	29	310
2.7200	2.7210	3	131
2.6060	2.6052	22	222
2.5030	2.5030	3	230
2.4140	2.4120	7	321
2.2560	2.2562	8	400
2.1260	2.1271	51	330
2.0188	2.0180	10	420
1.9243	1.9241	5	332
1.8435	1.8422	7	422
1.7700	1.7699	23	510
1.6480	1.6477	5	521
1.5946	1.5954	5	440
1.5470	1.5477	11	530
1.5037	1.5041	5	600
1.4635	1.4640	20	611
1.4270	1.4269	5	620
1.3933	1.3925	9	541

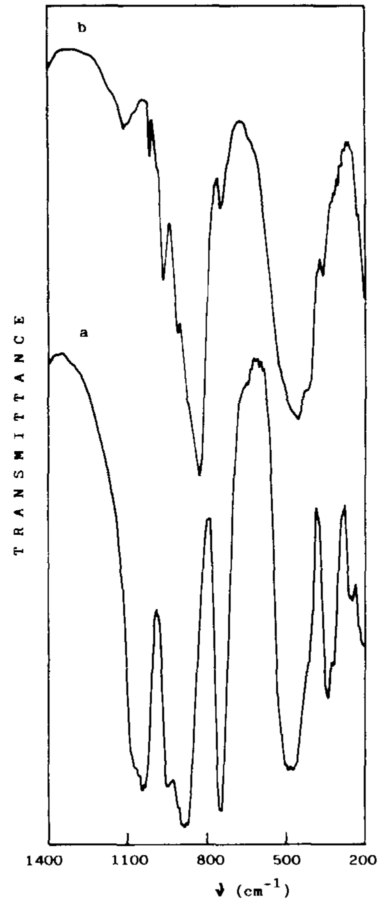


FIG. 3. Infrared spectra: (a) $VO(H_2AsO_4)_2$, (b) $Li_4VO(AsO_4)_2 \cdot 0.5H_2O$.

The mode bending O–As–O is also affected and passes from 492 cm^{-1} in the $VO(H_2AsO_4)_2$ to 460 cm^{-1} in the $Li_4VO(AsO_4)_2 \cdot 0.5H_2O$.

Another characteristic vibration in these compounds is that corresponding to the V=O stretching situated toward 960 cm^{-1} (*4*).

The DTA of this compound (Fig. 4a) shows a slight wide endothermic effect between 40 and 300°C, which is related to a loss of half a water molecule per formula. An exothermic effect occurs at 400°C and can be due to a structural transformation or a migration of the Li ions to thermodynamically more suitable positions. This effect takes place without loss of weight.

$Li_{2.4}Ni_{0.8}VO(AsO_4) \cdot 4H_2O$ (*LiNiVAs*)

The ion exchange Ni/Li in the lithium compound has been monitored by means of chemical analysis and X-ray diffraction. In the first stages of the exchange process, when the load of Ni is less than 0.8 atoms per formula a mixture of crystalline phases which correspond to the starting product and the new nickel derivative are present. The exchange reaction is relatively slow and difficult, and attempts to reverse the reaction have been unsuccessful. This may be due to the fact that the reactants are less soluble than the products.

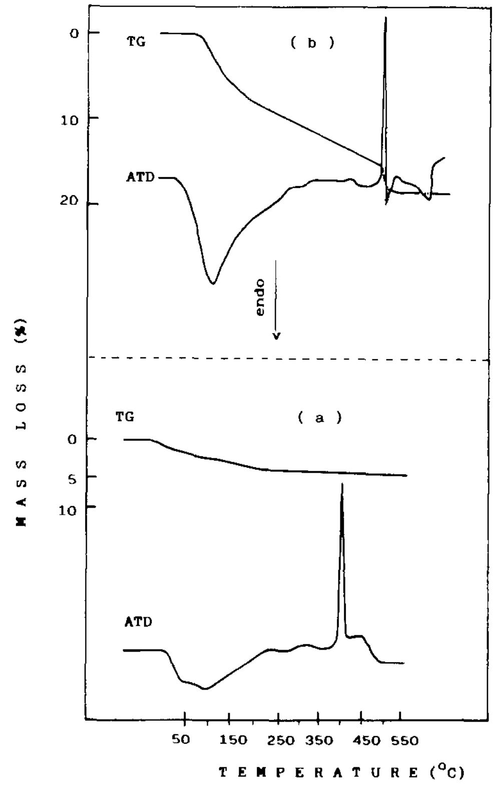


FIG. 4. Thermal analysis (TGA and DTA) of: (a) $Li_4VO(AsO_4)_2 \cdot 0.5H_2O$, (b) $Li_{2.4}Ni_{0.8}VO(AsO_4)_2 \cdot 4H_2O$.

TABLE III

EXPERIMENTAL AND CALCULATED LATTICE SPACINGS AND INTENSITIES OF $Li_{2.4}Ni_{0.8}VO(AsO_4)_2 \cdot 4H_2O$ [TETRAGONAL, $a = b = 9.106(2)$ Å; $c = 8.454(3)$ Å; $V = 700.98$ Å^3] $M_{20} = 40$

d_{obs} (Å)	d_{cal} (Å)	I/I_0	Assignment
6.4382	6.4388	19	110
4.5539	4.5530	28	200
4.2282	4.2269	87	002
3.6694	3.6688	100	211
3.5334	3.5335	16	112
3.2186	3.2195	63	220
3.0979	3.0977	48	202
2.8788	2.8795	40	310
2.5610	2.5611	33	222
2.3173	2.3173	9	213
2.1369	2.1368	63	411
2.1141	2.1135	14	004
2.0352	2.0362	7	420
2.0053	2.0043	10	402
1.9164	1.9170	12	204
1.8803	1.8807	9	323
1.7807	1.7803	8	501
1.7667	1.7668	11	224
1.7385	1.7383	25	413
1.6093	1.6097	10	440
1.5620	1.5617	18	530
1.4743	1.4741	16	611
1.4655	1.4649	17	532

When the Ni stoichiometry is the same or greater than 0.8 atoms per formula a single well-crystallized new phase with a well-defined diffractogram whose profile is similar to that of the HVAs appears. The X-ray diffraction pattern was indexed in the tetragonal system with a very good figure of merit. Loads greater than 0.8 (we have reached up to $Ni_{0.88}$) do not modify the diffractogram.

The IR spectrum of the LiNiVAs compound is similar to that described for the Li derivative (Fig. 3b) and contains the deformation and the stretching bands (δ H_2O, ν OH), being much more intense toward 1625 cm^{-1} and 3330 cm^{-1}, respectively.

The LiNiVAs thermogram is similar to that of Li, with the exception that there is a much clearer endothermic effect in the zone 40–320°C, associated to a loss of weight of 15% due to the greater quantity of water present in this material (Fig. 4b).

In the electronic spectrum of diffuse reflectance we can clearly observe (Fig. 5) the appearance of a wide band centered at 1200 nm that corresponds to one of the expected transitions ($^3A_{2g} \rightarrow {}^3T_{2g}$) of a Ni^{2+} aquocation in an octahedral field. The other transitions cannot be seen since they remain masked by those corresponding to the vanadium, which fall into same zone.

Structural Characteristics

The diffractograms of the three compounds HVAs, LiVAs, and LiNiVAs, appear very similar, indicating that their structures are closely related. These patterns were successfully indexed using the Latt Parm and TREOR programs (*12, 13*) with high figures of merit on primitive tetragonal (HVAs and LiNiVAs) and cubic (LiVAs) cells (Tables I, II, and III). In the case of the lithium compound, LiVAs, the diffractogram contains two amorphous background humps in the angular ranges 21 to 24° and 32–34° (2θ). We have tried to eliminate the amorphous humps by means of more ener-

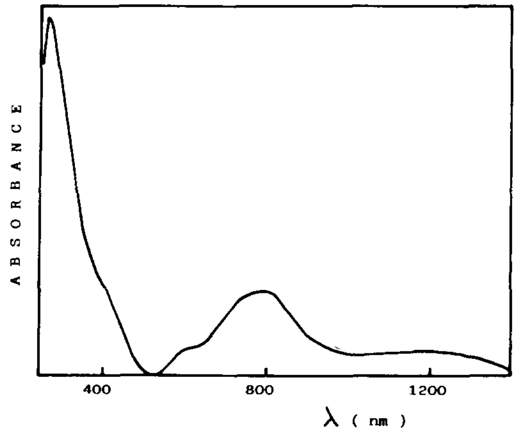
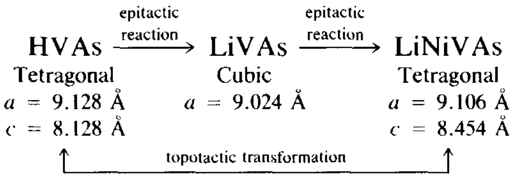


FIG. 5. Diffuse reflectance spectrum of $Li_{2.4}Ni_{0.8}VO(AsO_4)_2 \cdot 4H_2O$.



SCHEME 1

getic washings of the compound and repeated synthesis operations, but have had no success. According to the parameters found, some reflection lines could exist in those zones of the diffractogram, but they can also be due to remains of carbonated lithium hydroxide, which were not separated in the washing with acetone–ethanol.

In any case, the similarity of the *a* and *b* constants of all the compounds (range from 9.02 to 9.13 Å) and the *c* parameter in HVAs and LiNiVAs is outstanding. The value of *c* in LiVAs is also discrepant here, since this compound is indexed in the cubic system, while HVAs and LiNiVAs are tetragonal.

In Scheme 1, the structural transformations that take place in the exchange process are reflected. It is worthy of note that two consecutive epitactic reactions lead to a topotactic transformation with the same symmetry and slight variations in the cell parameters.

The reverse reaction LiNiVAs → LiVAs does not occur. The other reactions shown in Scheme 1 are reversible but a drastic loss of yield is observed due to the solubility of compounds.

In order to accurately resolve the structures and locate the lithium and hydrogen positions, a neutron powder diffraction study is in progress.

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References

1. J. W. JOHNSON, A. J. JACOBSON, J. F. BRODY, AND S. M. RICH, *Inorg. Chem.*, **21,** 3820 (1982).
2. G. CENTI, F. TRIFIRO, J. R. EBNER, AND V. M. FRANCHETTI, *Chem. Rev.* **88,** 55 (1988).
3. M. MARTINEZ-LARA, A. JIMENEZ-LOPEZ, L. MORENO-REAL, S. BRUQUE, B. CASAL, AND E. RUIZ-HITZKY, *Mater. Res. Bull.* **20,** 549 (1988).
4. M. MARTINEZ-LARA, L. MORENO-REAL, A. JIMENEZ-LOPEZ, S. BRUQUE-GAMEZ, AND A. RODRIGUEZ-GARCÍA, *Mater. Res. Bull.* **21,** 13 (1986).
5. G. LADWIG, *Z. Anorg. Allg. Chem.* **338,** 266 (1965).
6. J. W. JOHNSON, D. C. JOHNSTON, A. J. JACOBSON, AND J. F. BRODY, *J. Amer. Chem. Soc.* **106,** 8123 (1984).
7. N. G. CHERNORUKOV, N. P. EDGOROV, AND I. A. KORSHUNOV, *Russ. J. Inorg. Chem.* **23,** 1479 (1978).
8. N. G. CHERNORUKOV, I. A. KORSHUNOV, AND N. P. EDGOROV, *Russ. J. Inorg. Chem.* **23,** 1306 (1978).
9. C. J. BALLHAUSEN AND H. B. GRAY, *Inorg. Chem.* **1,** 111 (1962).
10. A. B. P. LEVER, "Inorganic Electronic Spectroscopy," 2nd Ed., Elsevier, Amsterdam (1984).
11. V. C. FARMER, "The Infrared Spectra of Minerals" (V. C. Farmer, Ed.), Mineralog. Soc., London (1970).
12. R. G. GARVEY, *Powder. Diffr.* **1,** 114 (1986).
13. P. E. WERNER, L. ERIKSSON AND M. WESTDAHL, *J. Appl. Crystallogr.* **18,** 367 (1985).