JOURNAL OF SOLID STATE CHEMISTRY **78**, 206–208 (1989)

The IR Spectra of the $(Cr_xFe_{1-x})VO_4$ Phases*

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Received March 24, 1988; in revised form August 12, 1988

The IR spectra of different solid solutions in the system $(Cr_xFe_{1-x})VO_4$ have been recorded and briefly discussed. They show the vibrational behavior which is characteristic of materials belonging to the α-$MnMoO_4$ structural type. The spectroscopic data are in complete agreement with the recently reported structural behavior of these phases.

Introduction

Although $CrVO_4$ and $FeVO_4$ belong to different structural types (*1, 2*), the solid solutions of composition $(Cr_xFe_{1-x})VO_4$ adopt the α-$MnMoO_4$ structure, which is different from those of the end members of the series (*3*). This behavior is rather unusual and probably represents a compromise between the regularity of the $CrVO_4$ structure and the distorted iron environments in $FeVO_4$.

In recent years we have made systematic studies on the spectroscopic behavior of phases adopting the $CrVO_4$ structural type (*4–6*). Also, the vibrational spectra of $FeVO_4$ and the isostructural $AlVO_4$ have been investigated in detail (*7*). It seems therefore interesting to obtain an insight into the vibrational characteristics of these unusual $(Cr_xFe_{1-x})VO_4$ solid solutions.

Experimental

Polycrystalline samples of composition $(Cr_{0.25}Fe_{0.75})VO_4$, $(Cr_{0.50}Fe_{0.50})VO_4$, and $(Cr_{0.75}Fe_{0.25})VO_4$ were prepared by solid state reactions, as described earlier (*3*). They were characterized by X-ray diffractometry. The powder diagrams show clearly the formation of continuous solid solutions.

The IR spectra were recorded on a Perkin-Elmer 580B spectrophotometer, using the KBr-pellet technique.

Results and Discussion

The IR spectra of the three investigated phases were, as expected, practically iden-

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* Proceedings, 36th Communication of the series "Orthovanadates and Related Compounds"; 35th Commun., see Ref. (*9*).

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0022-4596/89 $3.00

tical and show the spectral pattern which is characteristic of the α-$MnMoO_4$ structural type (cf., for example, (*8*)). As a typical example of these spectra, Fig. 1 shows that corresponding to the phase $(Cr_{0.50}Fe_{0.50})VO_4$. The exact band positions for the three investigated phases are given in Table I.

The only vanadate belonging to this structural type investigated so far is a low-temperature form of $InVO_4$ (*9*). Its spectrum is very similar to that of Fig. 1. The only difference is that in the present cases a doublet is seen around 850 cm^{-1} whereas for $InVO_4$ only one sharp band is observed in this region.

The structure of the mentioned doublet changes slightly with composition, as can be seen in Fig. 2. One may suspect that this splitting and its dependence on the composition could be related in some way to the distribution of the trivalent cations. But, it is not clear why only one of the vanadate-stretching modes is affected in such a dramatic way.

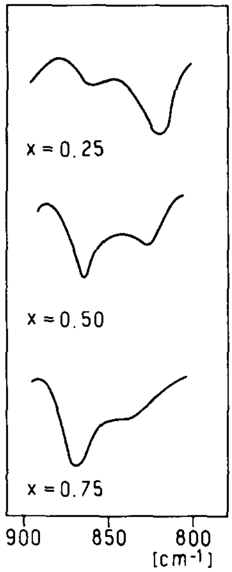

FIG. 2. The 850-cm^{-1} doublet in the $(Cr_xFe_{1-x})VO_4$ phases.

The spectral characteristics of the VO_4^{3-} ion in the α-$MnMoO_4$ environment have been discussed thoroughly in the case of the low-temperature form of $InVO_4$ (*9*). Due to the fact that the anions occupy two different sites in the lattice (C_2 and C_s), a great number of IR-active bands can be expected (six components for the antisymmetric stretching ν_3 and bending ν_4; four for the symmetric bending ν_2 and two for the symmetric stretching ν_1).

The following assignment for the bands

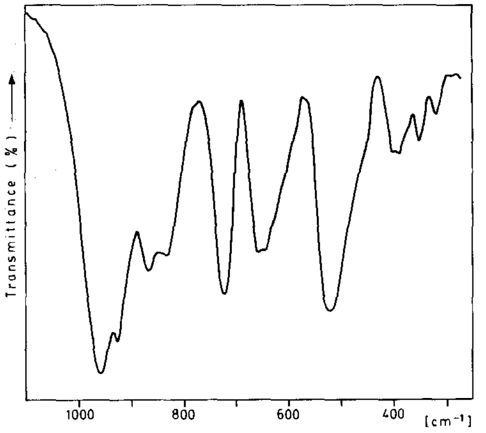

FIG. 1. Infrared spectrum of the phase $(Cr_{0.50}Fe_{0.50})VO_4$.

TABLE I

IR BANDS (cm^{-1}) OF THE THREE INVESTIGATED PHASES

$(Cr_{0.25}Fe_{0.75})VO_4$	$(Cr_{0.50}Fe_{0.50})VO_4$	$(Cr_{0.75}Fe_{0.25})VO_4$
951	956	958
922	924	927
862	865	870
821	830	836
714	720	731
638	650	663
630sh	642sh	635sh
500	518	531
381	400sh 388	416
346	350	353
320	320	320

Note. sh = shoulder.

observed in Fig. 1 can be proposed: the strong or medium intensity bands at 956, 865, 830, 720, and 650 (with a shoulder at 642) cm^{-1} could be the six expected ν_3 components whereas the weaker one, at 924 cm^{-1}, could be one of the two expected ν_1 modes. The strong band at 518 cm^{-1} is assignable to one of the antisymmetric bending components, whereas the remaining bands probably involve VO_4 bendings as well as $M^{III}O_6$ motions.

The great splitting in the stretching region seems to be typical for this structural type and is surely related to the very different V–O distances present in this structure which, for example, in the case of $(Cr_{0.20}Fe_{0.80})VO_4$, covers a range between 1.661 and 1.838 Å (*3*).

As can be seen from the data presented in Table I, practically all equivalent bands are displaced to higher wavenumbers as the unit cell volume diminishes from $(Cr_{0.25}Fe_{0.75})VO_4$ to $(Cr_{0.75}Fe_{0.25})VO_4$. This is the expected trend, which indicates a slight reinforcement of the V–O bonds in the same direction. A fully similar behavior was found and extensively discussed, in the case of the lanthanide orthovanadates, $LnVO_4$, belonging to the zircon structural type (*10, 11*) and in other related phases (*12*).

The commented dependence of the vibrational frequencies on the lattice parameters additionally confirms the formation of a continuous solid solution in the investigated system.

To conclude, this brief spectroscopic study has shown that the phases in the $(Cr_xFe_{1-x})VO_4$ system present a vibrational behavior which is characteristic of the α-$MnMoO_4$ materials. Therefore, the results are coincident with those of the structural studies and also confirm the formation of continuous solid solutions between $CrVO_4$ and $FeVO_4$ in the investigated compositional limits.

Acknowledgments

This work is supported by CONICET and CIC-Provincia de Buenos Aires. This research is also a part of a project devoted to the chemistry and biochemistry of vanadium which is granted by the Foundation "Volkswagenwerk" (Hannover, FRG).

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