JOURNAL OF SOLID STATE CHEMISTRY **65**, 351–355 (1986)

The Nasicon-like Copper(II) Titanium Phosphate $Cu_{0.50}Ti_2(PO_4)_3$

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Received January 20, 1986

$Cu_{0.50}Ti_2(PO_4)_3$ is a Nasicon-type phase with a cooperative Jahn–Teller distortion below 550°C. Crystal field, electron paramagnetic resonance, and magnetic data seem to be consistent with an octahedral surrounding and a $d^1_{x^2-y^2}$ ground state of Cu^{2+}. © 1986 Academic Press, Inc.

Introduction

Nasicon-type ceramics have been extensively studied for a long time as fast sodium ion conductors (*1*, *2*) and more recently as low thermal expansion materials (*3*). Among the members of the Nasicon group the first complete crystal structure investigation has been reported for $NaZr_2(PO_4)_3$ (*4*). The lattice consists of a three-dimensional network made up of PO_4 tetrahedra sharing corners with ZrO_6 octahedra and a three-dimensionally linked interstitial space where sodium atoms may occupy four available positions.

Due to the zeolitic morphology of the skeleton structure copper compounds could be of interest as active catalysts for oxidative deshydrogenation reaction (*5*). Therefore, we have undertaken a general study of copper Nasicon-type phosphates which at present time have been very poorly investigated (*6*). In a previous paper a copper(I) titanium phosphate was described in the scope of a comparison of solid solutions $M_xNb_{1-x}Ti_{1+x}(PO_4)_3$ and $M_{1+x}Cr_xTi_{2-x}(PO_4)_3$ (M = Na, Cu) (*7*). Simultaneously Mbandza *et al.* analyzed in detail some physical properties of $CuTi_2(PO_4)_3$ (*8*).

A recent structural investigation of $CuTi_2(PO_4)_3$ by neutron diffraction confirms that this compound belongs to the Nasicon family: the copper atoms are decentered from the position occupied by the sodium atoms in the octahedral site usually called M1 (*9*).

In this paper the relationships between structure and physical properties of a new copper titanium phosphate $Cu_{0.50}Ti_2(PO_4)_3$ are reported.

Preparation

$Cu_{0.50}Ti_2(PO_4)_3$ has been obtained by oxidation of $CuTi_2(PO_4)_3$ at 500°C:

$$4\ CuTi_2(PO_4)_3 + O_2 \rightarrow 4\ Cu_{0.50}Ti_2(PO_4)_3 + 2\ CuO \quad (1)$$

CuO is removed by washing out shortly the reaction products by a diluted and warm nitric acid solution ($t < 5$ mn). Then the isolated phosphate is filtered, washed

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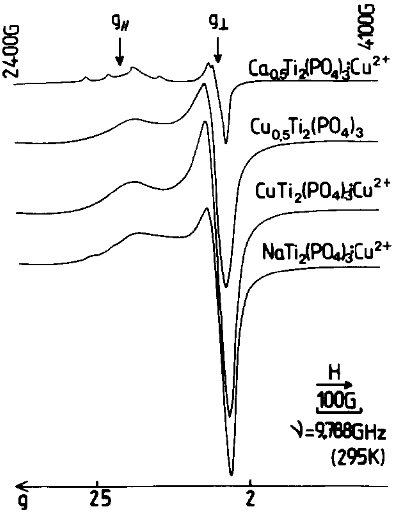

FIG. 1. EPR spectra of $Cu_{0.50}Ti_2(PO_4)_3$ and of some Cu^{2+}-doped titanium phosphates.

with warm water and dried at 600°C for 15 hr. The obtained powder is blue–green.

The oxidation of $CuTi_2(PO_4)_3$ investigated by thermogravimetric analysis corresponds to a weight gain which is perfectly consistent with reaction (1).

The copper rates have been determined by atomic absorption on the one hand in the cupric oxide solution (A) and on the other hand in a solution B obtained by attacking $Cu_{0.50}Ti_2(PO_4)_3$ successively with a mixture of concentrated HF and $HClO_4$ and with aqua regalis and subsequent dilution with water. In both cases the calculated and experimental copper concentrations are in good agreement:

sol. A calcd: 50%, found: 50.6%
sol. B calcd: 50%, found: 50.6%.

Structural Investigation

At room temperature the X-ray diffraction powder pattern can be indexed assuming a monoclinic cell: $a_m = 14.57 \pm 0.02$ Å, $b_m = 8.410 \pm 0.005$ Å, $c_m = 17.52 \pm 0.02$ Å, $\beta = 123.60 \pm 0.02°$. Simple relationships exist between the parameters of the monoclinic cell (m) and those of the usual hexagonal cell (h) of the Nasicon structure:

$$a_m = a_h\sqrt{3},\ b_m = a_h,\ c_m = \tfrac{2}{3}\sqrt{3a_h^2 + c_h^2},\quad \cos(\beta - 90°) = \frac{2c_h}{3c_m}.$$

Accordingly $a_h \simeq 8.41$ Å and $c_h \simeq 21.88$ Å.

There are eight $Cu_{0.50}Ti_2(PO_4)_3$ formula units per unit cell ($d_{exp} = 3.05 \pm 0.01$, $d_{calcd} = 3.07\ g \cdot cm^{-3}$).

A reversible allotropic transition occurs at 550°C. The high temperature variety is rhombohedral and the parameters of the corresponding hexagonal cell (t = 800°C) are $a_h = 8.400 \pm 0.005$ Å, $c_h = 21.90 \pm 0.03$ Å. It seems that the material has a near-zero thermal expansion.

EPR Study

The effect of the local and cooperative Jahn–Teller distortion has been investigated by EPR. The spectrum of $Cu_{0.50}Ti_2(PO_4)_3$ has been compared with those of $NaTi_2(PO_4)_3 : Cu^{2+}$, $Ca_{0.50}Ti_2(PO_4)_3 : Cu^{2+}$, and $CuTi_2(PO_4)_3 : Cu^{2+}$ (Fig. 1).

The EPR parameters collected in Table I show no significant variations with the tita-

TABLE I

EPR PARAMETERS FOR SOME Cu^{2+}-DOPED TITANIUM PHOSPHATES AND FOR $Cu_{0.50}Ti_2(PO_4)_3$

	$g_{\|}$	$g_{\perp}$	g^a	T (K)
$NaTi_2(PO_4)_3$:Cu^{2+}	2.366	2.072	2.174	300
$CuTi_2(PO_4)_3$:Cu^{2+}	2.360	2.060	2.164	300
$Ca_{0.50}Ti_2(PO_4)_3$:Cu^{2+}	2.370	2.060	2.168	300
	2.325	2.061	2.153	4.2
$Cu_{0.50}Ti_2(PO_4)_3$	2.324	2.066	2.155	32
	2.330	2.067	2.158	300

[a] $g = \sqrt{\dfrac{g_{\|}^2 + 2g_{\perp}^2}{3}}$.

nium phosphate composition. Cu^{2+} is located in similar sites characterized by $d_{x^2-y^2}$ ground state, i.e., a $d_{z^2}^2 d_{x^2-y^2}^1$ electronic configuration. The distortion of the coordination octahedron due to face sharing with both adjacent TiO_6 octahedra, induces a cooperative deformation of the whole structure at low temperature. The static character of this distortion vanishes at the temperature structural transition.

Magnetic and Optical Properties

The magnetic susceptibility has been measured between 4.2 and 900 K with a Faraday-type balance (Fig. 2). Below 120 K $\chi^{-1} = f(T)$ is a straight line running through the origin. Above 120 K the curve progressively concaves toward the T axis. This evolution results from the increasing influence of the temperature independent paramagnetism term (TIP). The entire curve fits with the equation:

$$\chi[2Cu_{0.50}Ti_2(PO_4)_3] = \frac{0.432}{T} + 200 \times 10^{-6} \text{ uem CGS.} \quad (2)$$

The diffuse reflection spectrum is compared with those of TiO_2 and of the phosphate $Ca_{0.5}Ti_2(PO_4)_3$ doped or not with Cu^{2+} (Fig. 3).

The spectra can be divided into three regions labeled A, B, C as the energy decreases.

In the A region the charge transfer transition $O^{2-} \rightarrow Ti^{4+}$ has been observed. The corresponding band gaps are TiO_2, 3 eV; $Ca_{0.50}Ti_2(PO_4)_3$ (doped or not with Cu^{2+}), 3.54 eV; and $Cu_{0.50}Ti_2(PO_4)_3$, 3.26 eV.

In the B region a broad additional absorption band arises. It is located between 350 and 600 nm but exists only as far as Cu^{2+} is present. The absorption edge, 2.18 eV, is independent of the phosphate composition.

The C region corresponds to the crystal field transitions for Cu^{2+}. The appearance of an unresolved broad band with a shoulder in the lowest energy region is consistent with a tetragonally distorted coordination octahedron of Cu^{2+} with a possible orthorhombic component.

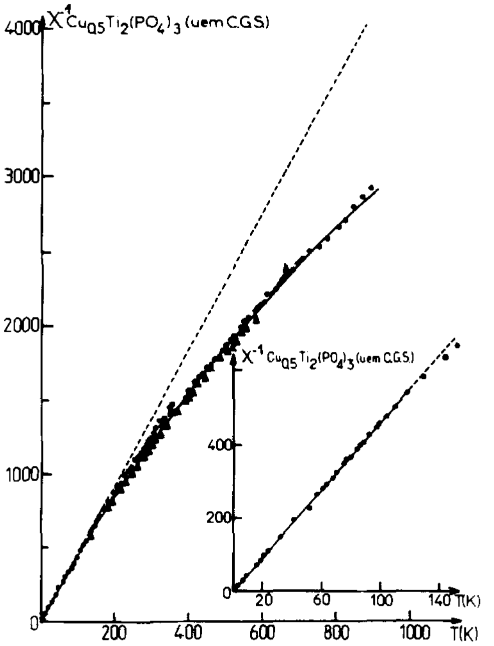

FIG. 2. Thermal variation of the reciprocal susceptibility of $Cu_{0.50}Ti_2(PO_4)_3$ (solid curve corresponds to Eq. (2)).

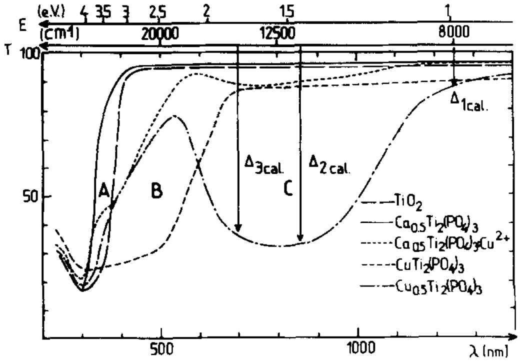

FIG. 3. Diffuse reflection spectra of TiO_2, $CuTi_2(PO_4)_3$, $Cu_{0.50}Ti_2(PO_4)_3$, and $Ca_{0.50}Ti_2(PO_4)_3$ doped or not with Cu^{2+}.

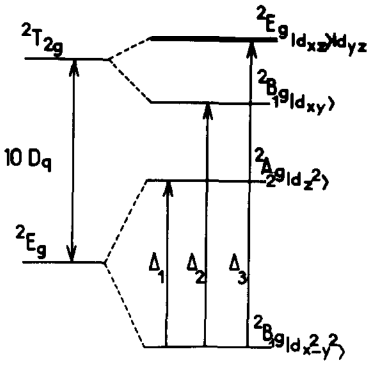

FIG. 4. Energy level diagram of Cu^{2+} in $Cu_{0.50}Ti_2(PO_4)_3$ assuming a tetragonally elongated octahedral environment.

Discussion

TiO_2 has a Ti $3d$ conduction band edge at 3 eV above the O^{2-} $2p^6$ valence band (*10*). The band gap increase observed for the phosphates results from the structural features of the Nasicon-type structure in the covalent skeleton, all oxygen atoms are connected with both PO_4 and TiO_6 groups. The strong covalent character of the P–O bonds stabilizes the O^{2-} $2p$ band and in the copper-free phosphates, E_g shows a similar increase, i.e., about 0.5 eV. The band gap width, 3.26 eV, found for $Cu_{0.50}Ti_2(PO_4)_3$ is probably a consequence of the Cu^{2+} surrounding which is able to bring about a cooperative distortion of the TiO_6 octahedra.

The absorption band in the B region may be the result of two mechanisms:

(i) a $Cu^{2+} \rightarrow Ti^{4+}$ charge transfer formally formulated as

$$Cu^{2+}(d^1_{x^2-y^2}) + Ti^{4+}(d^0) \rightarrow Cu^{3+}(d^0_{x^2-y^2}) + Ti^{3+}(d^1_{t2g})$$

(ii) a $O^{2-} \rightarrow Cu^{2+}$ charge transfer:

$$O^{2-}(2p^6) + Cu^{2+}(d^1_{x^2-y^2}) \rightarrow O^{-}(2p^5) + Cu^{+}(d^2_{x^2-y^2})$$

As observed by Blasse and Dirksen (*11*) for the charge transfer of type $M^{n+} \rightarrow Ti^{4+}$, the ionization potential value of M^{n+} can be used as a rough reference to predict the energy of the transition: the $Cu^+ \rightarrow Ti^{4+}$ transition energy must occur at a lower energy than the $Cu^{2+} \rightarrow Ti^{4+}$ one. The optical band gap of $CuTi_2(PO_4)_3$ (Fig. 3) is about 1.77 eV. The valence band edge consists of the $3d^{10}$ orbitals of Cu^+ and the interband transition corresponds to the charge transfer:

$$Cu^+(3d^{10}) + Ti^{4+}(3d^0) \rightarrow Cu^{2+}(3d^9) + Ti^{3+}(3d^1)$$

As a consequence the absorption edge value found in the B region is consistent for $Cu_{0.50}Ti_2(PO_4)_3$ with mechanism (i), but the mechanism (ii) cannot be completely excluded.

The thermal variation of the magnetic susceptibility of $Cu_{0.50}Ti_2(PO_4)_3$ precludes magnetic interactions between Cu^{2+} nearest neighbors, so that the EPR parameters have to be discussed within the context of local deformation of the copper sites.

The energy level diagram of Cu^{2+} with a $d_{x^2-y^2}$ ground state configuration, assuming an elongated tetragonal distortion of the octahedral site is given in Fig. 4. The $d_{x^2-y^2}$ orbital contains the unpaired electron. For such a geometry $g_\parallel$ and $g_\perp$ are related to the spin-orbit coupling λ and to the transitions Δ_2 and Δ_3 by the expressions (*12*)

$$g_\parallel = g_e - \frac{8k_\parallel^2\lambda}{\Delta_2(^2B_{1g} \rightarrow {}^2B_{2g})}$$

$$g_\perp = g_e - \frac{2k_\perp^2\lambda}{\Delta_3(^2B_{1g} \rightarrow {}^2E_g)}$$

where $k_\parallel$ and $k_\perp$ are the respective orbital reduction factors.

The center of the shoulder of the reflection spectrum in the C region may be assigned to the $\Delta_3(^2B_{1g} \rightarrow {}^2A_{1g})$ transition with $\Delta_3 \simeq 8000\ cm^{-1}$. This value is of the same order of magnitude as those found for oxides containing tetrahedral groups such as SiO_4, SO_4, etc. (*12*). The $g_\parallel$ and $g_\perp$ values allow us to give an estimate of the four quantities $k_\parallel$, $k_\perp$, Δ_2, and Δ_3 which must be in agreement with the crysal field absorption band (i.e., in the C region). We find: $k_\parallel = k_\perp \simeq 0.75$, $\Delta_2 \simeq 11.700\ \mathrm{cm}^{-1}$, $\Delta_3 \simeq 14.300\ \mathrm{cm}^{-1}$.

By introducing those values in the usual relations giving the thermal variation of the magnetic susceptibility for Cu^{2+} in a tetragonally elongated octahedron (*12*), i.e.,

$$\chi_\parallel = \frac{N\beta^2}{3k_BT} \cdot 3\left(1 - \frac{4k_\parallel\lambda}{\Delta_2}\right)^2 + \frac{8N\beta^2k_\parallel^2}{\Delta_2}$$

$$\chi_\perp = \frac{N\beta^2}{3k_BT} \cdot 3\left(1 - \frac{k_\perp\lambda}{\Delta_3}\right)^2 + \frac{2N\beta^2k_\perp^2}{\Delta_3}$$

$$\chi = \tfrac{1}{3}\chi_\parallel + \tfrac{2}{3}\chi_\perp$$

where the constants have their classical values, the calculated susceptibility for 2 $Cu_{0.50}Ti_2(PO_4)_3$ becomes

$$\chi = \frac{0.456}{T} + 47 \times 10^{-6}\ \text{uem CGS}.$$

The experimental and calculated Curie constants are in good agreement. On the other hand the calculated TIP term is about four times lower than the experimental one. This difference has not yet been explained and a parallel investigation of the isomorphous phosphate $Cu_{0.50}Zr_2(PO_4)_3$ is in progress.

Nevertheless the following remarks can be formulated:

(1) The magnitude of the k and Δ_i ($i = 1, 2, 3$) parameters obtained from both EPR and diffuse reflection spectra are close to those generally found for such materials (*14, 15*).

(2) On the contrary different numerical simulations taking into account the measured TIP term have led to k and/or Δ_i parameters without physical meaning.

Finally the problem of the existence of a solid solution $Cu_{0.5+x}Ti_2(PO_4)_3$ in which Cu^+ and Cu^{2+} coexist is still opened and will require appropriate investigation.

References

1. J. B. GOODENOUGH, H. Y-P. HONG, AND J. KAFALAS, *Mater. Res. Bull.* **11**, 203 (1976).
2. Proceed. Int. Conf. on Fast Ion Transport in Solids, Lake Geneva (P. VASHISHTA, J. N. MUNDY, AND G. K. SHENOY, Eds.), North-Holland, Amsterdam (1979).
3. J. ALAMO AND R. ROY, *J. Amer. Ceram. Soc.* No. 5, C78 (1984).
4. L. HAGMAN AND P. KIERKEGAARD, *Acta Chem. Scand.* **22**, 1822 (1968).
5. A. CLEARFIELD AND S. P. PACK, *J. Catal.* **51**, 431 (1978).
6. P. C. YAO AND D. J. FRAY, *Solid State Ionics* **8**, 35 (1983).
7. A. EL JAZOULI, A. SERGHINI, R. BROCHU, J. M. DANCE, AND G. LE FLEM, *C.R. Acad. Sci. (Paris)* **300**, No. 11, 493 (1985).
8. A. MBANDZA, E. BORDES, AND P. COURTINE, *Mater. Res. Bull.* **20**, 251 (1985).
9. J. L. SOUBEYROUX, A. EL JAZOULI, AND G. LE FLEM, *Mater. Res. Bull.*, in press.
10. K. MIZUSHIMA, M. TANAKA, AND S. IIDA, *J. Phys. Soc. Japan* **32**, 1519 (1972).
11. G. BLASSE AND G. G. DIRKSEN, *Chem. Phys. Lett.* **77**, No. 1, **9** (1981).
12. F. MABBS AND D. J. MACHIN, "Magnetism and Transition Metal Complexes," Chapman & Hall, London (1973).
13. O. SCHMITZ-DUMONT, H. FENDEL, M. HASSANEIN, AND H. WEISSENFELD, *Mh. Chem.* **97**, 1661 (1966).
14. N. SATYANARYANA AND S. RADHAKRISHNA, *Solid State Commun.* **54**, 981 (1985).
15. D. REINEN AND C. FREIBEL, Structure Bonding **37**, (1979).