

The Nasicon-like Copper(II) Zirconium Phosphate $\text{Cu}_{0.5}\text{Zr}_2(\text{PO}_4)_3$ and Related Compounds

A. EL JAZOULI,* M. ALAMI,† R. BROCHU,† J. M. DANCE,*
G. LE FLEM,* AND P. HAGENMULLER*

*Laboratoire de Chimie du Solide du CNRS, Université de Bordeaux I, 351
Cours de la Libération, 33405 Talence Cedex, France; and †Département de
Chimie, Faculté des Sciences, Université Mohamed V, Avenue Ibn Batouta,
Rabat, Maroc

Received October 29, 1986

A new family of Nasicon-like zirconium phosphates of formula $M_{0.5}\text{Zr}_2(\text{PO}_4)_3$ with $M = \text{Ca}, \text{Cu}, \text{Sr}, \text{Cd}$ or Pb has been described. The physical properties of the copper compound have been investigated in detail in which Cu^{2+} induces a Jahn-Teller distortion below 520°C . Crystal field, electron paramagnetic resonance, and magnetic data are consistent with an elongated octahedral surrounding of the Cu^{2+} ions. © 1987 Academic Press, Inc.

The Nasicon structure has been initially described by Hagman and Kierkgaard (1) for the $\text{NaA}_2(\text{PO}_4)_3$ ($A = \text{Ge}, \text{Ti}, \text{Zr}$) phosphates. The crystal structure consists of a three-dimensional network formed by PO_4 tetrahedra sharing corners with MO_6 octahedra. The site occupied by sodium is a distorted octahedron formed by triangular faces of two AO_6 octahedra along the c -axis of the hexagonal cell. This site is usually called M_1 .

Materials belonging to this structural family have been extensively studied for a long time as fast sodium ion conductors (2, 3) and low thermal expansion ceramics (4). Recently we have undertaken a general study of the copper compounds belonging to this structural family. Up until now the following phases have been successively described: $\text{CuZr}_2(\text{PO}_4)_3$ (5), $\text{CuTi}_2(\text{PO}_4)_3$ (6), $\text{Cu}_x\text{Nb}_{1-x}\text{Ti}_{1+x}(\text{PO}_4)_3$, and $\text{Cu}_{1+x}\text{Cr}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ (7). More recently it has been shown

that the oxidation of $\text{CuTi}_2(\text{PO}_4)_3$ leads to $\text{Cu}_{0.5}\text{Ti}_2(\text{PO}_4)_3$ which is also a Nasicon-type phase with a cooperative Jahn-Teller distortion below 550°C (8). Such an evolution which does not alter the covalent $\text{Ti}_2(\text{PO}_4)_3$ network could induce catalytic properties for oxidative-dehydrogenation reactions.

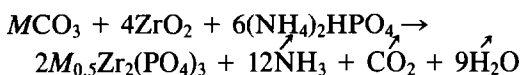
In this context we report here the oxidation reaction of $\text{CuZr}_2(\text{PO}_4)_3$ which leads, in a parallel way, to formation of $\text{Cu}_{0.5}\text{Zr}_2(\text{PO}_4)_3$. This new compound is characterized by its structural, magnetic, and optical features. An accurate analysis of the optical properties by diffuse reflectance technique in the visible and the UV needs identification of possible electronic transfer mechanisms and involves a comparison with similar copper-free zirconium phosphate such as $M_{0.5}\text{Zr}_2(\text{PO}_4)_3$ ($M = \text{Ca}, \text{Sr}, \text{Cd},$ or Pb). Thus two new phosphates have been obtained: $\text{Cd}_{0.5}\text{Zr}_2(\text{PO}_4)_3$ and $\text{Pb}_{0.5}\text{Zr}_2(\text{PO}_4)_3$.

TABLE I
CHEMICAL ANALYSIS OF
 $\text{Cu}_{0.5}\text{Zr}_2(\text{PO}_4)_3$

	$\frac{\text{Cu}}{\text{Zr}}$	$\frac{\text{Cu}}{\text{P}}$	$\frac{\text{Zr}}{\text{P}}$
Exp.	0.27	0.18	0.66
Calc.	0.25	0.17	0.67

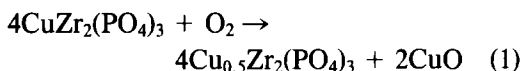
I. Preparation

The copper-free phosphates $M_{0.5}\text{Zr}_2(\text{PO}_4)_3$ ($M = \text{Ca}, \text{Sr}, \text{Cd}, \text{Pb}$) have been obtained from a stoichiometric mixture of $M\text{CO}_3$, ZrO_2 , and $(\text{NH}_4)_2\text{HPO}_4$. The corresponding reaction is



The mixtures were heated at 400°C for 24 hr; then at 800°C for 24 hr, and finally at 1350°C for 48 hr in air.

$\text{Cu}_{0.5}\text{Zr}_2(\text{PO}_4)_3$ has been obtained by oxidation of $\text{CuZr}_2(\text{PO}_4)_3$ at 500°C under oxygen:



$\text{CuZr}_2(\text{PO}_4)_3$ was prepared by a method previously described by Serghini (9) by heating a stoichiometric mixture of ZrP_2O_7 , ZrO_2 , and Cu_2O .

CuO coming from reaction (1) is removed

by washing out briefly the reaction products by diluted and warm nitric acid solution ($t < 5$ mn). The isolated phosphate is then filtered, washed with warm water, and dried at 600°C for 15 hr. A chemical analysis (Table I) gives a composition close to the theoretical value corresponding to $\text{Cu}_{0.5}\text{Zr}_2(\text{PO}_4)_3$. All $M_{0.5}\text{Zr}_2(\text{PO}_4)_3$ phases are white except the copper compound which is blue-green.

II. Structural Investigation

The X-ray diffraction patterns of the copper-free phosphates can be indexed assuming a rhombohedral cell. The parameters of the equivalent hexagonal cells are given in Table II. The order of magnitude of the data involves a Nasicon-type structure with a space group $R\bar{3}2$ different from that of $\text{NaZr}_2(\text{PO}_4)_3$ $R\bar{3}c$ due to the presence of additional reflexions, $h0l$, $0kl:l = 2n + 1$ and $00l:l = 3n$. There are six $M_{0.5}\text{Zr}_2(\text{PO}_4)_3$ formula units per unit cell. The experimental and calculated densities are given in Table II.

At room temperature the X-ray diffraction pattern of $\text{Cu}_{0.5}\text{Zr}_2(\text{PO}_4)_3$ can be indexed assuming a monoclinic cell:

$$\begin{aligned} a_m &= 15.31 \pm 0.04 \text{ \AA} \\ b_m &= 8.84 \pm 0.02 \text{ \AA} \\ c_m &= 18.29 \pm 0.05 \text{ \AA} \\ \beta &= 123.90 \pm 0.02^\circ \end{aligned}$$

TABLE II
CRYSTALLOGRAPHIC DATA FOR THE $M_{0.5}\text{Zr}_2(\text{PO}_4)_3$ PHOSPHATES
($M = \text{Ca}, \text{Cu}, \text{Sr}, \text{Cd}, \text{Pb}$)

$M_{0.5}\text{Zr}_2(\text{PO}_4)_3$	$a_h \pm 0.02 \text{ \AA}$	$c_h \pm 0.02 \text{ \AA}$	$V \pm 5 \text{ \AA}^3$	$d_{\text{calc.}}$	$d_{\text{exp.}} \pm 0.02$
$M = \text{Cd}$	8.85	22.28	1511	3.45	3.41
$M = \text{Ca} (15)$	8.80	22.60	1516	3.20	3.14
$M = \text{Sr} (16)$	8.70	23.38	1532	3.32	3.24
$M = \text{Pb}$	8.70	23.42	1532	3.71	3.66
$M = \text{Cu}$	8.84	22.77	1540	3.23	3.24

TABLE III
CRYSTALLOGRAPHIC DATA FOR THE
 $MZr_2(PO_4)_3$ PHOSPHATES
($M = Li, Na, K, Rb, Cs$)

$MZr_2(PO_4)_3$	a (Å)	c (Å)	V (Å ³)
$M = Li$	8.843	22.286	1509
$M = Na$	8.815	22.749	1530
$M = K$	8.720	23.94	1575
$M = Rb$	8.66	24.38	1582
$M = Cs$	8.62	24.86	1600

Simple relationships exist between the parameters of the monoclinic cell (m) and those of the usual hexagonal cell (h): $a_m = a_h\sqrt{3}$, $b_m = a_h$, $c_m = 2/3\sqrt{3a_h^2 + c_h^2}$, $\cos(\beta - 90^\circ) = (2/3)(c_h/c_m)$. Accordingly, $a_h = 8.84$ Å; $c_h = 22,76$ Å.

There are eight $Cu_{0.5}Zr_2(PO_4)_3$ formula units per unit cell ($d_{exp.} = 3.24 \pm 0.02$ g cm⁻³, $d_{calc.} = 3.23$ g cm⁻³).

A reversible allotropic transition occurs at 520°C. The high temperature variety is rhombohedral and the parameters of the corresponding hexagonal cell (at 800°C) are: $a_h = 8.84 \pm 0.04$ Å, $c_h = 22.77 \pm 0.05$ Å. $Cu_{0.5}Zr_2(PO_4)_3$ has a near-zero thermal expansion.

All these results can be analyzed within the scope of the structural data characterizing the Nasicon-type phosphates.

Assuming that the divalent cations occupy generally half of the M_1 sites, the following distinguishes the copper phosphate from the others.

When $M = Ca, Sr, Cd,$ or Pb , a size increase of the divalent ion leads to increasing c -parameters and decreasing a -parameters. Such an evolution usually observed in Nasicon-type phosphates (10) has been detected for instance for the zirconium series: $MZr_2(PO_4)_3$ ($M = Li, Na, K, Rb, Cs$) (11) (Table III). The M_1 coordination polyhedron shares two faces with adjacent ZrO_6 octahedra along the c -axis. Occupancy by a larger ion leads to a higher

c -value. Due to the elastic character of the network this expansion results in a correlative decrease of a .

Due to the lack of detailed information concerning the structure of $Cu_{0.5}Zr_2(PO_4)_3$, it is difficult to explain the rather large value of the unit cell volume. This anomaly has also been observed for $Cu_{0.5}Ti_2(PO_4)_3$ (8). Nevertheless the local surrounding of Cu^{2+} has been investigated by electron paramagnetic resonance (EPR).

The EPR spectrum of $Cu_{0.5}Zr_2(PO_4)_3$ is compared with those of $Cu_{0.5}Ti_2(PO_4)_3$ (8) and $CuZr_2(PO_4)_3 : Cu^{2+}$ in Fig. 1. The EPR data collected in Table IV show no significant evolution with the variation of the phosphate composition. The Cu^{2+} are located in a similar site characterized by a $d_{z^2}^2d_{x^2-y^2}^1$ electronic configuration. The Jahn-Teller distortion involves an elongated CuO_6 octahedron with two large and four short $Cu-O$ bonds. For $Cu_{0.5}Zr_2(PO_4)_3$ a new EPR shoulder appears centered at $g' = (g_{||} + g_{\perp})/2$ ($g_{||}$ and g_{\perp} are the axial components of the g tensor). According to Reinen (12), it could be due to dipolar magnetic interactions between two nearest

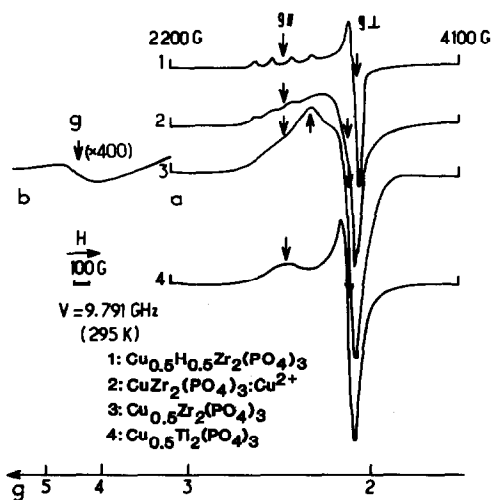


FIG. 1. EPR spectra of $Cu_{0.5}Zr_2(PO_4)_3$ and of some copper Nasicon-like phosphates.

TABLE IV
EPR PARAMETERS FOR SOME COPPER NASICON-TYPE PHOSPHATES

	$g_{\parallel z}$	$g_{\perp x}$	$g_{\perp y}$	g^*	$A_{\parallel} (G)$	$A_{\perp x} (G)$	$A_{\perp y} (G)$
$\text{Cu}_{0.5}\text{Zr}_2(\text{PO}_4)_3$	2.371	2.079	2.079	2.181		No observed	
$\text{CuZr}_2(\text{PO}_4)_3 : \text{Cu}^{2+}$	2.345	2.074	2.074	2.168	126	19.4	19.4
$\text{Cu}_{0.5}\text{H}_{0.5}\text{Zr}_2(\text{PO}_4)_3 : \text{Cu}^{2+}$	2.359	2.063	2.069	2.168	118	13.9	13.3
$\text{Cu}_{0.5}\text{Ti}_2(\text{PO}_4)_3$	2.33	2.067	2.067	2.153		No observed	

Note. $g^* = \sqrt{(g_z^2 + g_x^2 + g_y^2)}/3$.

neighboring Cu^{2+} ions. This hypothesis is corroborated by the detection of a weak and relatively broad line ($g'' = 4.37$) at half field (Fig. 1). This half field line can be assigned to a $\Delta m_s = 2$ transition which results from copper pair interactions. Thus a certain proportion of Cu^{2+} is probably not located in M_1 but within the large size vacancies in the $3d$ -covalent framework. The rate of these shifted Cu^{2+} ions is however very low, as shown later by the magnetic study (Sect. IV).

III. Optical Properties

The diffuse reflectance spectra have been recorded for all $M_{0.5}\text{Zr}_2(\text{PO}_4)_3$ investigated

phases (Fig. 2). The spectra of the copper-free phosphates exhibit a single absorption band at about 245 nm (5.06 eV). The location of the maximum is independent of the nature of cation. The spectra are similar to those of $\text{NaZr}_2(\text{PO}_4)_3$ and ZrP_2O_7 , where zirconium also occupies oxygen octahedra. The absorption can be assigned thus to an electronic $\text{O}^{2-} \rightarrow \text{Zr}^{4+}$ transfer.

The spectrum of $\text{Cu}_{0.5}\text{Zr}_2(\text{PO}_4)_3$ is more complex. It also shows at about 250 nm a broad absorption band (I) with a rather broad maximum, but in addition a large band (II) located between 500 and 1300 nm corresponding to the crystal field transitions of Cu^{2+} .

The diffuse reflectance spectra of Cu_2

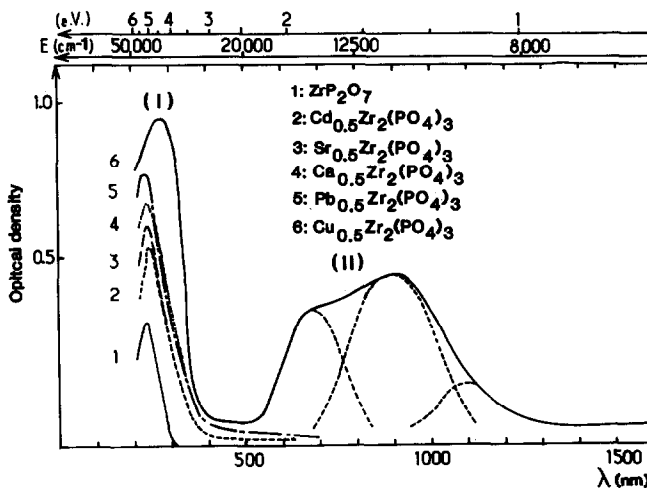


FIG. 2. Diffuse reflection spectra of ZrP_2O_7 and of $M_{0.5}\text{Zr}_2(\text{PO}_4)_3$ ($M = \text{Ca}, \text{Cu}, \text{Sr}, \text{Cd}, \text{Pb}$).

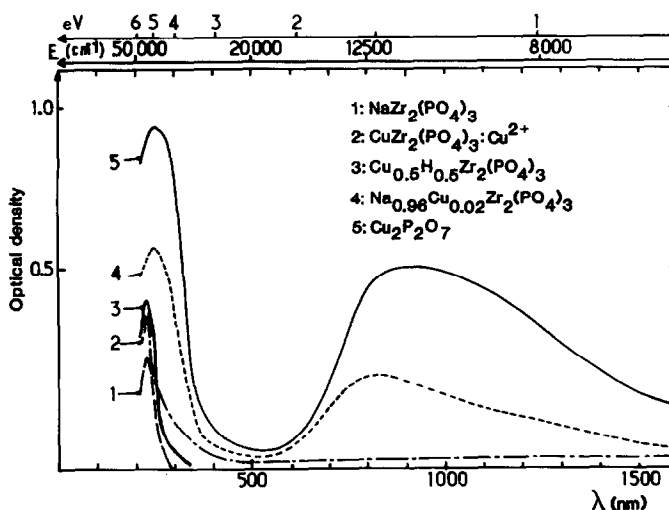


FIG. 3. Diffuse reflection spectra of $\text{Cu}_2\text{P}_2\text{O}_7$ and of zirconium Nasicon-type phosphates containing different Cu^{2+} rates.

$\text{P}_2\text{O}_7\alpha$ and of several zirconium phosphates are given in Fig. 3. The spectrum of the copper pyrophosphate exhibits a band overlapping the (I) region of Fig. 2. Curves 2 and 3 of Fig. 3 concern materials without Cu^{2+} or only doped with Cu^{2+} and display sharp bands at 230 nm, whereas curve 4, established for a Cu^{2+} -rich material, exhibits clear broadening of this band. As a consequence one may assume that band (I) of $\text{Cu}_{0.5}\text{Zr}_2(\text{PO}_4)_3$ corresponds to both $\text{O}^{2-} \rightarrow \text{Cu}^{2+}$ and $\text{O}^{2-} \rightarrow \text{Zr}^{4+}$ transfers.

This conclusion has been confirmed by following experience. By the action of hydrogen on $\text{Cu}_{0.5}\text{Zr}_2(\text{PO}_4)_3$ at 400°C we obtain a new Nasicon-type phosphate with composition close to $\text{Cu}_{0.5}\text{H}_{0.5}\text{Zr}_2(\text{PO}_4)_3$, the EPR and diffuse reflectance spectra of which are given in Figs. 1 and 3, respectively. The presence of an EPR hyperfine structure is consistent with the low rate of remaining Cu^{2+} (<5%). The width of band (I) is strongly reduced and the location of its maximum has been detected at 228 nm, a value very close to those observed for the ZrP_2O_7 and $M_{0.5}\text{Zr}_2(\text{PO}_4)_3$ compounds ($M \neq \text{Cu}$).

IV. Magnetic Study

The magnetic susceptibility of $\text{Cu}_{0.5}\text{Zr}_2(\text{PO}_4)_3$ has been measured between 4.2 and 900 K with a Faraday-type balance (Fig. 4). At low temperature $\chi^{-1} = f(T)$ is a straight line running through the origin. Above 120 K the curve progressively becomes concave toward the T -axis. This evolution results from the increasing influence of the temperature-independent paramagnetism term (TIP). The whole magnetic curve fits with equation

$$\chi[2\text{Cu}_{0.5}\text{Zr}_2(\text{PO}_4)_3] = \frac{0.452}{T} + 100 \cdot 10^{-6} \text{ uem CGS.} \quad (1)$$

V. Discussion

The properties of $\text{Cu}_{0.5}\text{Zr}_2(\text{PO}_4)_3$ are very similar to those of $\text{Cu}_{0.5}\text{Ti}_2(\text{PO}_4)_3$. The main difference results from the location of the $\text{O}^{2-} \rightarrow \text{Zr}^{4+}$ electronic transfer, which occurs as expected at higher energy than the $\text{O}^{2-} \rightarrow \text{Ti}^{4+}$ one (4.13 eV) (δ). This difference reflects the more ionic character of the

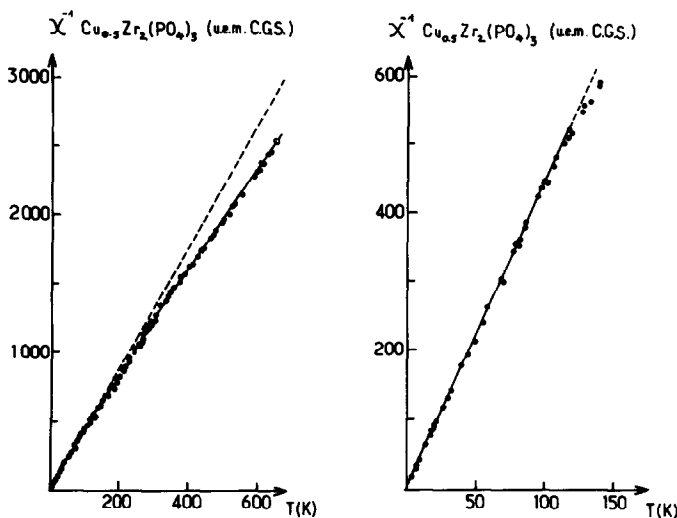


FIG. 4. Thermal variation of the reciprocal susceptibility of $\text{Cu}_{0.5}\text{Zr}_2(\text{PO}_4)_3$ (the solid curve corresponds to Eq. (1)).

Zr–O bond. The thermal variation of $\text{Cu}_{0.5}\text{Zr}_2(\text{PO}_4)_3$ magnetic susceptibility precludes magnetic interactions between Cu^{2+} nearest neighbors (except some above-mentioned dipolar magnetic interactions due to the limited presence of copper pairs).

The energy level diagram of Cu^{2+} with a $d_{x^2-y^2}$ configuration, assuming an elongated tetragonal distortion of the octahedral M_1 site is given in Fig. 5. For such a geometry g_{\parallel} and g_{\perp} are related to the spin-orbit coupling λ_0 and to the transition energies Δ_2 and Δ_3 by the expressions (13)

$$g_{\parallel} = g_e - \frac{8k^2\lambda_0}{\Delta_2(2B_{1g} \rightarrow 2B_{2g})} \quad (2)$$

$$g_{\perp} = g_e - \frac{2k^2\lambda_0}{\Delta_3(2B_{1g} \rightarrow 2E_g)} \quad (3)$$

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

Absorption band II can be divided into three components, the maxima of which correspond respectively to $\Delta_1 = 9260 \text{ cm}^{-1}$, $\Delta_2 = 11,300 \text{ cm}^{-1}$, and $\Delta_3 = 14,290 \text{ cm}^{-1}$. These values are comparable to those

found for $\text{Cu}_{0.5}\text{Ti}_2(\text{PO}_4)_3$: $\Delta_1 = 8000 \text{ cm}^{-1}$, $\Delta_2 = 11,700 \text{ cm}^{-1}$, and $\Delta_3 = 14,300 \text{ cm}^{-1}$ (8).

The g_{\parallel} and g_{\perp} values obtained from Eqs. (2) and (3) allow us to estimate the orbital reduction factors: $k_{\parallel} = 0.79$ and $k_{\perp} = 0.82$.

By introducing those values in the usual relations giving the thermal variation of the magnetic susceptibility for Cu^{2+} and using

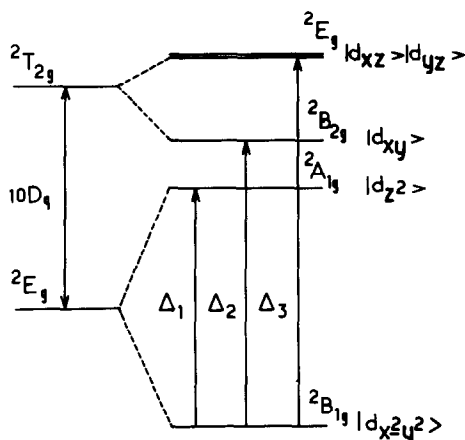


FIG. 5. Energy level diagram of Cu^{2+} in $\text{Cu}_{0.5}\text{Zr}_2(\text{PO}_4)_3$ assuming a tetragonally elongated octahedra environment.

$\lambda_0 = -830 \text{ cm}^{-1}$ (13), the calculated susceptibility for $2\text{Cu}_{0.5}\text{Zr}_2(\text{PO}_4)_3$ becomes

$$\chi[2\text{Cu}_{0.5}\text{Zr}_2(\text{PO}_4)_3] = \frac{0.464}{T} + 55.10^{-6} \text{ uem CGS.}$$

The experimental and calculated values are thus in good agreement and very close to those determined for the titanium phosphate (8):

$$\chi[2\text{Cu}_{0.5}\text{Ti}_2(\text{PO}_4)_3] = \frac{0.456}{T} + 47.10^{-6} \text{ uem CGS.}$$

VI. Conclusion and Prospects

This paper describes the basic properties of a new Nasicon-derived phosphate $\text{Cu}_{0.5}\text{Zr}_2(\text{PO}_4)_3$. The compound has been characterized by its optical and magnetic properties. A more detailed structural study is actually achieved by neutron diffraction.

The presence of several types of vacancies within the lattice and the ability of Cu^{2+} to be easily reduced suggest the possibility of catalytic properties. Thus a reversible intercalation of hydrogen has been observed and the obtained phase has a composition close to $\text{Cu}_{0.5}\text{H}_{0.5}\text{Zr}_2(\text{PO}_4)_3$ (14). The reduction of Cu^{2+} to Cu^+ leads to color change in removing the $\text{O}^{2-} \rightarrow \text{Cu}^{2+}$ electronic transfer band from the absorption spectrum (Fig. 3) and induces a yellow green luminescence under 250 nm excitation. The correlation between these various

parameters requires a more detailed investigation which is in progress.

References

1. L. HAGMAN AND P. KIERKGAARD, *Acta Chem. Scand.* **22**, 1822 (1968).
2. J. B. GOODENOUGH, H. Y. P. HONG, AND J. KAFALAS, *Mater. Res. Bull.* **11**, 203 (1976).
3. P. VASHISHTA, J. N. MUNDY, AND G. R. SHENOY (Eds.), "Proceedings, Int. Conf. on Fast Ion Transport in Solids, Lake Geneva," North-Holland, Amsterdam (1979).
4. J. ALAMO AND R. ROY, *J. Amer. Ceram. Soc.*, No. 5, C78 (1984).
5. P. C. YAO AND D. J. FRAY, *Solid State Ionics* **8**, 35 (1983).
6. A. MBANDZA, E. BORDES, AND P. COURTINE, *Mater. Res. Bull.* **20**, 251 (1985).
7. A. EL JAZOULI, A. SERGHINI, R. BROCHU, J. M. DANCE, AND G. LE FLEM, *C.R. Acad. Sci. (Paris)*, **300**(11), 493 (1985).
8. A. EL JAZOULI, J. L. SOUBEYROUX, J. M. DANCE, AND G. LE FLEM, *J. Solid State Chem.* **65**, 351 (1986).
9. A. SERGHINI IDRISSE, "Thèse de 3ème Cycle," University of Rabat, Morocco (1984).
10. F. CHERKAOUI, J. C. VIALA, C. DELMAS, AND P. HAGENMULLER, *Solid State Ionics* (in press).
11. B. MATKOVIC, B. PRODIC, AND M. SLUKIC, Proceedings du Colloque International sur les phosphates minéraux solides, *Bull. Soc. Chim. Fr.*, 1777 (1968).
12. D. REINEN, C. FRIEBEL, AND V. PROPACH, *Z. Anorg. Allg. Chem.* **408**, 187 (1974).
13. F. MABBS AND D. J. MACHIN, "Magnetism and Transition Metal Complexes," Chapman & Hall, London (1973).
14. G. LE POLLES, A. EL JAZOULI, R. OLAZCUAGA, J. M. DANCE, G. LE FLEM, AND P. HAGENMULLER, *Mat. Res. Bull.* **22**, 1171 (1987).
15. M. KINOSHITA AND M. INOUE, *J. Chem. Soc. Japan* **8**, 1219-1223 (1980).
16. N. G. CHERNORUKOV, I. A. KORSHUNOV, AND T. V. PROFEVA, *Sov. Phys. Crystallogr. (Engl. Transl.)* **23**(4), 475 (1978).