



Full paper / Mémoire

Chimie douce preparation of $\text{Cu}_x\text{Zn}_{3-x}\text{V}_2\text{O}_7(\text{OH})_2 \cdot y\text{H}_2\text{O}$ isostructural to trigonal zinc pyrovanadate

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Abstract

New $\text{Cu}_x\text{Zn}_{3-x}\text{V}_2\text{O}_7(\text{OH})_2 \cdot y\text{H}_2\text{O}$ ($0 < x \leq 1.5$) isostructural to zinc pyrovanadate $\text{Zn}_3\text{V}_2\text{O}_7(\text{OH})_2 \cdot 2\text{H}_2\text{O}$, were successfully prepared by using a chimie douce technique. The method consists in mixing zinc nitrate and copper nitrate with a boiling solution of vanadium oxide (obtained by reacting V_2O_5 with few millilitres of 30 vol.% H_2O_2 followed by addition of distilled water). When ammonium hydroxide NH_4OH 10% was added ($\text{pH} \approx 6$), a precipitate was obtained. Using powder X-ray diffraction data, the crystal structures of as-prepared samples were determined by Rietveld refinement. Copper substitutes zinc in the zinc pyrovanadate lattice and is found to introduce distortion in the structure, which is mainly due to the Jahn–Teller effect. Distortion becomes more pronounced when the amount of copper is increased. This restricts the amount of copper which can be incorporated in the hexagonal zinc pyrovanadate lattice. **To cite this article:** K. Melghit, C. R. Chimie 11 (2008).

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Résumé

De nouveaux composés $\text{Cu}_x\text{Zn}_{3-x}\text{V}_2\text{O}_7(\text{OH})_2 \cdot y\text{H}_2\text{O}$ ($0 < x \leq 1.5$) isostructuraux au pyrovanadate de zinc $\text{Zn}_3\text{V}_2\text{O}_7(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ ont été préparés avec succès en utilisant la chimie douce. La méthode consiste à mélanger le nitrate de zinc et le nitrate de cuivre avec une solution bouillante d'oxyde de vanadium (obtenue en faisant réagir V_2O_5 avec quelques millilitres de H_2O_2 30% vol. puis par ajout d'eau distillée). Quand l'hydroxyde d'ammonium NH_4OH 10% est ajouté, un précipité se forme ($\text{pH} \approx 6$). En utilisant des données de diffraction de rayons X sur poudre, les structures cristallines des échantillons préparés ont été déterminées par raffinement Rietveld. Le cuivre substitue le zinc dans la structure du pyrovanadate de zinc. La structure présente des distorsions, qui sont surtout liées à l'effet Jahn–Teller. La distorsion devient plus prononcée quand la quantité de cuivre est augmentée. Cela restreint la quantité de cuivre qui peut être incorporé dans la maille hexagonale du pyrovanadate de zinc. **Pour citer cet article :** K. Melghit, C. R. Chimie 11 (2008).

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1. Introduction

Compounds of transition metal oxides find many applications in numerous industries, such as in lithium rechargeable batteries and heterogeneous catalysis. Zinc pyrovanadate $Zn_3V_2O_7(OH)_2 \cdot 2H_2O$ is a layered compound with interesting crystal structure feature. It is prepared first by a hydrothermal technique [1]. Before that, copper pyrovanadate $Cu_3V_2O_7(OH)_2 \cdot 2H_2O$ was prepared by a solution method at room pressure [2,3]. Both of them show similar layered crystalline structures, although they crystallize in different crystal systems. Copper pyrovanadate adopts a monoclinic lattice in contrast to zinc pyrovanadate, which adopts a hexagonal lattice. Their crystalline structures consist of MO_6 octahedral ($M = Zn$ or Cu) layers joined by two tetrahedral VO_4 units along the c axis. The two tetrahedral VO_4 s have one common oxygen and they form pyrovanadate group V_2O_7 . A mixture of zinc and copper pyrovanadate phases ($Cu_xZn_{1-x}V_2O_7(OH)_2 \cdot 2H_2O$ ($x = 1.0, 0.95, 0.90, 0.70,$ and 0.60), isostructural to monoclinic copper pyrovanadate (Volborthite), were recently reported [4,5]. They are prepared by using a solution method, where long reaction time is needed (2 days). Recently, new simple chimie douce method, at normal pressure, successfully leads to zinc pyrovanadate with a short reaction time (15 min) and high yield [6]. The objective of the present study is to incorporate copper in the zinc pyrovanadate lattice using the same method and to investigate the effect of copper on the zinc pyrovanadate crystalline structure.

2. Experimental

In the present preparation, the same method as in Ref. [6] was used. Different molar ratios of Cu/Zn : 0.9/2.1, 1.5/1.5 and 2.1/0.9, which correspond to 30, 50 and 70 at.% Cu were used. About 0.250 g of V_2O_5 (BDH, England) was mixed with about 3 mL of 30 vol.% H_2O_2 (Fluka). An exothermic reaction took place immediately. After a few minutes, before the mixture dried, about 400 mL of distilled water was added and heated until boiling. A yellow orange clear solution with pH 2 was obtained. At the same time amount of $Cu(NO_3)_2 \cdot 2.5H_2O$ (ACROS Organics) and $Zn(NO_3)_2 \cdot 6H_2O$ (Rasayan laboratory) were dissolved in 50 mL of distilled water and added to the boiling vanadium oxide solution ($\sim 100^\circ C$). The mass ratios $Cu(NO_3)_2 \cdot 2.5H_2O/Zn(NO_3)_2 \cdot 6H_2O$ used were: 0.288 g/0.859 g (for 30 at.% Cu), 0.480 g/0.613 g (for 50 at.% Cu) and 0.671 g/0.368 g (for 70 at.% Cu). When ammonium hydroxide NH_4OH 10% was added, a precipitate

was obtained at $pH \approx 6$. The stirring was maintained for 15 min. The products were dried at room temperature and analyzed with a powder X-ray Philips 1710 diffractometer and a JEOL JSM-840A scanning electron microscope equipped with an Oxford EDAX. The effects of temperature on the weight loss were investigated by thermal analyses TGA (2960 Universal TA Instruments, under normal atmosphere and with a heating rate of $10^\circ C \text{ min}^{-1}$, between room temperature and $600^\circ C$).

3. Results and discussion

EDAX analyses of the as-prepared samples show that the initial compositions of zinc and copper used are maintained in the final products (Table 1). Also, the present reactions show high yields of products (more than 90%). The as-prepared samples were analyzed by powder X-ray diffraction (Fig. 1). All diffraction peaks present on the powder X-ray diffraction patterns of 30 and 50 at.% Cu-containing samples are indexed by the hexagonal lattice of zinc pyrovanadate. The sample containing 70 at.% Cu presents a different pattern where new peaks appear. The attempts to index this pattern were unsuccessful, although several tests were carried out with different known indexing programs. Thus, the purity of the sample becomes questionable. A careful inspection of the pattern indicates that the present phase is a mixture of both hexagonal zinc pyrovanadate and monoclinic copper pyrovanadate. This is clear in Fig. 2. The powder X-ray diffraction pattern of 70 at.% Cu-containing sample was successfully fitted ($R_p = 11.6$ and $R_{wp} = 8.5$) using the Rietveld analysis (profile matching with constant scale factor) available in FULLPROF program [8]. The unit cells and space groups of both zinc pyrovanadate and copper pyrovanadate were used as input data in the program. This indicates that the hexagonal structure of zinc pyrovanadate is unstable to accommodate high amount of copper such as 70 at.% Cu. It is worth noting that the mixture ($Cu_xZn_{1-x}V_2O_7(OH)_2 \cdot 2H_2O$ ($x = 0.70$), with similar composition, 70 at.% Cu, and prepared using

Table 1
EDAX analysis of as-prepared samples

Experiments	Elements	Initial at.%	Product at.%
1	Zn	70	69
	Cu	30	31
2	Zn	50	48
	Cu	50	52
3	Zn	30	27
	Cu	70	72

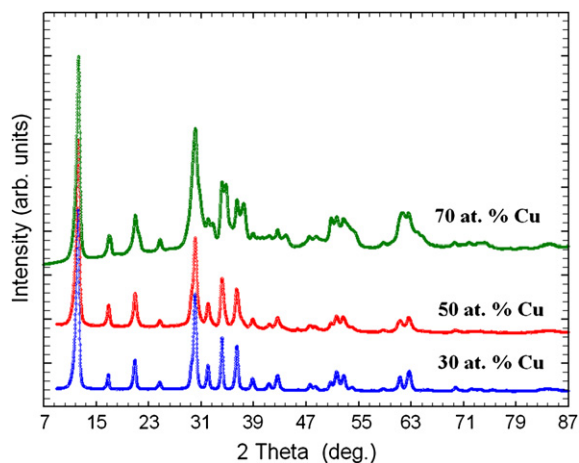


Fig. 1. Powder X-ray diffraction of as-prepared samples with different amounts of copper.

a different solution method, was reported to be a single-phase isostructural to monoclinic copper pyrovanadate [4]. Fig. 3 shows micrographs of scanning electron microscope of 30 and 50 at.% Cu-containing samples. They show homogeneous particles with platelet shape. Thermogravimetry analysis (TGA) curves for the as-prepared samples, 30 and 50 at.% Cu, are very similar (Fig. 4). They show about three different slopes which probably are related to three different types of water: adsorbed water (about $0.7\text{H}_2\text{O}$), which is lost first when the samples are heated from room temperature to $150\text{ }^\circ\text{C}$, followed by bonded water (about $2\text{H}_2\text{O}$),

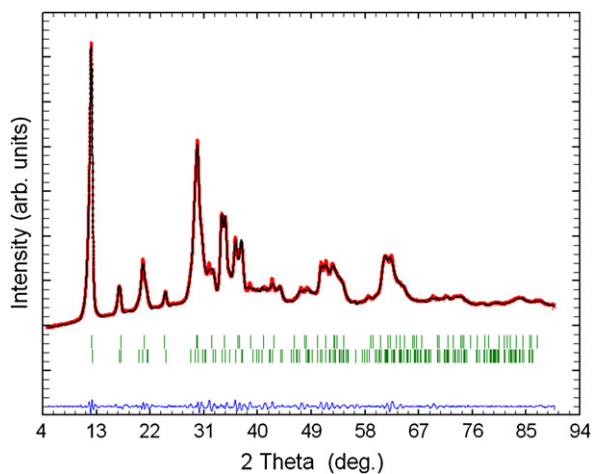


Fig. 2. Rietveld plot for 70 at.% Cu-containing sample. The upper trace shows the observed data as dots, while the calculated pattern is represented by the solid line. The lower trace is a plot of the difference between observed and calculated data. The vertical markers show the positions calculated for Bragg reflections for both zinc and copper pyrovanadate.

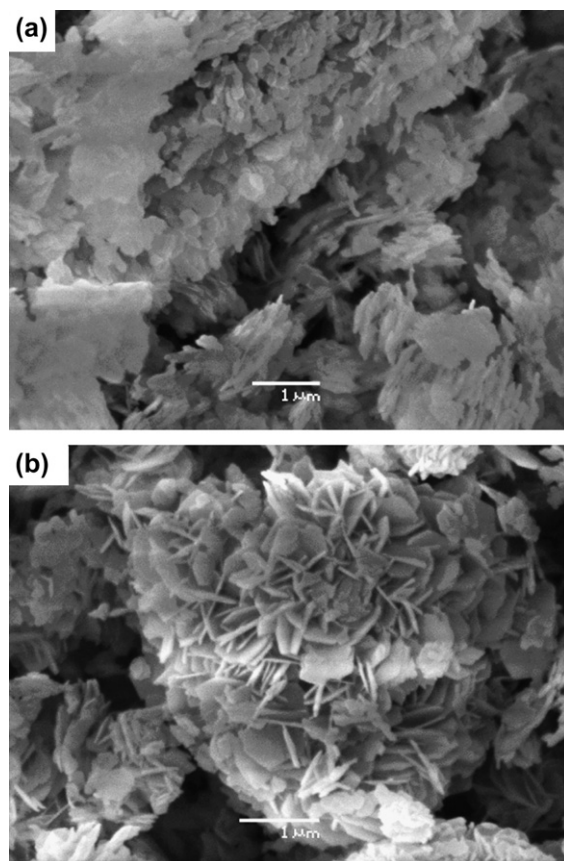


Fig. 3. SEM micrographs of (a) 30 at.% Cu-containing sample (b) 50 at.% Cu-containing sample.

which is lost between $150\text{ }^\circ\text{C}$ and $250\text{ }^\circ\text{C}$; at the end, above $250\text{ }^\circ\text{C}$, hydroxyl groups, participating in the crystalline structure, are lost (about $1\text{H}_2\text{O}$). This will lead to structural transformation and probably formation of zinc and copper orthovanadates [7]. From

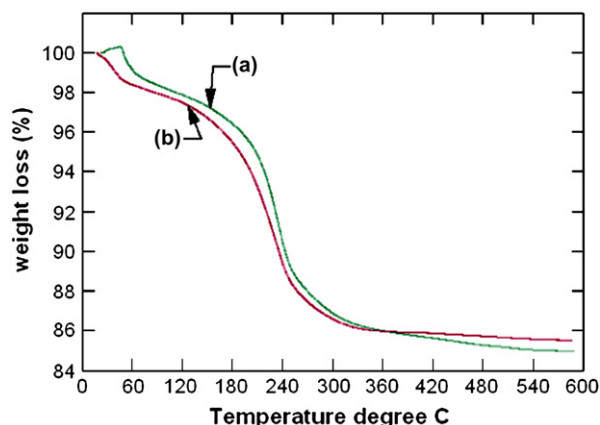


Fig. 4. TGA curves (a) 30 at.% Cu-containing sample (b) 50 at.% Cu-containing sample.

EDAX analysis and TGA study, the chemical formulae of both 30 and 50 at.% Cu-containing samples are $\text{CuZn}_2\text{V}_2\text{O}_7(\text{OH})_2 \cdot 2.8\text{H}_2\text{O}$ and $\text{Cu}_{1.5}\text{Zn}_{1.5}\text{V}_2\text{O}_7(\text{OH})_2 \cdot 2.7\text{H}_2\text{O}$, respectively. To study the effect of copper incorporation on the crystalline structure of zinc pyrovanadate, the crystal structures of as-prepared samples were investigated by the Rietveld profile analysis using the FULLPROF program [8]. The structural parameters of zinc pyrovanadate [1] were used as input data. The Pseudo-Voigt function was used to describe individual line profiles. The background was refined as linear interpolation between a set of background points with refinable heights. The parameters refined include the scale factor, overall B factor, zero point correction, cell parameters, isotropic thermal and positional parameters for all atoms, and three coefficients to describe the angular dependence of line breadths, asymmetry factors and shape parameters. In the refinement, the displacement parameters for the same atoms were constrained to vary in the same manner. The occupancy factor values for copper and zinc were taken from EDAX analysis. The refinement converges to $R_p = 7.60\%$ and $R_{wp} = 8.60\%$ in the case of 30 at.% Cu-containing sample and $R_p = 7.30\%$; $R_{wp} = 7.10\%$ in the case of 50 at.% Cu-containing sample. Table 2 shows the details of the Rietveld refinement. Figs. 5 and 6 show the final Rietveld plot. Table 3 shows the refined fractional atomic coordinates and Table 4 shows the bond distances and angles, respectively, for 30 and 50 at.% Cu-containing samples. For comparison, the bond distances and angles of pure zinc

Table 2

Details of Rietveld refinements of 30 and 50 at.% Cu-containing sample

	30 at.% Cu	50 at.% Cu
Wavelength (Å)	1.54056	1.54056
Step length	0.02	0.02
2θ range (°)	9.0–120.0	9.0–120.0
Symmetry	Trigonal	Trigonal
Lattice parameters		
a (Å)	6.0318(3)	6.0422(4)
c (Å)	7.1730(4)	7.1936(7)
Volume (Å ³)	226.01(2)	227.44(3)
Space group	$P\text{-}3m1$ (No. 164)	$P\text{-}3m1$ (No. 164)
Z	1	1
No. of reflections	168	179
No. of structural parameters	17	17
No. of profile parameters	10	10
Background information	Linear interpolation	Linear interpolation
R_p	0.076	0.073
R_{wp}	0.086	0.071
R_{exp}	0.062	0.088
R_b	0.015	0.014
R_f	0.018	0.025

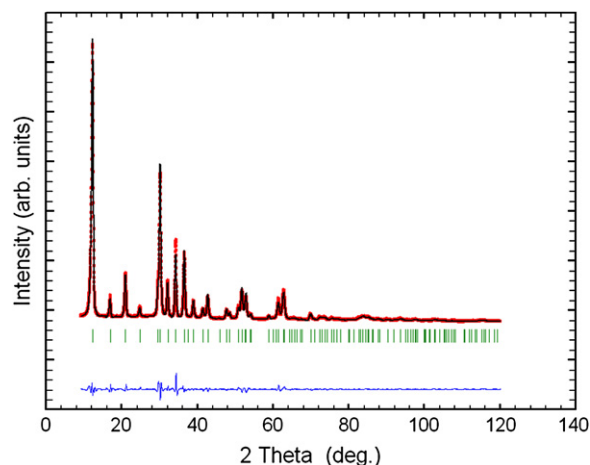


Fig. 5. Final Rietveld plot for 30 at.% Cu-containing sample. The upper trace shows the observed data as dots, while the calculated pattern is represented by solid line. The lower trace is a plot of the difference between observed and calculated. The vertical markers show the positions calculated for Bragg reflections.

pyrovanadate are also displayed (Table 4). Similar to zinc pyrovanadate, the Cu-containing samples show only one type of both tetrahedral VO_4 and octahedral MO_6 ($M = \text{Zn}$ or Cu) groups. The VO_4 has one common oxygen O3 along the c axis (Fig. 7a and b) that form the pyrovanadate group V_2O_7 . The other three oxygens O2 of VO_4 assure connection between tetrahedral and octahedral layers. Oxygen O1 is only common to octahedral MO_6 . This structure left empty cavities which were occupied by water molecules

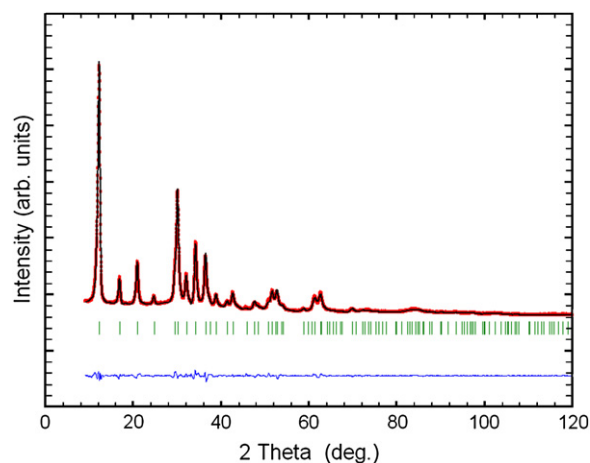


Fig. 6. Final Rietveld plot for 50 at.% Cu-containing sample. The upper trace shows the observed data as dots, while the calculated pattern is represented by solid line. The lower trace is a plot of the difference between observed and calculated. The vertical markers show the positions calculated for Bragg reflections.

Table 3

Fractional atomic coordinates and isotropic atomic displacement parameters of 30 and 50 at.% Cu-containing samples

Atom	Site	X (30)	X (50)	Y (30)	Y (50)	Z (30)	Z (50)	Biso (Å ²) (30)	Biso (Å ²) (50)	Occu. (30)	Occu. (50)
Zn	3e	0.5	0.5	0	0	0	0	2.66(99)	3.00(99)	0.167	0.125
Cu	3e	0.5	0.5	0	0	0	0	2.66(99)	3.00(99)	0.083	0.125
V	2c	0	0	0	0	0.2539(3)	0.2556(3)	0.80(99)	0.36(99)	0.167	0.167
O1	2d	0.6667	0.6667	0.3333	0.3333	0.8829(9)	0.9138(13)	4.88(99)	6.70(99)	0.5	0.5
O2	6i	0.1434(5)	0.1404(5)	0.2867(11)	0.2808(11)	0.8173(4)	0.8223(5)	4.88(99)	6.70(99)	0.083	0.083
O3	1b	0	0	0	0	0.5	0.5	4.88(99)	6.70(99)	0.167	0.167
Ow	2d	0.6667	0.6667	0.3333	0.3333	0.4901(29)	0.4642(22)	4.88(99)	6.70(99)	0.167	0.167

Table 4

Selected bond distances (Å) and angles (°) with their standard deviations of 30, 50 at.% Cu-containing samples and pure zinc pyrovanadate (0 at.% Cu) [1]

0 at.% Cu	30 at.% Cu		50 at.% Cu		
<i>Tetrahedron: VO₄</i>					
V–O2: 3 × 1.695(2)	O2–V–O2: 3 × 110.52(12)	V–O2: 3 × 1.582(3)	O2–V–O2: 3 × 110.1(2)	V–O2: 3 × 1.573(3)	O2–V–O2: 3 × 108.0(2)
V–O3: 1.781(1)	O2–V–O3: 3 × 108.40(9)	V–O3: 1.765(2)	O2–V–O3: 3 × 108.8(2)	V–O3: 1.758(2)	O2–V–O3: 3 × 110.9(2)
<i>Octahedron MO₆ (M = Zn or Cu)</i>					
Zn–O1: 2 × 1.941(2)	O1–Zn–O1: 179.98(13)	M–O1: 2 × 1.933(3)	O1–M–O1: 180.0(3)	M–O1: 2 × 1.851(3)	O1–M–O1: 180.0(3)
Zn–O2: 4 × 2.226(2)	O2–Zn–O2: 2 × 179.99(8)	M–O2: 4 × 2.287(3)	O2–M–O2: 2 × 180.0(3)	M–O2: 4 × 2.287(3)	O2–M–O2: 2 × 180.0(3)
	O1–Zn–O2: 2 × 94.24 (11)		O1–M–O2: 2 × 92.6(1)		O1–M–O2: 2 × 96.6(2)
	O1–Zn–O2: 2 × 85.76(11)		O1–M–O2: 2 × 87.4(2)		O1–M–O2: 2 × 83.4(3)
	O2–Zn–O2: 2 × 94.37(8)		O2–M–O2: 2 × 97.4(2)		O2–M–O2: 2 × 99.7(2)
	O2–Zn–O2: 2 × 85.63(8)		O2–M–O2: 2 × 82.6(2)		O2–M–O2: 2 × 80.3(2)

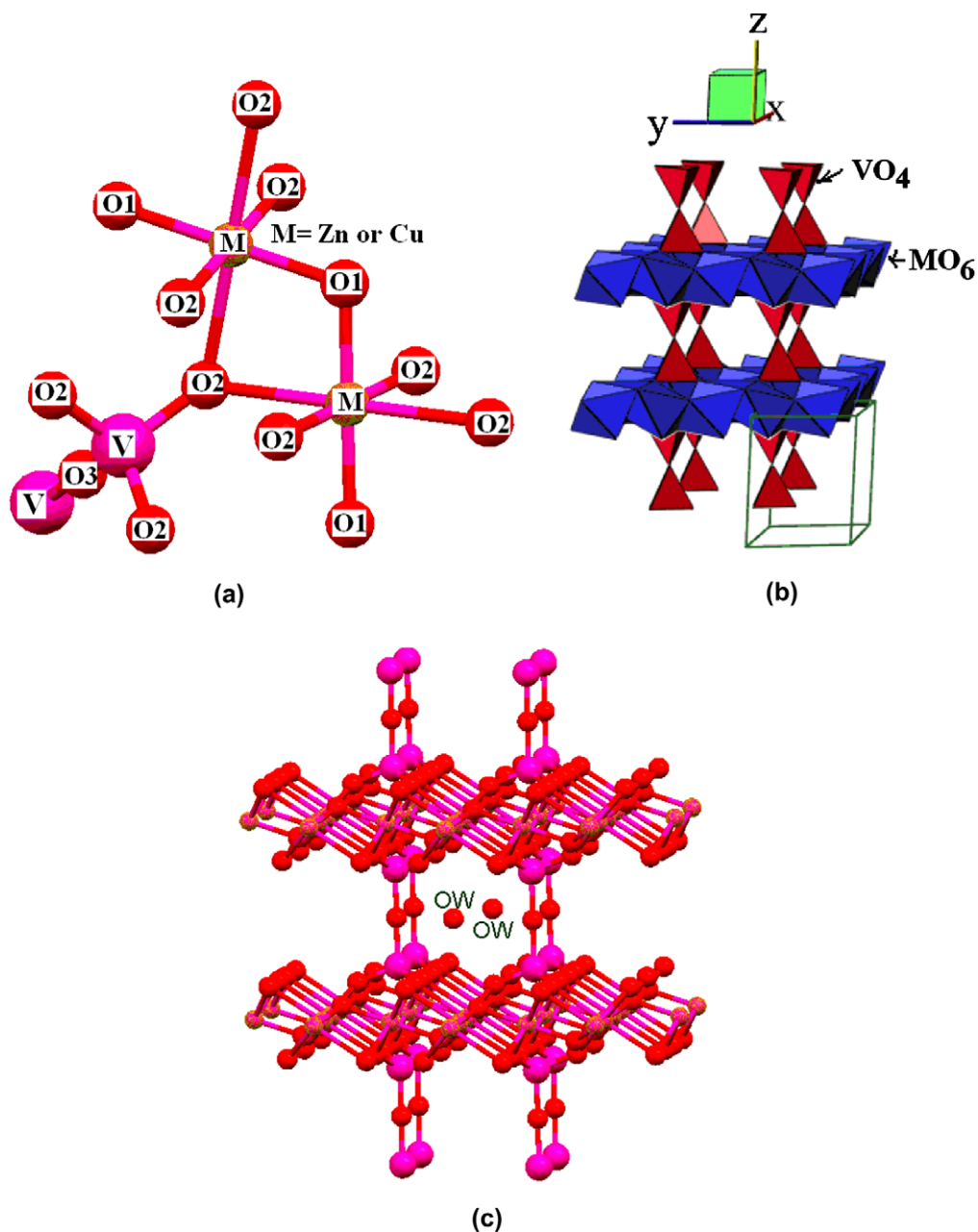


Fig. 7. View of the structure (figures displayed by mercury [10] and balls and stick [11]).

(Fig. 7c); the water oxygen position in the present refinement was found to be different from the water oxygen position reported in the zinc pyrovanadate structure [1]. Two molecules of water are present in each unit cell cavity. This is consistent with the TGA curve, which shows loss of two bonded molecules of water by unit formula, between 150 °C and 250 °C. The bond distances and angles comparison (Table 4) shows The V–O bonds' distances of the

Cu-containing samples become shorter and a noticeable decrease in the V–O₂ bond distance can be seen: V–O₂ in 30 at.% Cu-containing sample is 1.582 Å, which is much shorter compared to pure zinc pyrovanadate 1.695 Å and it decreases further for the 50 at.% Cu-containing sample (1.573 Å). The V–O bond distance calculated from ionic radii of vanadium V⁺⁵ and O⁻² in tetrahedral coordination is 1.735 Å [9]. This indicates that as copper substitutes zinc in

the zinc pyrovanadate lattice, the V–O2 bond distance becomes much shorter, which increases the distortion in the tetrahedral VO₄. The octahedral MO₆ for 30 at.% Cu-containing sample shows similar M–O1 bond distance as zinc pyrovanadate; however, the bond distance M–O2 increases from 2.23 Å to 2.29 Å. Probably this is the cause of the Jahn–Teller effect. Also the angle O2–M–O2 has a higher value of 97.4° compared to pure zinc pyrovanadate sample (94.4°). The sample with 50 at.% Cu shows a larger distortion of the MO₆ octahedron, in which both M–O1 and M–O2 bond distances are changed: the M–O2 bonds become longer (2.29 Å), which is similar to the M–O₂ bond distance value in the 30 at.% Cu-containing sample, and the M–O1 bond distance becomes shorter (1.85 Å), compared to pure zinc pyrovanadate (1.94 Å). The Jahn–Teller effect in the present sample is more accentuated, which should be expected as the amount of copper in the sample is higher. Also the O2–M–O2 angles are changed, while one O2–M–O2 is increased, from 97.4° for 30 at.% Cu-containing sample to 99.7° for 50 at.% Cu-containing sample, the other one O2–M–O2 is decreased, from 82.6° for 30 at.% Cu-containing sample to 80.3° for 50 at.% Cu-containing sample. This indicates that the incorporation of copper in the zinc pyrovanadate lattice induces distortion in both tetrahedral and octahedral groups. The octahedral groups are more distorted (both bond distances and angles are changed) compared to tetrahedral groups, where only bond distances are changed. This distortion increases with a larger amount of copper. This explains why the X-ray diffraction pattern of 70 at.% Cu-containing sample shows a mixture of phases. It seems that 70 at.% Cu amount has exceeded the limit of copper allowed by the zinc pyrovanadate lattice. The incapacity of the zinc pyrovanadate hexagonal lattice to incorporate more copper is essentially related to the structure distortion. This is probably mainly due to the Jahn–Teller effect. For this reason pure copper pyrovanadate, although its structural features is similar to that of hexagonal zinc pyrovanadate, adopts the lower symmetry lattice, a monoclinic lattice that seems to tolerate octahedral distortion much better compared to the hexagonal lattice.

4. Conclusions

New copper zinc pyrovanadate compounds are obtained by using a simple, room pressure, chimie douce method. The amount of copper incorporated in the zinc pyrovanadate lattice is limited by the distortion caused, which is mainly due to the Jahn–Teller effect. The simplicity and the high product yield make the present method suitable for preparing transition metal oxides, especially oxides based on vanadium, which are potential candidates for many industrial applications.

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