Characterization of yellow and red inorganic pigments from $\text{Mg}_{0.5}\text{Cu}_{1.5}\text{V}_x\text{P}_{2-x}\text{O}_7$ ($0 \leq x \leq 2$) solid solutions

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Abstract

The structural characterization of $\text{Mg}_{0.5}\text{Cu}_{1.5}\text{V}_x\text{P}_{2-x}\text{O}_7$ ($0.0 \leq x \leq 2.0$) compositions was performed and the colour parameters of these materials measured. Solid solutions in the $\alpha\text{-Cu}_2\text{P}_2\text{O}_7$, $\beta\text{-Cu}_2\text{P}_2\text{O}_7$ and $\beta\text{-Cu}_2\text{V}_2\text{O}_7$ structures were obtained by incorporation of V(V) in the $\alpha\text{-Cu}_2\text{P}_2\text{O}_7$ and $\beta\text{-Cu}_2\text{P}_2\text{O}_7$ structures and P(V) in the $\beta\text{-Cu}_2\text{V}_2\text{O}_7$ structure. Solid solutions with the $\alpha\text{-Cu}_2\text{P}_2\text{O}_7$ structure are obtained at 500–600 °C when the vanadium:phosphorus ratio is lower than 2/3 ($x \leq 1.2$). At 600 °C, these materials have a bright yellow colour. In these compositions, the transition to the $\beta\text{-Cu}_2\text{P}_2\text{O}_7$ structure occurs at 800 °C. This transition modifies the colour but it keeps the yellow colouration for compositions. At 1000 °C, the $\text{Cu}_3\text{P}_2\text{O}_8$ phase coexists with the $\beta\text{-Cu}_2\text{P}_2\text{O}_7$ phase and the yellow colouration is lost. Solid solutions with the $\beta\text{-Cu}_2\text{V}_2\text{O}_7$ structure are obtained at 600–800 °C when the amount of vanadium is high ($x \geq 1.5$). The increase in the amount of vanadium in $\text{Mg}_{0.5}\text{Cu}_{1.5}\text{V}_x\text{P}_{2-x}\text{O}_7$ ($0.0 < x \leq 2.0$) compositions changes the colour of the materials from yellow to red at 600 °C (the $\text{Mg}_{0.5}\text{Cu}_{1.5}\text{P}_2\text{O}_7$ composition, $x = 0.0$, is pale green). The colour of the materials darkens with increasing temperature and compositions with $x > 1.5$ melted at 1000 °C.

Keywords $\alpha\text{-Cu}_2\text{P}_2\text{O}_7$ · $\beta\text{-Cu}_2\text{P}_2\text{O}_7$ · $\beta\text{-Cu}_2\text{V}_2\text{O}_7$ · Structure · Solid solutions · Colour · Pigment

1 Introduction

Most Cu and Mg diphosphates and divanadates present monoclinic structures. The coordination number (C.N.) of Cu(II) is 4 or 5 in these structures, while the coordination number of Mg(II) is 6 in almost all of them. The different coordinations of Cu and Mg are due to the small differences in variables of the fractional coordinates to accommodate the atoms when structures with the same space group and atoms at the same crystallographic sites are considered; e.g. C.N.(Cu) = 4 in $\beta\text{-Cu}_2\text{P}_2\text{O}_7$ and C.N.(Mg) = 6 in $\beta\text{-Mg}_2\text{P}_2\text{O}_7$, both with the spatial group: C 1 2/m 1. The

change from V(V) to P(V) modifies the C.N. of the Mg(II) ion in $\alpha\text{-Mg}_2\text{X}_2\text{O}_7$ ($\text{X} = \text{V}, \text{P}$) but the C.N. of Cu(II) is the same in the structure of $\text{Cu}_2\text{X}_2\text{O}_7$ ($\text{X} = \text{V}, \text{P}$) with the spatial group: C 1 2/c 1 [1–10]. Figure 1 shows the $\alpha\text{-Cu}_2\text{P}_2\text{O}_7$, $\beta\text{-Cu}_2\text{P}_2\text{O}_7$ (two unit cell) and $\beta\text{-Cu}_2\text{V}_2\text{O}_7$ structures and their XRD simulated profiles. The data used in this figure were obtained from the Inorganic Crystal Structure Database [10]. The FullProf program in the WinPlotr Suite was used to obtain this simulation. The structures were drawn with the Studio program included in the aforementioned software suite [11–13]. The differences between the unit cell from $\alpha\text{-Cu}_2\text{P}_2\text{O}_7$ and $\beta\text{-Cu}_2\text{P}_2\text{O}_7$ (with $c = 9.174$

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Fig. 1 Representation of the unit cells in α - $\text{Cu}_2\text{P}_2\text{O}_7$, β - $\text{Cu}_2\text{P}_2\text{O}_7$ (two unit cells) and β - $\text{Cu}_2\text{V}_2\text{O}_7$ structures and their XRD simulated profiles. Details from 15° to 25° 2θ are included in the inset

$\text{\AA}$ and $c = 4.576 \text{ \AA}$, respectively, and similar values of a and b parameters) are due to the slightly different relative position of the oxygen atoms. These differences give rise to the coordination number of 4 in the β - $\text{Cu}_2\text{P}_2\text{O}_7$ structure (CuO_4 square) and of 5 in the α - $\text{Cu}_2\text{P}_2\text{O}_7$ structure (CuO_5 pyramid). Figure 1 includes the bonds smaller than $2.5 \text{ \AA}$ (first coordination). In both the α - $\text{Cu}_2\text{P}_2\text{O}_7$ and β - $\text{Cu}_2\text{V}_2\text{O}_7$ structures, one of the oxygen atoms occupies 4e sites and all the other atoms occupy 8f sites (S. G.: C 1 2/c 1), although their x , y and z values are different. Hence, the relative three-dimensional position of the

atoms is different. The position of CuO_5 pyramids in the α - $\text{Cu}_2\text{P}_2\text{O}_7$ and β - $\text{Cu}_2\text{V}_2\text{O}_7$ structures can be seen in Fig. 1. The α - $\text{Cu}_2\text{P}_2\text{O}_7$ to β - $\text{Cu}_2\text{P}_2\text{O}_7$ transition occurs at 100°C [4] and the α - $\text{Cu}_2\text{V}_2\text{O}_7$ to β - $\text{Cu}_2\text{V}_2\text{O}_7$ transition at 710°C . The latter transition is reversible [1]. $\text{Cu}_2\text{V}_2\text{O}_7$ melts at 790°C [14]. The presence of Mg(II) in $\text{Mg}_y\text{Cu}_{2-y}\text{V}_2\text{O}_7$ compositions increases the melting point and the materials develop the monoclinic α - $\text{Mg}_2\text{V}_2\text{O}_7$ or triclinic $\text{Mg}_2\text{V}_2\text{O}_7$ crystalline phase with black, black-brown or yellow-brown colouration when $y = 1.5, 1.75$ or 2.0 at 1000°C [15]. $\text{Mg}_2\text{V}_2\text{O}_7$ melts at 1132°C [16]. The presence of P(V) in these compositions

could also increase the melting point. The melting point of $\text{Mg}_2\text{P}_2\text{O}_7$ is 1382 °C [17].

The colour of most phosphates is light, while intense colours are obtained from vanadates. Colour is often associated with transition metal ions. The d–d electronic transitions in transition metal ions give rise to many of the familiar colours of transition metal compounds; e.g. the various shades of blue and green associated with different copper(II) complexes. Charge transfer effects in which an electron is transferred between an anion and a cation are often responsible for intense colours as in, for example, permanganates (purple) and chromates (yellow) [18].

The absence of a charge transfer band in the visible wavelength range explains the pale blue or weak greenish-blue colours in $\alpha\text{-Cu}_2\text{P}_2\text{O}_7$ and $\text{Mg}_x\text{Cu}_{2-x}\text{P}_2\text{O}_7$ ($0.0 \leq x \leq 1.5$) solid solutions. The average Cu–O distance is 2.035 Å and the coordination number is 5 in $\alpha\text{-Cu}_2\text{P}_2\text{O}_7$. The incorporation of Mg(II) ions via substitution of Cu(II) ions when solid solutions are formed decreases the biggest M–O (M = Mg, Cu) distance, although significant changes in the M–O distances for the four nearest oxygen atoms to M (Cu, Mg) are not detected [19].

The colour of $\text{Mg}_2\text{V}_2\text{O}_7$ is pale yellow, almost white. This is related to the position of the charge transfer band of V(V) in spectra (≈ 380 nm). Two different crystallographic vanadium ions with average V–O distances of 1.819 and 1.755 Å are present in the monoclinic $\alpha\text{-Mg}_2\text{V}_2\text{O}_7$ structure. There are not chromophore ions in the isostructural $\text{Mg}_2\text{P}_2\text{O}_7$ compound, which is white in colour [15, 18].

The nature of the bonding between chromophore ions and oxygen ions affects the colour of the materials considerably. The bond length can be used to explain the displacement of the bands in the visible ultraviolet spectrum. Interatomic Cu–O distances are smaller in vanadate structures than in phosphate structures. The Cu–O bond is stronger in vanadates than in phosphates because the V–O bond is weaker than the P–O bond. Interatomic V–O distances are slightly greater than interatomic P–O distances, $r(\text{P(V)}) < r(\text{V(V)})$. The O(–II) ion is bonded to the non-metal P(V) ion with a strong covalent bond, whereas the V–O bond is weaker because it is bonded to the V(V) transition metal ion. The average Cu–O distance is 2.0069 Å in $\beta\text{-Cu}_2\text{V}_2\text{O}_7$ and 2.0346 Å in $\alpha\text{-Cu}_2\text{P}_2\text{O}_7$, both monoclinic structures (S. G.: C 1 2/c 1) with a Cu(II) coordination number equal to 5 and a V(V) or P(V) coordination number equal to 4. At 600 °C, red–brown and orange materials can be obtained from $\text{Mg}_y\text{Cu}_{2-y}\text{V}_2\text{O}_7$ solid solutions with the $\beta\text{-Cu}_2\text{V}_2\text{O}_7$ structure when $0.5 \leq y \leq 1.25$ [15]. The red–brown colour is obtained from these solid solutions when the average M–O distances are the shortest ($y = 0.5$).

A yellowish mineral, volborthite, with the chemical formula $\text{Cu}_3\text{V}_2\text{O}_7(\text{OH})_2 \cdot 2\text{H}_2\text{O}$, has been identified in historic mural paintings [20]. Iron oxides, ferrous sulphate, Pb_3O_4 ,

lead chromate, mercury sulfide, cadmium sulfide and cadmium selenide can be used as inorganic raw materials in the preparation of red paint pigments [21]. Their utilization is increasingly regulated or even already banned by governmental authorities. As a consequence, safer substitutes with equivalent stability and coloristic features are attracting growing attention. The most commonly used non-hazardous red pigments are based on iron oxides, because of their nontoxicity, high chemical stability, frequent occurrence in nature and low costs, however the colours shown by iron red pigments are far less vivid as the hues of the cadmium sulfoselenides ($\text{Cd}(\text{S,Se})$), lead chromate (PbCrO_4), or arsenic sulfide (As_4S_4) compounds [22].

Interest in finding environmentally friendly red and yellow pigments is still high. Some compounds and solid solutions have been published but they have problems with temperature-stability (metastable phases) or the compositions are too expensive to be produced. A bright red pigment is obtained at 750 °C from $(\text{Bi}_{1.95}\text{Zr}_{0.05})_{0.8}\text{Fe}_{0.4}\text{O}_{3+6}$ with the metastable $\beta\text{-Bi}_2\text{O}_3$ tetragonal structure, $L^* = 49.9$, $a^* = 31.1$, $b^* = 25.8$ [22]. From the yellow $\text{Bi}_2\text{Ce}_2\text{O}_7$ pigment with pyrochlore structure, increasing calcination temperature leads to a considerable shift in tones and primarily to weakening of the yellow to yellow–orange tone [23]. In solid solutions in the $\text{CeO}_2\text{--Fe}_2\text{O}_3\text{--Pr}_6\text{O}_{11}$ system, a red pigment with $L^* = 43$, $a = 18.67$ and $b^* = 17.40$ is obtained from $\text{Ce}_{0.8}\text{Fe}_{0.08}\text{Pr}_{0.12}\text{O}_{1.90}$ composition [24]. Brilliant colours, varying from bright yellow to deep red, depending on the O/N ratio can be obtained from $\text{Ca}_{1-x}\text{La}_x\text{TaO}_{2-x}\text{N}_{1+x}$ solid solutions with perovskite structure and $L^* = 77.70$, $a^* = 7.07$, $b^* = 83.86$ ($x = 0.05$) to $L^* = 31.62$, $a^* = 49.29$, $b^* = 39.29$ ($x = 0.90$). The oxynitrides can be exposed to temperatures as high as 720 °C during the short period of processing to give lead-free enamels [25]. The substitution of Bi(III) for Ca(II) in the $\text{Ca}_{10}\text{Cu}_y(\text{PO}_4)_6\text{O}_2\text{H}_{2-y-\delta}$ red–violet pigment with hydroxyapatite structure changes the colour to yellow [26]. The doping of Pr^{4+} or Tb^{4+} for Ce^{4+} in $\text{La}_2\text{Ce}_2\text{O}_7$ with disordered defect fluorite type structure changes the light yellow colour or soft orange to dark orange, $L^* = 51.35$, $a^* = 15.94$, $b^* = 17.57$ [27].

The aim of this study is to investigate the possible formation of $\text{Mg}_{0.5}\text{Cu}_{1.5}\text{V}_x\text{P}_{2-x}\text{O}_7$ ($0.0 \leq x \leq 2.0$) solid solutions with $\alpha\text{-Cu}_2\text{P}_2\text{O}_7$, $\beta\text{-Cu}_2\text{P}_2\text{O}_7$ and $\beta\text{-Cu}_2\text{V}_2\text{O}_7$ structures and to monitor the evolution of the colour of these materials with composition and temperature to try obtain yellow and red inorganic pigments without lead, chromate, cadmium, sulfide or mercury.

2 Experimental

$\text{Mg}_{0.5}\text{Cu}_{1.5}\text{V}_x\text{P}_{2-x}\text{O}_7$ ($0.0 \leq x \leq 2.0$) compositions were synthesized via the chemical co-precipitation method. The starting materials were $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (Scharlau), CuCl_2 (Acros Organic, 99%), NH_4VO_3 (Alfa-Aesar, 99%) and H_3PO_4 (Merck, 99%).

The stoichiometric amount of NH_4VO_3 , a 0.5 M solution of H_3PO_4 in water, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and CuCl_2 were added to water to obtain a final volume of 200 mL. Samples were vigorously stirred for two days at room temperature. Subsequently, an ammonia aqueous solution (Scharlab, 25%) was added until reaching pH = 10 and precipitation of materials occurred. Following the co-precipitation process, the materials were dried using IR-irradiation. Only water is evacuated in this operation, the Mg:Cu:V:P molar ratio of the starting materials being preserved. The dry samples were fired at 300, 500, 600, 800 and 1000 °C for 2 h at each temperature.

The resulting materials were examined using a Panalytical X-ray diffractometer with CuK_α radiation to study the development of the crystalline phases at different temperatures. A structure profile refinement was carried out via the Rietveld method (Fullprof.2 k computer program) [11–13]. Unit cell parameters and interatomic distances in the developed structures were obtained to investigate the possible formation of solid solutions under these synthesis conditions. Diffraction patterns ranging between 6° and 110° (2 θ) were collected, using monochromatic CuK_α radiation, a step size of 0.02° (2 θ) and a sampling time of 10 s. The initial structural information was obtained from the Inorganic Crystal Structure Database [10]. This database includes standard cell [19], standard space group, fractional atomic coordinates and other information on crystalline phases found in the literature.

UV–vis–NIR spectroscopy (diffuse reflectance) allows the Cu(II) site and the V(V)–O and Cu(II)–O transfer charge bands in the samples to be studied. A Jasco V-670 spectrophotometer was used to obtain the UV–vis–NIR (ultraviolet visible near infrared) spectra in the 200 to 2500 nm range.

An X-Rite spectrophotometer (SP60, standard illuminant D65, an observer 10°, and a reference sample of MgO) was used to obtain CIEL*a*b* colour parameters on the fired samples: L* is the lightness axis (black (0) → white (100)), a* is the green (–) → red (+) axis, and b* is the blue (–) → yellow (+) axis [28].

Magnetic characterization of the $\text{Mg}_{0.5}\text{Cu}_{1.5}\text{V}_2\text{O}_7$ composition fired at 600 °C was performed on a MicroSense vibrating sample magnetometer (VSM, model EV9) equipped with EV1-LNA temperature control option. A

powder sample was compacted into a cylindrical pillbox that was pasted onto an acrylic rod by means of double-sided Scotch® tape and securely fixed by wrapping with Teflon tape. Subsequently, the temperature dependence of the magnetization curve ($M(T)$), was measured under a 10 kOe applied magnetic field in continuous mode from 100 to 300 K, applying a 6 K/min heating rate.

3 Results and discussion

Table 1 shows the evolution of the crystalline phases with composition and temperature in $\text{Mg}_{0.5}\text{Cu}_{1.5}\text{V}_x\text{P}_{2-x}\text{O}_7$ ($0.0 \leq x \leq 2.0$) compositions. When $x \leq 1.2$, the majority crystalline phase present is the $\alpha\text{-Cu}_2\text{P}_2\text{O}_7$ phase at 500 and 600 °C. Under the conditions employed in this study, a mixture of $\alpha\text{-Cu}_2\text{P}_2\text{O}_7$ to $\beta\text{-Cu}_2\text{P}_2\text{O}_7$ phases are detected at these temperatures, the $\beta\text{-Cu}_2\text{P}_2\text{O}_7$ phase being the majority crystalline phase present at 800 and 1000 °C. The $\beta\text{-Cu}_2\text{P}_2\text{O}_7$ crystalline phase is stable at 1000 °C when $x < 1.0$, although other phases can also be detected. When $x > 1.2$, the majority crystalline phase present is the $\beta\text{-Cu}_2\text{V}_2\text{O}_7$ phase. This crystalline phase is stable up to 800 °C in all the compositions ($x \geq 1.2$). Compositions with $x \geq 1.8$ melt at 1000 °C. $\text{Cu}_2\text{V}_2\text{O}_7$ melts at 790 °C, with the presence of Mg(II) increasing the melting point of these compositions slightly [14]. The $\beta\text{-Cu}_2\text{V}_2\text{O}_7$ structure was not detected at 1000 °C. At this temperature, the crystalline phases with $\text{Cu}_3\text{P}_2\text{O}_8$, $\text{Mg}_3\text{P}_2\text{O}_8$ and $\alpha\text{-Mg}_2\text{V}_2\text{O}_7$ structures developed and were detected instead of the crystalline phase with the $\beta\text{-Cu}_2\text{V}_2\text{O}_7$ structure or together with the crystalline phase with the $\beta\text{-Cu}_2\text{P}_2\text{O}_7$ structure.

Figure 2 shows the variation in unit cell parameters in the $\alpha\text{-Cu}_2\text{P}_2\text{O}_7$ and $\beta\text{-Cu}_2\text{V}_2\text{O}_7$ structures at 600 °C. The discontinuity in the variation of the unit cell parameters is due to the change in the structure developed in the compositions at this temperature: the $\alpha\text{-Cu}_2\text{P}_2\text{O}_7$ structure when $x \leq 1.2$ and the $\beta\text{-Cu}_2\text{V}_2\text{O}_7$ structure when $x \geq 1.5$. Tables 2, 3 and 4 show the unit cell parameters in the $\alpha\text{-Cu}_2\text{P}_2\text{O}_7$, $\beta\text{-Cu}_2\text{P}_2\text{O}_7$ and $\beta\text{-Cu}_2\text{V}_2\text{O}_7$ structures, respectively. The increase detected in the unit cell parameters in the three structures can be associated with the partial substitution of the P(V) ion by the V(V) ion ($r(\text{P(V)}) < r(\text{V(V)})$ in C.N. = 4). The variation in these parameters with composition confirms the formation of solid solutions in these structures in a partial compositional range. The presence of small amounts of other crystalline phases may be due to the instability of the prepared solid solutions at high temperature. When $0.0 \leq x \leq 1.2$, the solid solutions with the $\alpha\text{-Cu}_2\text{P}_2\text{O}_7$ structure were obtained at 600 °C and the solid solutions with the $\beta\text{-Cu}_2\text{P}_2\text{O}_7$ structure at 800 °C. When $1.5 \leq x \leq 2.0$, the $\beta\text{-Cu}_2\text{V}_2\text{O}_7$ solid solutions were obtained at 600 and 800 °C. The increase in the unit cell

Table 1 Evolution of crystalline phases with temperature in $\text{Mg}_{0.5}\text{Cu}_{1.5}\text{V}_x\text{P}_{2-x}\text{O}_7$ compositions

x	500 °C	600 °C	800 °C	1000 °C
0.0	$\alpha\text{CP(s)}$, $\beta\text{CP(m)}$, CP (vw)	$\alpha\text{CP(s)}$, $\beta\text{CP(m)}$, CP (vw)	$\beta\text{CP(s)}$, CP (vw)	$\beta\text{CP(s)}$, CP (vw)
0.3	$\alpha\text{CP(m)}$, $\beta\text{CP(m)}$, $\alpha\text{CV(w)}$, CP (vw)	$\alpha\text{CP(s)}$, $\beta\text{CP(m)}$, CP(vw)	$\beta\text{CP(s)}$, CP(vw)	$\beta\text{CP(s)}$, CP(m), MC(vw), T(vw)
0.6	$\beta\text{CP(s)}$, $\alpha\text{CP(m)}$, $\alpha\text{CV(w)}$, CP (vw)	$\alpha\text{CP(s)}$, $\alpha\text{CV(m)}$, $\beta\text{CP(w)}$, CP(vw)	$\beta\text{CP(s)}$, CP(vw)	CP(s), $\beta\text{CP(m)}$, T(w), $\alpha\text{MV(w)}$, $\alpha\text{MV(vw)}$,
0.9	$\alpha\text{CP(s)}$, $\alpha\text{CV(s)}$, CP (vw)	$\alpha\text{CP(s)}$, $\alpha\text{CV(m)}$, CP(vw)	$\beta\text{CP(s)}$, $\alpha\text{CV(m)}$, $\beta\text{CV(w)}$, $\alpha\text{MP(vw)}$, $\alpha\text{MV(vw)}$, CP(vw)	CP(s), $\beta\text{CP(m)}$, $\alpha\text{MV(m)}$, $\beta\text{CV(w)}$, MP2(w), $\gamma\text{CV(vw)}$
1.2	$\alpha\text{CP(s)}$, $\gamma\text{CV(w)}$, $\alpha\text{MV(w)}$	$\alpha\text{CP(s)}$, $\alpha\text{CV(vw)}$, $\alpha\text{MV(vw)}$	MP(s), $\beta\text{CV(m)}$, $\alpha\text{MP(m)}$, $\beta\text{CP(m)}$, $\alpha\text{MV(w)}$	MP(m), $\alpha\text{MP(m)}$, $\alpha\text{MV(w)}$, $\gamma\text{CV(w)}$, $\beta\text{CP(w)}$
1.5	$\alpha\text{MV(s)}$, $\alpha\text{CP(m)}$, V(w), $\gamma\text{CV(vw)}$, $\beta\text{CV(vw)}$	$\beta\text{CV(s)}$, $\alpha\text{CP(m)}$, MP1(w), $\alpha\text{MV(vw)}$	$\beta\text{CV(s)}$, MP1(m), $\alpha\text{MV(vw)}$, $\beta\text{CP(vw)}$	$\beta\text{CV(s)}$, $\alpha\text{MP(m)}$, $\alpha\text{MV(m)}$, MP2(m), $\gamma\text{CV(w)}$, $\beta\text{CP(vw)}$
1.8	$\alpha\text{CP(s)}$, $\alpha\text{CV(m)}$, $\alpha\text{MP(m)}$, $\gamma\text{CV(vw)}$, MP2(vw), $\beta\text{CV(vw)}$, $\alpha\text{MV(vw)}$	$\beta\text{CV(s)}$, MP1(vw)	$\beta\text{CV(s)}$, MP1(m), $\alpha\text{MV(vw)}$	–
2.0	$\beta\text{CV(s)}$, $\alpha\text{MV(vw)}$	$\beta\text{CV(s)}$, $\alpha\text{MV(vw)}$	$\beta\text{CV(s)}$, $\alpha\text{MV(vw)}$, $\alpha\text{CV(w)}$	–

Crystalline phases: $\alpha\text{CP}=\alpha\text{-Cu}_2\text{P}_2\text{O}_7$, $\beta\text{CP}=\beta\text{-Cu}_2\text{P}_2\text{O}_7$, $\alpha\text{MP}=\alpha\text{-Mg}_2\text{P}_2\text{O}_7$, $\text{CP}=\text{Cu}_3\text{P}_2\text{O}_8$ (triclinic), $\text{MP1}=\text{Mg}_3\text{P}_2\text{O}_8$ (monoclinic, $\beta=90.99^\circ$), $\text{MP2}=\text{Mg}_3\text{P}_2\text{O}_8$ (monoclinic, $\beta=120.94^\circ$), $\text{MP}=\text{Mg}_3\text{P}_2\text{O}_8$ (orthorhombic), $\text{V}=\text{V}_2\text{O}_3$, $\alpha\text{CV}=\alpha\text{-Cu}_2\text{V}_2\text{O}_7$, $\beta\text{CV}=\beta\text{-Cu}_2\text{V}_2\text{O}_7$, $\gamma\text{CV}=\gamma\text{-Cu}_2\text{V}_2\text{O}_7$, $\alpha\text{MV}=\alpha\text{-Mg}_2\text{V}_2\text{O}_7$, $\text{MC}=\text{MgCu}_2\text{V}_2\text{O}_8$, $\text{T}=\text{Mg}_2\text{V}_2\text{O}_7$ (triclinic)

Diffraction peak intensity: s = strong, m = medium, w = weak, vw = very weak

Fig. 2 Variation in unit cell parameters in (diamond) the $\alpha\text{-Cu}_2\text{P}_2\text{O}_7$ structure ($x \leq 1.2$) and (square) the $\beta\text{-Cu}_2\text{V}_2\text{O}_7$ structure ($x \geq 1.5$) obtained from $\text{Mg}_{0.5}\text{Cu}_{1.5}\text{V}_x\text{P}_{2-x}\text{O}_7$ compositions fired at 600 °C

parameters with composition is greater in the $\alpha\text{-Cu}_2\text{P}_2\text{O}_7$ and $\beta\text{-Cu}_2\text{P}_2\text{O}_7$ structures than in the $\beta\text{-Cu}_2\text{V}_2\text{O}_7$ structure.

Figure 3 shows the variation in the M–O (M = Mg, Cu) and X–O (X = P, V) distances in the $\alpha\text{-Cu}_2\text{P}_2\text{O}_7$ and $\beta\text{-Cu}_2\text{V}_2\text{O}_7$ structures (developed when $x \leq 1.2$ and when $x \geq 1.5$, respectively) obtained from $\text{Mg}_{0.5}\text{Cu}_{1.5}\text{V}_x\text{P}_{2-x}\text{O}_7$ compositions fired at 600 °C. These changes in distances

Table 2 Unit cell from the $\alpha\text{-Cu}_2\text{P}_2\text{O}_7$ structure fired at 600 °C

x	a(Å)	b(Å)	c(Å)	β(°)
0.0	6.8443(3)	8.1188(3)	9.1478(2)	109.285(2)
0.3	6.8883(5)	8.1594(5)	9.2495(3)	108.756(5)
0.6	7.1534(6)	8.1451(5)	9.5332(7)	110.657(6)
0.9	7.1487(5)	8.1626(5)	9.5758(6)	110.333(5)
1.2	7.2106(4)	8.1460(5)	9.6974(4)	110.422(4)

Table 3 Unit cell from the $\beta\text{-Cu}_2\text{P}_2\text{O}_7$ structure fired at 800 °C

x	a(Å)	b(Å)	c(Å)	β(°)
0.0	6.7511(2)	8.1628(2)	4.5463(2)	107.997(2)
0.3	6.8401(2)	8.1667(2)	4.6027(1)	108.498(2)
0.6	7.0135(2)	8.1747(2)	4.7037(2)	109.596(2)
0.9	7.0807(4)	8.1533(4)	4.7676(2)	110.197(4)

Table 4 Unit cell obtained from the $\beta\text{-Cu}_2\text{V}_2\text{O}_7$ structure fired at 600 and 800 °C

T(°C)	x	a(Å)	b(Å)	c(Å)	β(°)
600	1.5	7.6168(3)	8.0624(2)	10.0340(3)	110.553(4)
600	1.8	7.6512(3)	8.0792(3)	10.0974(4)	110.565(3)
600	2.0	7.6445(2)	8.1030(2)	10.1146(3)	110.609(2)
800	1.5	7.6359(3)	8.0334(4)	10.0526(5)	110.603(5)
800	1.8	7.6372(5)	8.0811(5)	10.1092(5)	110.547(4)
800	2.0	7.6462(3)	8.0934(4)	10.1120(5)	110.547(3)

Fig. 3 Variation in M–O (M=Mg, Cu) and X–O (X=P, V) distances in **a** the α - $\text{Cu}_2\text{P}_2\text{O}_7$ structure ($x \leq 1.2$) and **b** the β - $\text{Cu}_2\text{V}_2\text{O}_7$ structure ($x \geq 1.5$) obtained from $\text{Mg}_{0.5}\text{Cu}_{1.5}\text{V}_x\text{P}_{2-x}\text{O}_7$ compositions fired at 600 °C

may be associated with structural changes and are due to changes in bond strength when solid solutions are formed. The mean distances increase with increasing x depending on the greater amount of V(V) in the compositions when solid solutions with both α - $\text{Cu}_2\text{P}_2\text{O}_7$ and β - $\text{Cu}_2\text{V}_2\text{O}_7$ structures are formed. The difference between the mean M–O (M=Mg, Cu) and the mean X–O (X=P, V) is greater in the α - $\text{Cu}_2\text{P}_2\text{O}_7$ structure than in the β - $\text{Cu}_2\text{V}_2\text{O}_7$ structure. M–O distances are greater in the α - $\text{Cu}_2\text{P}_2\text{O}_7$ structure. In both structures, four oxygen atoms are closer to M(II) (M=Mg, Cu) and the bond with the fifth oxygen atom is weaker and is more distant. The smaller difference between the mean M–O (M=Mg, Cu) distance and the mean X–O (X=P, V) distance in the solid solutions with the β - $\text{Cu}_2\text{V}_2\text{O}_7$ structure (with a greater amount of V(V) than P(V)) is due to lower covalence in the X–O bond in this structure than in the solid solutions with the α - $\text{Cu}_2\text{P}_2\text{O}_7$ structure (greater amount of P(V) than V(V)). The M–O (M=Mg, Cu) bond is slight smaller in the β - $\text{Cu}_2\text{V}_2\text{O}_7$ solid solutions. The covalence in the M–O (M=Mg, Cu) bond is higher in these solid solutions than in the α - $\text{Cu}_2\text{P}_2\text{O}_7$ solid solutions.

Figure 4 shows the UV–vis–NIR spectra of $\text{Mg}_{0.5}\text{Cu}_{1.5}\text{V}_x\text{P}_{2-x}\text{O}_7$ ($0 \leq x \leq 2$) compositions fired at 300, 600 and 1000 °C. A d–d transition is allowed from the Cu(II)

ion (d^9). Bands due to d–d transitions are not expected from V(V) or P(V) ions, but the charge transfer band of V(V) can be superimposed onto the charge transfer band of Cu(II). Both the position of these bands due to d–d transitions and the charge transfer band position in the spectra are related to the chemical bonds and colouration of the materials. The colour of the materials varies depending on where the bands appear: 650–800 (green), 580–650 (blue), 580–550 (violet), 490–550 nm (red), 450–490 (orange) or 400–450 (yellow) [29]. In the studied compositions containing Cu(II), two defined bands can be observed. The maximum due to the d–d transition falls outside the visible region of the spectrum (about 850 nm) and the charge transfer band is the most important component of the colour of these materials. At 300 °C, in the $\text{Mg}_{0.5}\text{Cu}_{1.5}\text{P}_2\text{O}_7$ composition ($x = 0.0$) and when $x \leq 0.9$, the band at 600–1200 nm can be assigned to the d–d transition of Cu(II) and the band at 350–625 nm to the charge transfer band of Cu(II) and V(V) ($x > 0.0$). With increasing x ($x > 0.9$), the definition of the bands is lost and the absorbance is ≥ 1 in the 200–1300 nm range (Fig. 4a). At 600 °C, two well defined bands can be observed in the spectra when $x > 0.0$. When $x = 0.0$, the charge transfer band moves to a smaller wavelength and falls outside the visible spectrum (Fig. 4b).

Fig. 4 UV-vis-NIR spectra of $\text{Mg}_{0.5}\text{Cu}_{1.5}\text{V}_x\text{P}_{2-x}\text{O}_7$ ($0.0 \leq x \leq 2.0$) compositions fired at **a** 300, **b** 600 and **c** 1000 °C

The band at 620–1300 nm can be assigned to the d–d transition of Cu(II), while the band at 350–625 nm corresponds to the charge transfer band (Cu(II) and V(V)). The increase in the amount of vanadium in the compositions changes the colour of the materials from yellow to red when $x \neq 0.0$. At this temperature, the $\text{Mg}_{0.5}\text{Cu}_{1.5}\text{P}_2\text{O}_7$ composition ($x = 0.0$) is pale green, whereas yellow materials are obtained when $x \leq 0.9$, orange materials when $x = 1.2$ and red materials when $x \geq 1.5$. These results can be related to the formation of solid solutions with the $\alpha\text{-Cu}_2\text{V}_2\text{O}_7$ structure when $x \leq 1.2$ (yellow materials) and solid solutions with the $\beta\text{-Cu}_2\text{V}_2\text{O}_7$ structure when $x \geq 1.5$ (red materials) detected by XRD. The high amounts of vanadium give rise to broad charge transfer bands. The position of the charge transfer band extends towards longer wavelengths, i.e. lower energies, with increasing x (the amount of vanadium increases), extending the maximum range in absorbance to 550 nm, and its shape changes when the $\beta\text{-Cu}_2\text{V}_2\text{O}_7$

structure develops ($x \geq 1.5$). The sum of both V–O and Cu–O charge transfer bands contributes to the band at 350–625 nm, although the variation in the amount of vanadium appears to contribute more to the position of its maximum. The increase in the amount of vanadium weakens the X–O ($X = \text{P}, \text{V}$) bonds (increase of the distances). The four X–O ($X = \text{P}, \text{V}$) distances are between 1.50 and 1.56 Å when $x = 0.3$, 1.54 and 1.60 Å when $x = 1.2$ ($\alpha\text{-Cu}_2\text{V}_2\text{O}_7$ structure), while the V–O distances are between 1.60 and 1.75 Å when $x = 2.0$ ($\beta\text{-Cu}_2\text{V}_2\text{O}_7$ structure). The difference between the smallest and longest of these distances (0.06 when $x = 0.3$, 0.06 when $x = 1.2$ and 0.15 when $x = 0$) may be related to the width of the charge transfer band. At 1000 °C in the composition without vanadium ($x = 0.0$), the charge transfer band also falls outside the visible spectrum. At this temperature (1000 °C) and when $x > 0.0$, the absorbance is high over the entire wavelength range. The minimum between the d–d transition and charge transfer band is lost (Fig. 4c). This could be due to the high number of different distances in the phases including $\text{Cu}_3\text{X}_2\text{O}_8$ ($X = \text{P}, \text{V}$) present in compositions with a strong diffraction intensity at this temperature (Table 3). Heating in oxidizing atmosphere provoke a partial sinterization of the samples without changes in the oxidation state of the vanadium. The pale green colour of the $\text{Mg}_{0.5}\text{Cu}_{1.5}\text{P}_2\text{O}_7$ ($x = 0.0$) composition remains at 1000 °C.

In the $\beta\text{-Cu}_2\text{V}_2\text{O}_7$ structure, the Cu(II) ions are surrounded by oxygen atoms and form edge-sharing CuO_5 polyhedra. In the CuO_5 polyhedra, the Cu–O bond length along the a axis is much longer than the other four Cu–O bond lengths on the bc plane due to Jahn–Teller distortion. This anisotropic environment gives rise to the strong magnetic anisotropy of this compound [30].

On this scenario, the $\text{Mg}_{0.5}\text{Cu}_{1.5}\text{V}_2\text{O}_7$ ($x = 2.0$) composition may be considered a paramagnetic substance in the temperature range studied here (100–300 K), where the unpaired electrons from the Cu(II) ions (one electron from each Cu(II) ion) are oriented at random on the structure. But under strong applied magnetic field the magnetic dipole moment will be oriented towards the field direction and partial misalignment of spins is achieving during heating, giving a response that is inversely proportional to temperature. Thus, the temperature dependency of the inverse of the molar magnetic susceptibility, χ_m^{-1} , between 100 and 300 K, is included in Fig. 5. The curve provides a good fit to the Curie–Weiss law ($\chi_m = \frac{C_m}{T - \theta}$) depicted by the dotted line (see Table 5). From the molar Curie constant, C_m , we have established the effective magnetic moment, μ_{eff} for Cu(II) ions assuming that the remaining atoms are non-magnetic. The effective moment obtained ($\mu_{\text{eff}} = \sqrt{\frac{3k_B}{N_A} \frac{1}{\mu_B}} \sqrt{C_m} \approx 2.827 \sqrt{C_m} [\mu_B]$) is in accordance with the $\mu_{\text{observed}} = 1.7\text{--}2.2$ reported in Cu^{2+} complexes.

Fig. 5 Dependence of the inverse of the magnetic susceptibility with temperature for $\text{Mg}_{0.5}\text{Cu}_{1.5}\text{V}_2\text{O}_7$ ($x=2.0$) composition fired at 500 °C

Table 5 Molar Curie constant (C_m), Weiss constant (θ) and effective magnetic moment (μ_{eff}) of Cu(II) ions for the $\text{Mg}_{0.5}\text{Cu}_{1.5}\text{V}_2\text{O}_7$ composition fired at 500 °C

Calcination temperature (°C)	C	θ (K)	μ_{eff} (B.M.)
500	0.463	− 25.4	1.92(4)

Moreover, the Weiss constant, θ , is negative, which points out that the $\text{Mg}_{0.5}\text{Cu}_{1.5}\text{V}_2\text{O}_7$ sample behaves an antiferromagnetic order, but its onset should be below the lower temperature reached.

The CIE L^* a^* and b^* parameters of $\text{Mg}_{0.5}\text{Cu}_{1.5}\text{V}_x\text{P}_{2-x}\text{O}_7$ ($0 \leq x \leq 2$) compositions fired at 300, 500, 600, 800 and 1000 °C are shown in Table 6. At 600 °C, a progressive and interesting change from yellow to red is obtained. This fact is related with the progressive change in the unit cell parameters (Fig. 2) and Cu–O distances (Fig. 3). The values of $b^*(+)$, amount of yellow colouration, in compositions with $0.3 \leq x \leq 1.2$ are high. The $b^* = +50.93$ value obtained from the $\text{Mg}_{0.5}\text{Cu}_{1.5}\text{V}_{0.9}\text{P}_{1.1}\text{O}_7$ ($x=0.9$) composition fired at 600 °C is comparable to the $b^* = 55.52$ value obtained from $\text{Ni}_2\text{P}_2\text{O}_7$ fired at 1000–1200 °C [31] and better than the $b^* = 47.81$ from $\text{Ni}_2\text{V}_2\text{O}_7$ fired at 600 °C [32]. In these compositions, the majority crystalline phase presents the $\alpha\text{-Cu}_2\text{P}_2\text{O}_7$ structure. When x decreases, the yellow colour of the samples becomes paler (the b^* value is smaller). In these compositions, the b^* values become smaller with increasing temperature ($b^* < 32$ at 800 °C and $b^* < 14$ at 1000 °C). When the temperature increases, the colour of the materials turns beige at 800 °C and dark at 1000 °C. The values of $b^*(+)$, amount of red colouration, are higher in compositions with $1.2 \leq x \leq 2.0$. The b^* values range between +20.14 and 22.61 at 600 °C and only between +2.67 and +0.88 at 800–1000 °C. When $x > 1.2$, the majority crystalline phase presents the $\beta\text{-Cu}_2\text{V}_2\text{O}_7$ structure. Hence,

the $\alpha\text{-Cu}_2\text{P}_2\text{O}_7$ structure is associated with yellow colourations of materials, the $\beta\text{-Cu}_2\text{P}_2\text{O}_7$ structure ($x \neq 0.0$) with brown colourations and the $\beta\text{-Cu}_2\text{V}_2\text{O}_7$ structure with red colourations at 600 °C. $\text{Mg}_{0.5}\text{Cu}_{1.5}\text{V}_x\text{P}_{2-x}\text{O}_7$ ($0 < x \leq 2$) solid solutions fired at 600 °C might be used in the preparation of yellow–orange–red paint pigments.

With increasing temperature, all the CIE L^* a^* and b^* parameters decrease and the colour of the $\text{Mg}_{0.5}\text{Cu}_{1.5}\text{V}_x\text{P}_{2-x}\text{O}_7$ ($0 \leq x \leq 2$) compositions tends towards dark brown. The evolution towards dark colour was also detected from $\text{Mg}_y\text{Cu}_{2-y}\text{V}_2\text{O}_7$ solid solutions [15]. It can relate to the development of $\text{Cu}_3\text{P}_2\text{O}_8$, $\text{Mg}_2\text{P}_2\text{O}_8$, $\alpha\text{-Mg}_2\text{P}_2\text{O}_7$, $\alpha\text{-Mg}_2\text{V}_2\text{O}_7$ structures. These crystalline phases are more stable at high temperature than the $\alpha\text{-Cu}_2\text{P}_2\text{O}_7$ and $\beta\text{-Cu}_2\text{V}_2\text{O}_7$ structures. Stable structures are associated with dark colorations of materials and can be used as ceramic pigments due to the development of the crystalline phases with higher thermal stability.

4 Conclusions

$\text{Mg}_{0.5}\text{Cu}_{1.5}\text{V}_x\text{P}_{2-x}\text{O}_7$ ($0.0 \leq x \leq 2.0$) compositions were synthesized via the chemical co-precipitation method. Structural characterization of these materials and the increase in the unit cell parameters with composition (amount of vanadium) in the $\alpha\text{-Cu}_2\text{P}_2\text{O}_7$, $\beta\text{-Cu}_2\text{P}_2\text{O}_7$ and $\beta\text{-Cu}_2\text{V}_2\text{O}_7$ structures confirm the formation of solid solutions in these structures in a partial compositional range. Results are consistent with the substitution of the P(V) ion by the V(V) ion in the $\alpha\text{-Cu}_2\text{P}_2\text{O}_7$ (at 500–600 °C when $0.0 \leq x \leq 1.2$) and $\beta\text{-Cu}_2\text{P}_2\text{O}_7$ (at 800–1000 °C when $0.0 \leq x \leq 1.2$) structures or with the substitution of the V(V) ion by the P(V) ion in the $\beta\text{-Cu}_2\text{V}_2\text{O}_7$ structure (at 600–800 °C when $x \geq 1.5$) ($r(\text{P(V)}) < r(\text{V(V)})$ in C.N. = 4).

The charge transfer band is the most important component of the colour of these materials. High amounts of vanadium give rise to broad charge transfer bands. At 600 °C, when $x > 0.0$, the d–d transition of Cu(II) (620–1300 nm) and the charge transfer band of Cu(II) and V(V) (350–625 nm) can be observed in the spectra, as two well defined bands. The extension of the maximum absorbance range of the charge transfer band increases with x . Hence, yellow materials are obtained when $0.0 < x \leq 0.9$, orange materials when $x = 1.2$ and red materials when $x \geq 1.9$ (maximum range in absorbance to 350–550 nm). The shortest Cu–O distances may be associated with the $\beta\text{-Cu}_2\text{V}_2\text{O}_7$ structure and the red colour of these materials.

Optimal yellow material with $b^* = +50.93$ value and optimal red material with $a^* = 22.61$ were obtained from the $\text{Mg}_{0.5}\text{Cu}_{1.5}\text{V}_{0.9}\text{P}_{1.1}\text{O}_7$ ($x=0.9$) and $\text{Mg}_{0.5}\text{Cu}_{1.5}\text{V}_{1.8}\text{P}_{0.2}\text{O}_7$ ($x=1.8$) compositions fired at 600 °C.

Table 6 CIE L* a* b* colour parameters and observed colour in $\text{Mg}_{0.5}\text{Cu}_{1.5}\text{V}_x\text{P}_{2-x}\text{O}_7$ ($0 \leq x \leq 2$) compositions

x	CIE L* a* b* Parameter	300 °C	500 °C	600 °C	800 °C	1000 °C
0.0	L*	67.07	85.29	85.47	87.41	81.85
	a*	−3.74	−5.59	−3.71	−8.09	−8.88
	b*	+33.58	+5.89	+6.30	+1.05	+1.17
		Yellowish green	Pale green	Pale green	Pale green	Pale green
0.3	L*	50.69	48.07	70.69	51.41	44.82
	a*	+0.50	+2.58	+0.07	+11.41	−1.68
	b*	+19.87	+9.78	+40.40	+26.83	+1.50
		Greenish brown	Brown	Yellow	Reddish beige	Dark grey
0.6	L*	42.96	46.34	68.66	54.25	43.13
	a*	−0.46	+3.65	+5.73	+5.49	−1.25
	b*	+13.22	+9.94	+41.31	+31.23	+8.72
		Greenish brown	Brown	Yellow	Yellowish beige	Dark green
0.9	L*	40.59	57.71	64.82	53.07	42.14
	a*	−1.73	+10.03	+8.67	+3.56	+2.56
	b*	+11.55	+36.12	+50.93	+29.52	+13.79
		Dark green–brown	Beige	Yellow	Yellowish beige	Brown
1.2	L*	33.07	42.80	47.16	31.38	34.56
	a*	−2.46	+1.09	+21.42	+1.98	+2.67
	b*	+6.42	+7.33	+37.91	+5.48	+7.02
		Dark green–brown	Brown	Orange	Dark brown	Reddish dark red
1.5	L*	34.41	31.19	42.73	29.45	31.62
	a*	−4.39	−2.11	+20.14	+2.17	+2.20
	b*	+8.40	+0.30	+20.12	+4.10	+4.39
		Dark green	Black–dark green	Orange–red	Black–very dark brown	Dark red
1.8	L*	33.34	42.71	42.09	31.71	–
	a*	−3.21	+3.31	+22.61	+0.80	–
	b*	+6.87	+10.22	+17.14	+3.29	–
		Dark green	Brown	Garnet red	Black–very dark brown	–
2.0	L*	33.32	34.87	38.34	33.37	–
	a*	−3.10	+22.33	+20.33	+2.19	–
	b*	+6.76	+15.65	+15.59	+6.94	–
		Dark green	Red	Garnet red	Very dark Brown	–

$\text{Mg}_{0.5}\text{Cu}_{1.5}\text{V}_x\text{P}_{2-x}\text{O}_7$ ($0 < x \leq 2$) solid solutions fired at 600 °C might be used in the preparation of yellow–orange–red paint pigments. The colour of the materials darkens with increasing temperature. Hence, these pigments might be used in paints or as an additive in materials that do not need to exceed 600 °C.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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