RbCuPO$_4$ – a maximum copper tetrahedral framework adopting the zeotype ABW structure

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The sky blue RbCuPO$_4$-ABW is the first reported maximum copper (framework ratio 1 : 1) zeotype framework, consisting of alternating PO$_4$ and flattened CuO$_4$ (Cu–O 1.89–1.95 Å) tetrahedra; a second metastable very pale green–blue phase can also be produced by quenching, with conversion to the purely four-coordinate copper material accomplished by application of slight mechanical pressure.

The incorporation of transition metals into frameworks, including zeolites, is of great interest due to the properties potentially imparted by the presence of d-metal centres including catalytic activity, colour and magnetic ordering phenomena. Zeolite structures containing first row transition metals have received most attention, although in general the levels of substitution have been low, presumably due to the reduced stability of tetrahedral coordination over higher coordination environments (5- and 6-fold) in the aqueous media used to synthesise the majority of framework materials. Work to date has centred on the first row transition metals that do show appreciable tetrahedral coordination chemistry to oxygen, namely Co^{2+} and Zn^{2+}. Frameworks containing high levels of Co^{2+} were first described by Chippindale *et al.*[1] and were extended by Stucky and coworkers, using hydrothermal methods, to include the ABW and related semi-condensed frameworks such as Na-CoPO$_4$, KCoPO$_4$, NH$_4$CoPO$_4$ and RbCoPO$_4$.[2] We completed this series by synthesising CsCoPO$_4$ ABW using a solid state route.[3] Until recently, the levels of other transition metals that could be doped into most zeolite structure types remained low, at around 5% of the tetrahedral sites. However, synthesis of other maximum transition-metal ABW related frameworks has now been achieved by our group to include CsFeSiO$_4$[4] and RbNiPO$_4$.[5]

We have found that the zeotype structures that permit high levels of transition metal substitution are generally denser, in terms of tetrahedral units per unit volume, and exist with low levels of hydration, for example the ABW, CAS, ANA and BIK zeolite families.[6] In terms of transition metal substitutions, the ANA structure type is the most versatile with transition metal substituted leucite[7] and pollucite[8,9] phases described in the literature. However the levels of substitution in this system are limited through compound stoichiometry at 16.6% of the framework sites, *i.e.* to the one trivalent tetrahedral site.

Here we describe the synthesis and structural characterisation of the ABW-type structure material RbCuPO$_4$, where half of the tetrahedral framework sites are occupied by copper.

A polycrystalline sample of RbCuPO$_4$-ABW was produced as follows. Stoichiometric amounts of Cu(MeCO$_2$)$_2$ (Aldrich, 99.9%), (NH$_4$)$_2$HPO$_4$ (Aldrich, 99%) and RbOH (Aldrich, 50% solution by weight in water) were dissolved in dilute nitric acid. 100 ml ethanol was then added to the solution and the pH slowly raised by the addition of ammonia solution until precipitation occurred. The resulting mixture was slowly evaporated to give a thick gel paste, which was decomposed over 12 h in a furnace at 250 °C. The powder was thoroughly ground in an agate pestle and mortar before being fired at 650 °C and then 750 °C, each for 12 h. Soluble impurities were removed by washing with deionised water followed by firing for 12 h at 750 °C. Powder

X-ray diffraction patterns were collected for preliminary phase identification and subsequent Rietveld analysis using a Siemens D5000 diffractometer (Cu-Kα_1 radiation; λ = 1.54056 Å). GSAS was used for Rietveld refinement of the powder X-ray data.[10]

Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were performed using a Polymer Laboratories STA1500 DTA/TGA balance. The sample was heated in air at a rate of 5 °C min^{-1} from room temperature to 600 °C, held for 30 min at this temperature and then cooled back to room temperature at 10 °C min^{-1}. Diffuse reflectance UV–VIS spectra were obtained from a Lambda19 spectrophotometer with solid state attachment. The Kubelka–Munk function was applied to the data to compensate for the effects of particle size. Elemental analysis was carried out using a JEOL JSM-6400 SEM equipped with a TRACOR series II energy dispersive X-ray analysis system.

Inspection of the powder X-ray diffraction (PXD) pattern of the as-synthesised material showed that the majority phase present could be indexed on an orthorhombic unit cell with a = 8.5262(4) Å, b = 5.3562(3) Å and c = 8.9064(4) Å. There were also several weaker peaks that were indexed on a monoclinic unit cell with a = 5.0424(8) Å, b = 8.5880(2) Å, c = 9.6434(2) Å and α = 91.51(1)°. Both unit cells were consistent with structure types that have been previously reported for the ABW-type framework.[11]

Grinding the product followed by further PXD pattern collection showed that the proportion of the two phases present was altered, with the orthorhombic phase growing in intensity. Quenching the reaction from above 600 °C to RT without any grinding gave the monoclinic phase as the major phase (*ca.* 9 : 1 ratio). Pelletisation of the product under 6 tonnes cm^{-2} for 10 min followed by regrinding gave essentially *only* the orthorhombic product and increased the intensity of the blue colouration of the product. We have also recently found that nickel doping into RbCuPO$_4$ stabilises the monoclinic ABW subtype and details of the new sub-structure will be published elsewhere.[12]

Data for Rietveld profile analysis on the orthorhombic phase were collected over a period of 16 h between 10 and 110° using a step size of 0.02°. The initial model used for the refinement was that of Henry and Weller for CsFeSiO$_4$.[4] Weak constraints (standard deviation 0.01 Å) were placed upon bond lengths in the refinement due to the poor definition of the oxygen positions from powder X-ray diffraction data. A few weak impurity peaks (<5% of the maximum peak intensity) were also excluded from the refinement. The final refinement profile is illustrated in Fig. 1 and the structural model is given in Table 1. Derived bond lengths and relevant framework bond angles are given in Table 2. It can be seen from Table 2 that the phosphate tetrahedra are much more regular than the cuprate polyhedra, which are flattened in accordance with the expected Jahn–Teller distortion found in other four-coordinate Cu^{II} compounds.[13]

TGA showed the orthorhombic phase to be a non-hydrated framework, as no weight losses were observed between RT and 800 °C. Fig. 2 illustrates the DTA trace obtained for the orthorhombic phase between RT and 600 °C. It can be seen that
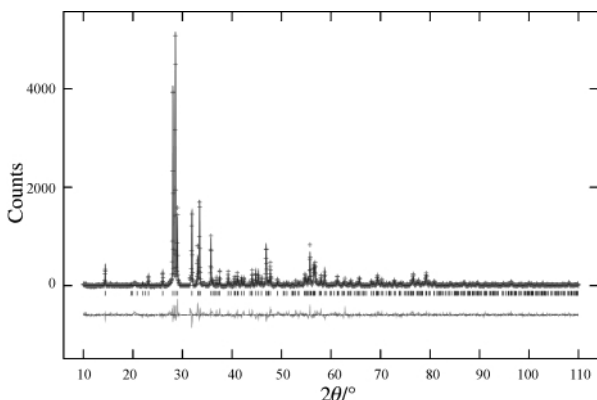
Fig. 1 Final profile fit obtained from the powder X-ray diffraction data for RbCuPO₄. The observed data are crosses, the calculated profile pattern the solid line and the lower continuous line the difference plot. Tick marks show the allowed reflection positions.

Table 1 Atomic coordinates for RbCuPO$_4^a$

Atom	Multi-plicity	x	y	z	$10^2 U_{iso}/\text{Å}^2$
Rb	4e	0.1768(4)	0.4719(20)	0.5199(4)	2.80(14)
Cu	4e	0.4140(9)	−0.0303(20)	0.3268(7)	4.48(25)
P	4e	0.0791(18)	−0.0146(27)	0.1837(14)	4.0(3)
O1	4e	0.1419(25)	0.028(5)	0.0294(14)	4.4(7)
O2	4e	−0.0621(23)	−0.1769(27)	0.1682(33)	4.4(7)
O3	4e	0.0534(31)	0.2262(30)	0.2667(24)	4.4(7)
O4	4e	0.2302(23)	−0.1355(34)	0.2249(31)	4.4(7)

^{a} Space group $Pc2_1n$: a = 8.5261(4) Å, b = 5.3562(2) Å, c = 8.9064(4) Å, R_p = 12.57%, R_{wp} = 16.72%, R_{F^2} = 17.06% for 315 observations.

Table 2 Derived bond distances (Å) and angles (°) for RbCuPO₄ (e.s.d.s are given in parentheses)

P–O1	1.490(6)	O1–P–O2	107.0(17)
P–O2	1.492(6)	O1–P–O3	112.1(19)
P–O3	1.504(7)	O1–P–O4	90.1(16)
P–O4	1.486(6)	O2–P–O3	115.3(17)
Cu–O1	1.892(11)	O2–P–O4	117.9(17)
Cu–O2	1.905(12)	O3–P–O4	112.2(15)
Cu–O3	1.951(12)	O1–Cu–O2	80.9(12)
Cu–O4	1.896(12)	O1–Cu–O3	132.1(11)
		O1–Cu–O4	107.3(12)
		O2–Cu–O3	127.5(12)
		O2–Cu–O4	113.3(12)
		O3–Cu–O4	95.8(12)

there are two phase transitions on heating, at 410 and 550 °C, only one of which is reversible on cooling. It is thought that the first transition is the orthorhombic–monoclinic phase transition but the second transition is yet to be characterised. The first transition can be assigned as the orthorhombic–monoclinic phase interconversion because it is absent on cycling and rapid cooling is known to give the monoclinic phase. Further investigation is planned using variable temperature powder neutron diffraction in order to study the copper coordination sphere, the orthorhombic–monoclinic phase transition and the high temperature polymorph.

Elemental analysis using EDAX confirmed the ratio of Rb:Cu:P to be 1:1:1 within experimental error and the UV–VIS spectrum showed an absorption centred at approximately 610 nm in the visible region, which is consistent with that expected for copper coordinated to four oxygen atoms, *e.g.* CaCu(MeCO₂)₄.6H₂O,[13] and the observed sky blue colour.
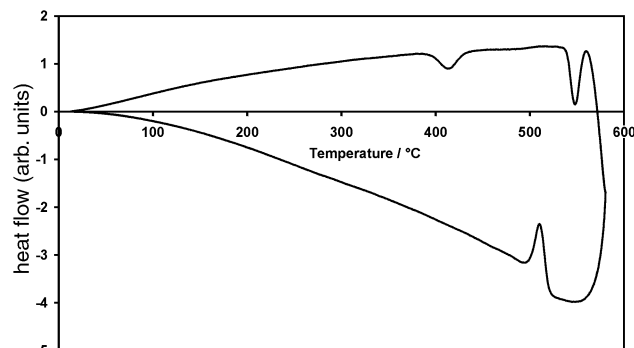

Fig. 2 DTA trace of RbCuPO₄ between RT and 600 °C showing two transitions, the first at 410 °C is irreversible under the experimental conditions and the second at 550 °C in the heating cycle and 510 °C in the cooling cycle is reversible.

In this case, the small pore size, illustrated by the fact that the extra-framework counter cation cannot be ion exchanged, either in solution or by melt methods, means that the material is very unlikely to be a selective catalyst, with any activity being restricted to the surfaces of the particles. However, we have shown that high levels of transition metals can be doped into zeotype frameworks using this experimental route, which may lead to new catalytic materials in the future.

We have successfully synthesised the first maximum copper framework (1:1 framework species ratio) with a zeolite topology, RbCuPO₄-ABW. Two structurally similar phases exist at room temperature with the proportions being determined by the final heating regime, cooling conditions and subsequent grinding. Slow cooling followed by grinding gives a framework containing purely four-coordinate copper whereas quenching without grinding gives a metastable monoclinic phase as the major phase (*ca.* 9:1 ratio). This second phase, which is very pale green-blue, can be converted back to the purely four-coordinate Cu containing framework by the application of moderate pressure (*e.g.* mechanical grinding or pelletisation). This transition is readily observed by the marked colour change.

Notes and references

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