DALTON
FULL PAPER

Synthesis and structural characterisation of $CsCoPO_4$-ABW

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The cobalt phosphate, $CsCoPO_4$, possessing the zeolite ABW framework topology has been synthesised using a solid state route. Rietveld refinement from powder neutron diffraction data has shown the material to be a direct structural analogue of $CsZnPO_4$ polymorph III. The framework is made up of alternating cobaltate and phosphate tetrahedra sharing vertices with caesium counter cations located in the channels formed. The presence of Co(II) tetrahedra, confirmed by UV visible spectroscopy, is responsible for the intense blue colour of the material. DTA analysis combined with preliminary variable temperature powder X-ray diffraction has shown the presence of a phase transition at approximately 171 °C to an orthorhombic unit cell probably isostructural with $CsZnPO_4$ polymorph II.

Introduction

The substitution of transition metal centres into the frameworks of zeolites has recently become a topic of great interest due to the increased catalytic properties of some of these materials. Examples include the introduction of iron into sodalite[1] for the partial oxidation of methane to methanol and cobalt into aluminophosphate zeolites for the autoxidation of cyclohexane[2] and *p*-cresol.[3] The redox properties of the transition metal, usually involving the divalent and trivalent states, are probably also crucial to such processes. However, for most transition metal species the level of incorporation of the divalent metal into the framework is low. This is probably a result of the lower stability of tetrahedral coordination for the larger transition metal, with respect to higher coordination environments, in particular octahedral coordination, discouraging their incorporation from aqueous media.

Until recently the level of iron that could be doped into a zeolite structure remained low, at around 5% of the tetrahedral sites, though the formation of the maximum iron content in the structure $CsFeSiO_4$[4] indicates that under the correct synthetic conditions higher substitution of transition metal is obtainable. The exception to this general behaviour is cobalt where the stability of divalent cobalt in tetrahedral sites allows significant levels of cobalt incorporation into several zeolite and other framework structures, *e.g.* NH_4CoPO_4,[5] CoAPO-5[2] and CoAPO-11.[3] A related problem associated with high levels of tetrahedral divalent transition metals in framework structures is hydrolysis to give higher co-ordinate species. Therefore, zeolite structures that permit high levels of framework substitution are generally denser frameworks that exist with low levels of hydration, such as the ABW framework.

One divalent species which has been studied in detail in terms of its incorporation into frameworks is Zn^{2+}, for example in the phases $NaZnSiO_3(OH)$[6] and $CsZnPO_4$.[7] Due to the similarity in size of Zn^{2+} and Co^{2+} there are many cobalt analogues of the zinco–phosphate systems. Indeed, $RbCoPO_4$, $KCoPO_4$ and NH_4CoPO_4 are all isostructural with their zinco–phosphate counterparts.[5] Three polymorphs of $CsZnPO_4$ have been described,[7] but to date there has been no structural report of the cobalt analogue. Napijalo *et al.*[8] claim to have synthesised $CsCoPO_4$ which crystallises with a triclinic unit cell with lattice parameters $a = 5.6(1)$ Å, $b = 9.9(2)$ Å, $c = 9.1(2)$ Å, $\alpha = 77.71(4)°$, $\beta = 87.35(6)°$, $\gamma = 53.98(3)°$ although without any structural details.

New frameworks with high levels of cobalt were first described by Chippindale *et al.*[9] Stucky and co-workers[5] extended the series to include several ABW and ABW related frameworks such as $NaCoPO_4$, $KCoPO_4$, NH_4CoPO_4 and $RbCoPO_4$. However, none of these publications reports an ABW with the composition $CsCoPO_4$. Here we present the synthesis of $CsCoPO_4$, adopting the ABW framework topology, and structural refinement from powder data along with preliminary studies into its physical properties.

Experimental

Polycrystalline $CsCoPO_4$ was prepared by grinding together $(NH_4)_2HPO_4$ (Aldrich, 99%), Cs_2CO_3 (Aldrich, 99.9%) and $Co(NO_3)_2\cdot 6H_2O$ (Aldrich, 98%) in the molar ratio 2:1:2. The resulting mixture was fired at 1000 °C for 24 hours then cooled to room temperature at 30 °C per hour. The product was found to be an intense blue colour. At significantly longer synthesis times a black amorphous, and as yet unknown, decomposition layer appeared on the surface of the powder.

Room temperature powder X-ray diffraction data were collected using a Siemens D5000 diffractometer (Cu-K$_{\alpha 1}$ radiation; $\lambda = 1.5406$ Å) over the range $10° < 2\theta < 100°$ for 15 hours. Powder neutron diffraction data were collected using the High Resolution Powder Diffractometer (HRPD) at the Rutherford Appleton Laboratory. A 10 g sample was loaded into an 11 mm diameter vanadium sample can and data were collected over a period of 6 hours at the one metre sample position. The high-resolution backscattering data were used for structural refinement. GSAS[10] was used for refinement of the powder X-ray and powder neutron diffraction data. Variable temperature powder X-ray diffraction patterns from $CsCoPO_4$ were obtained using an INEL CPS120 diffractometer (Cu-K$_\alpha$ radiation) at 21 °C and 190 °C with silicon powder as an internal standard. Preliminary indexing was carried out using the CRYSFIRE program.[11]

Differential thermal analysis was performed using a Polymer Laboratories STA1500 differential thermal analysis/thermogravimetric analysis balance. The sample was heated in air at a rate of 10 °C per minute from room temperature to 250 °C and then cooled at 10 °C per minute back to room temperature. Diffuse reflectance UV-visible spectra were obtained from a Lambda 19 spectrophotometer with solid state attachment. The Kubelka–Munk function was applied to the data to

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compensate for the effects of differing particle sizes. Both pure and diluted (30 wt.% TiO_2) samples were recorded.

Results and discussion

Inspection of the powder X-ray diffraction data showed $CsCoPO_4$ to adopt an ABW-type structure, where all the reflections could be indexed using a monoclinic unit cell with approximately the lattice parameters $a = 9.21$ Å, $b = 5.47$ Å, $c = 9.29$ Å, $\beta = 90.36°$. However, it was not possible to ascertain whether there was a doubling of a, as found by Blum *et al.* for $CsZnPO_4$,[7] from the X-ray data alone. Preliminary refinement of the structure, using the space group $P2_1$, proved satisfactory in supporting the ABW structure model. However, the domination of the X-ray scattering by caesium left many structural parameters poorly defined and in order to delineate the framework more accurately further investigation was carried out using the powder neutron diffraction data alone.

The initial neutron refinement model was NH_4LiSO_4 of Hasebe and Asahi[12] with NH_4^+ being replaced by Cs^+, Li^+ by Co^{2+} and S^{6+} by P^{5+}. It became apparent at an early stage in the refinement that there were several peaks in the powder neutron diffraction pattern that remained unindexed using the space group $P2_1$. Using powder data, it is notoriously difficult to distinguish between $P2_1$ and $P2_1$ plus a centre of inversion, due to peak overlap of hkl and $\bar{h}kl$ reflections. The result of the addition of an inversion centre would either be a disordered framework with an identical unit cell volume or an ordered framework with a doubled unit cell volume. The work of Blum *et al.*[7] on $CsZnPO_4$ polymorphs has demonstrated that the latter occurs when there is a mismatch between the radii of the framework cations. In order to assist in the assignment of the correct space group, LeBail type intensity extractions were performed, using the powder neutron data, in the possible space groups, $P2_1/a$ and $P2_1$, giving χ^2 of 2.3 and 5.5 respectively strongly supporting the former as the actual space group. For completeness, extractions were also performed in the other possible monoclinic space groups known for ABW-type materials but were discarded due to very poor fit statistics.

The neutron refinement was repeated using the model of Blum *et al.*[7] for $CsZnPO_4$ polymorph III as a starting point. The refinement proceeded smoothly, without the use of constraints, and converged to give χ^2 of 10.4 using isotropic temperature factors throughout. However, although introduction of anisotropic temperature factors reduced χ^2 to below 5.5, some of the resultant oxygen ellipsoids were found to be highly anisotropic. Two explanations can be given for this. The first is that there is some oxygen disorder between the hexagonal tridymite-like layers, which we have found previously from powder neutron refinements of other known ABW materials. The second is that the data set as collected does not yield enough intensity information to be able to refine 150+ variables without introduction of a significant number of constraints to the model. It is thought that the results from the Rietveld refinement are a combination of these two factors. Therefore, we present here only the results of the model with isotropic thermal parameters and no oxygen disorder. Fig. 1 shows the final fit obtained to the powder neutron data. Table 1 details the structural model and Table 2 the derived bond distances and angles from the unconstrained refinement. Further detailed investigations into the oxygen disorder are continuing but, as described above, a definitive elucidation of the structure with a reasonable number of variables may be precluded. The powder X-ray data were then fitted using the final neutron model, which confirmed the result giving χ^2 of 1.52 *cf.* 1.34 for the LeBail extraction.

The structure (Fig. 2) is comprised of alternating PO_4^{3-} and CoO_4^{6-} tetrahedra obeying an extension of Loewenstein's rule,[13] which states that the linking of tetrahedra centred on low charged T atoms through oxygen is unfavourable. There are two caesium positions within the main 8-ring channels, parallel to the b axis. The caesium atoms coordinate fully to the framework oxygen atoms on both sides of the channel effectively filling them and so, unlike the Li-ABWs,[14] contain no zeolitic water. The derived bond distances yield typical values for both Co–O and P–O bonds, 1.917–1.953 Å and 1.507–1.546 Å respectively. However, the bond angles are significantly distorted from ideal tetrahedral geometry (109.5°) varying from 102.7°–117.7°, with the cobaltate tetrahedra more distorted than the phosphate tetrahedra. Cobalt and other large transition metal divalent cations tend to form tetrahedra that are more distorted than those around higher charged elements, such as silicon and

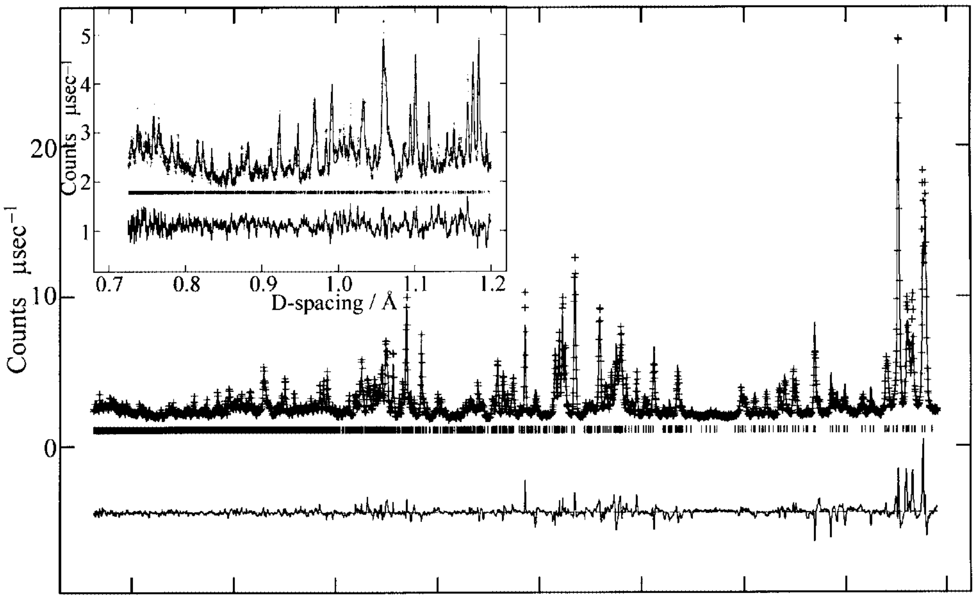

Fig. 1 Final profile fit obtained from the powder neutron diffraction data for $CsCoPO_4$. The crosses are the observed data, the upper continuous line the calculated profile pattern and the lower continuous line the difference plot. The tick marks show the allowed reflection positions. The inset illustrates an enlarged profile fit to the low D-spacing data.

Table 1 Atomic coordinates for $CsCoPO_4$

Atom	Multiplicity	x	y	z	100 x U_{iso}/Å^2
Cs1	4e	0.00383(21)	0.2434(15)	0.2076(4)	0.91(10)
Cs2	4e	0.24924(25)	0.7325(11)	0.6919(5)	2.16(12)
Co3	4e	0.0892(4)	0.2517(11)	0.5821(8)	2.09(22)
Co4	4e	0.1674(5)	0.7280(14)	0.0880(8)	2.85(27)
P5	4e	0.09634(20)	0.7498(10)	0.4169(4)	0.80(9)
P6	4e	0.34652(22)	0.7329(9)	0.0919(4)	1.15(10)
O7	4e	−0.01572(22)	0.2525(12)	0.5569(4)	1.98(11)
O8	4e	0.88751(29)	0.1996(13)	0.7399(5)	4.69(18)
O9	4e	0.86834(27)	0.0355(9)	0.5003(5)	2.68(16)
O10	4e	0.36823(33)	0.0145(9)	0.5268(6)	3.41(18)
O11	4e	0.26820(22)	0.7469(12)	0.1480(4)	1.67(11)
O12	4e	0.60057(25)	0.1999(10)	0.7859(5)	3.20(14)
O13	4e	0.35819(32)	0.8933(9)	0.9599(7)	3.32(16)
O14	4e	0.36461(31)	0.4637(9)	0.0570(6)	3.11(15)

[a] Space group $P2_1/a$: $a = 18.42806(16)$, $b = 5.47254(5)$, $c = 9.28972(10)$ Å, $\beta = 90.365(1)°$, $\chi^2 = 10.36$, $R_{wp} = 7.53\%$, $R_p = 6.54\%$, $R_{F**2} = 10.34\%$ for 3010 observations.

Table 2 Derived bond distances (Å) and angles (°) (estimated standard deviations are given in parentheses)

Co3–O7	1.947(9)	O7–Co3–O9	111.2(4)
Co3–O9	1.917(5)	O7–Co3–O10	110.0(4)
Co3–O10	1.927(5)	O7–Co3–O12	102.68(32)
Co3–O12	1.922(8)	O9–Co3–O10	103.53(33)
Co4–O8	1.939(4)	O9–Co3–O12	117.7(4)
Co4–O11	1.939(10)	O10–Co3–O12	111.8(4)
Co4–O13	1.943(5)	O8–Co4–O11	104.8(4)
Co4–O14	1.953(11)	O8–Co4–O13	104.8(4)
P5–O7	1.507(6)	O8–Co4–O14	106.1(5)
P5–O8	1.514(4)	O11–Co4–O13	110.3(5)
P5–O9	1.546(7)	O11–Co4–O14	116.6(4)
P5–O10	1.534(4)	O13–Co4–O14	113.1(5)
P6–O11	1.539(6)	O7–P5–O8	110.90(32)
P6–O12	1.537(6)	O7–P5–O9	109.8(4)
P6–O13	1.524(7)	O7–P5–O10	110.9(4)
P6–O14	1.546(4)	O8–P5–O9	104.8(4)
Cs1–O7	3.268(5)	O8–P5–O10	113.3(4)
Cs1–O7	3.491(9)	O9–P5–O10	106.93(33)
Cs1–O7	3.527(9)	O11–P6–O12	109.27(34)
Cs1–O8	3.180(9)	O11–P6–O13	112.4(4)
Cs1–O8	3.678(9)	O11–P6–O14	108.8(4)
Cs1–O9	3.874(7)	O12–P6–O13	111.4(4)
Cs1–O9	3.894(7)	O12–P6–O14	104.3(4)
Cs1–O10	3.711(8)	O13–P6–O14	110.4(4)
Cs1–O12	3.543(9)		
Cs1–O12	3.154(8)		
Cs1–O13	3.100(7)		
Cs1–O14	3.786(8)		
Cs1–O14	3.127(7)		
Cs2–O8	3.503(8)		
Cs2–O9	3.074(7)		
Cs2–O9	3.192(7)		
Cs2–O10	3.096(7)		
Cs2–O10	3.191(8)		
Cs2–O11	3.064(8)		
Cs2–O11	3.201(8)		
Cs2–O12	3.728(8)		
Cs2–O13	3.308(7)		
Cs2–O14	3.392(7)		

phosphorus. The ready distortion of the framework tetrahedra containing divalent cations, coupled with the high flexibility of the framework, accounts for the wide range of different sized counter cations (*e.g.* K^+, NH_4^+, Rb^+, Tl^+ and Cs^+) that have been reported for the ABW structure.

The proposed stoichiometry of the material was checked using EDAX measurements, which confirmed that the Cs : Co : P ratio was 1 : 1 : 1 within the experimental error of the technique. Further, the mass of the product obtained, compared with that expected from the starting materials if $CsCoPO_4$ were the only product, was correct thereby demonstrating no loss of the relatively volatile caesium and phosphorus. The lack of any impurity in the powder X-ray diffraction and powder neutron diffraction patterns is also consistent with the assigned product stoichiometry.

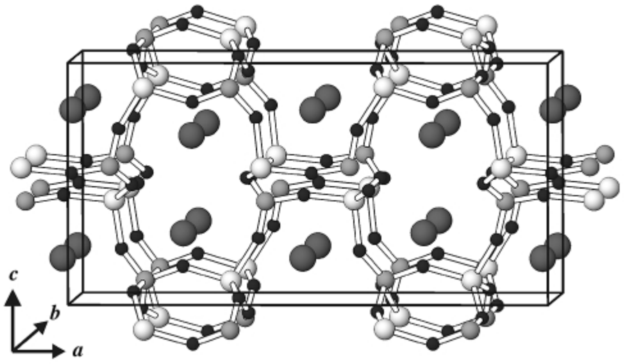

Fig. 2 Structure of $CsCoPO_4$ viewed just off the [010] direction illustrating the 8-ring channels. The small black spheres are oxygen, the large dark spheres are caesium, the light spheres are cobalt and the intermediate colour spheres are phosphorus.

TGA confirmed that $CsCoPO_4$ contains no zeolitic water, which was expected due to the size of the counter-cation. To date, no ABW materials have been discovered with Cs^+ as the counter-cation that contain zeolitic water. The presence of an reversible endothermic phase transition at 171 ± 5 °C was also observed in the DTA trace. Preliminary variable temperature powder X-ray diffraction studies show that the cell becomes orthorhombic with the lattice parameters $a = 9.194(8)$, Å, $b = 5.491(6)$ Å and $c = 9.416(9)$ Å. Initial indications suggest that the structure is analogous to $CsZnPO_4$ polymorph II.[7] Investigation of the changes to the structure, analysed using variable temperature powder neutron diffraction data, will be published elsewhere.

The UV visible spectra, Fig. 3, revealed the characteristic complex absorption envelope associated with tetrahedrally coordinated Co(II). The broad nature of the envelope can be ascribed to the distorted nature of the cobalt–oxygen tetrahedra (see Table 2) and the presence of two different cobalt sites within the structure.

Conclusions

The synthesis and characterisation of the final member of the alkali metal cobalt phosphate ABW series, $CsCoPO_4$, has been achieved. The structure is based on alternating PO_4^{3-} and CoO_4^{6-} tetrahedra and contains both 6- and 8-ring channels in which the caesium atoms are located on two different sites.

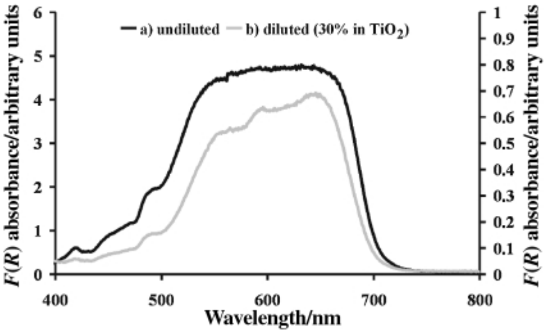

Fig. 3 Solid state UV visible spectra of $CsCoPO_4$ as prepared (a) and diluted (30% in TiO_2) $CsCoPO_4$ (b).

The caesium acts as a template around which the framework forms and, due to their large size, the structure is not hydrated. Powder neutron diffraction indicates that the structure is more complex and this is being investigated further with variable temperature powder neutron diffraction. $CsCoPO_4$ undergoes a phase transition at *ca.* 171 °C to a more simple structure, as shown by variable temperature powder X-ray diffraction, although the nature of this phase transition is yet to be fully described. $CsCoPO_4$ has two different tetrahedral cobalt sites that are distorted significantly away from a regular tetrahedron producing an intense broad absorption in the UV visible spectra and the resultant intense blue colouration.

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