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High temperature synthesis of a noncentrosymmetric site-ordered cobalt aluminophosphate related to the pollucite structure

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A straightforward synthesis of a transition metal-loaded derivative of the pollucite structure is presented, with non-centric cation ordering over the tetrahedral sites.

Complex open-framework oxides are intensively studied for applications in sorption, catalysis and ion-exchange.[1] Most current systems are based on tetrahedral silicate or aluminophosphate frameworks, so there is considerable interest in the introduction of transition metals, with their associated redox, optical and magnetic properties, into such materials. The tetrahedral sites in the MT_2O_4 ABW structure (where M is an extra-framework and T a tetrahedral framework-forming cation) can support 50% transition metal loading.[2,3] Pollucite ($CsAlSi_2O_6{\cdot}xH_2O$) is a naturally occurring mineral of MT_3O_6 composition with the analcime (ANA) topology[4] in which Si^{4+} and Al^{3+} are randomly distributed over the tetrahedral sites. Synthetic $M_2TSi_5O_{12}$ analogues (T^{2+} = Mg, Zn, Cd; M = Cs^+, Rb^+, K^+) prepared at high temperature are similarly disordered but synthesis under low temperature hydrothermal conditions does afford cation ordering.[5] Lithium substitution into the pollucite framework has recently been achieved, enhancing the density of extra-framework cations.[6] The synthesis of ordered transition-metal containing frameworks accessible without applied pressure and at higher metal loadings has yet to be accomplished. In this communication we present the cobalt-rich aluminophosphate $Cs_2Co_2Al(PO_4)_3$ derived from the pollucite structure where partial ordering of the transition metal cations over the tetrahedral sites produces an unusual non-centrosymmetric structure[7] despite synthesis at elevated temperatures expected to favour complete cation disorder.

Direct synthesis in air at high temperature† affords $Cs_2Co_2Al(PO_4)_3$ which laboratory X-ray diffraction identifies as having the pollucite structure with space group *Ia*3*d*. This space group symmetry would require complete disorder of the Co^{2+}, Al^{3+} and P^{5+} species over the tetrahedral sites of the framework and is observed in low temperature hydrothermal synthesis.[8] As this seemed chemically unfavourable due to the associated charge and size differences, we collected synchrotron X-ray powder diffraction data with improved signal-to noise ratio. This revealed extra reflections consistent with the loss of both classes of glide plane and the adoption of space group $I4_132$. This allows two distinct tetrahedral sites in the framework, and refinement (Fig. 1) of the data indicates that one is exclusively occupied by P^{5+} while the more similarly charged Co^{2+} and Al^{3+} occupy the other site in a disordered manner. This produces strict alternation of MO_4 (where M is 66% Co^{2+} and 33% Al^{3+}) and PO_4 tetrahedra (Fig. 2). The Co^{2+}/Al^{3+} site T–O mean distance of 1.83(1) Å contrasts with the P–O mean of 1.52(1) Å (consistent with other phosphates) and compares well with 1.86 Å predicted from the Co–O and Al–O tetrahedral distances of 1.93 Å and 1.74 Å. The complete site ordering determined from the superstructure intensities is thus consistent with the bond lengths, which are often a more sensitive test of the nature of the species occupying the sites when X-ray data are employed. Relevant bond lengths are given in the Fig. 2 caption. The bond valence sum at the P site indicates 100% occupancy by P^V. The difference between the two P–O bond lengths is consistent with that found in ALPO-53 and other synthetic aluminophosphates.[9]

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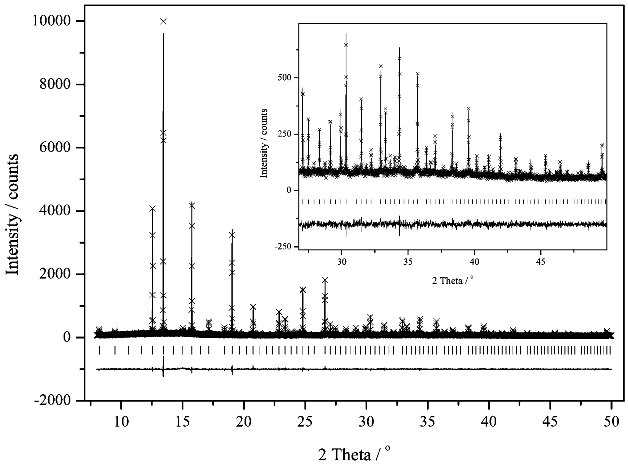

Fig. 1 Rietveld analysis of $Cs_2Co_2Al(PO_4)_3$ against synchrotron X-ray powder diffraction data collected on the 9.1 instrument. R_w = 9.07% $R(F^2)$ = 7.91%. λ = 0.803050 Å. Space group $I4_132$, a = 13.73267(3) Å, Cs1 on 8a 0.125, 0.125, 0.125 U = 0.039(1)Å^2; Cs2 on 8b 0.875, 0.875, 0.875 U = 0.058(1) Å^2 Co^{2+} (66.6%)/Al^{3+} (33.3%) on 24g 0.125, 0.8414(3), 0.0914(3) U = 0.026(2) Å^2 P on 24h 0.125, 0.6658(5), 0.5842(5) U = 0.036(3) Å^2 O1 on 48i 0.0942(9), 0.1150(9), 0.7098(8) U = 0.039(5) Å^2 O2 on 48i 0.892(1), 0.8475(9), 0.2662(8) U = 0.039(5) Å^2.

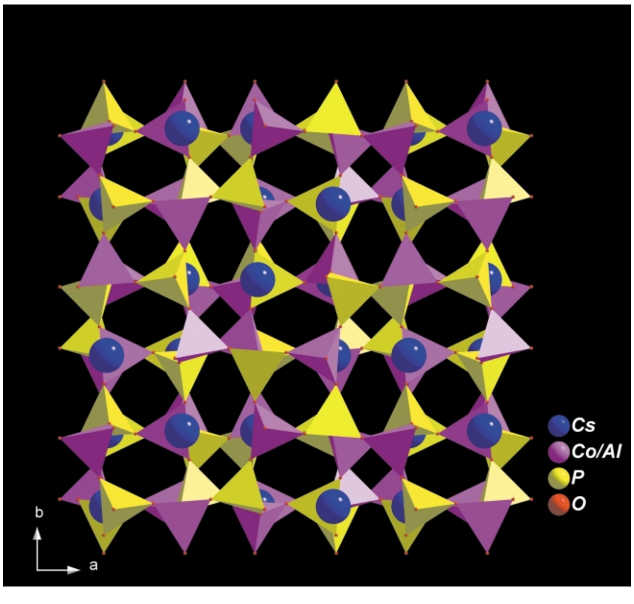

Fig. 2 The structure of $Cs_2Co_2Al(PO_4)_3$ showing the alternation of P^V (yellow) and Co^{2+}/Al^{3+} (magenta) tetrahedra from the cation site ordering which renders the structure non-centric. The view is along the [001] direction. Bond lengths within the tetrahedra are: Co/Al–O1 1.81(1) Å × 2 Co/Al–O2 1.85(1) Å × 2 P–O1 1.58(1) Å × 2 P–O2 1.46(1) Å × 2. The T–O–T angles are Co/Al–O1–P 140.2(9)° Co/Al–O2–P 136.4(9)°.

Both Cs^+ cations reside in large twelve-coordinate voids described by six 3.78(1) Å and six 3.23(1) Å contacts to O(1) and six 3.54(1) Å and six 3.41(1) Å contacts to O(2) (Fig. 3). Access to these sites is *via* six-membered and eight-membered rings; synthetic pollucites such as $CsTiSi_2O_{6.5}$ have been proposed for radioactive waste immobilisation.[10]

The cation ordering driven by the high metal loading destroys the centre of symmetry in the disordered pollucite parent structure. The partial ordering results in a chiral colouring of the network: the 432 point group is enantiomorphic and allows circular dichroic but not polar or piezoelectric behaviour.[11] This chiral decoration of the analcime structure has been found in non-transition metal containing $Na_{13}Al_{24}Si_{13}P_{11}O_{96}\cdot16H_2O$, where Al^{3+} forms the non-diluted site.[12] As for the synthetic $M_2TSi_5O_{12}$ pollucites, this ordered arrangement forms only under high pressure and much milder temperature conditions (210 °C) than those employed here. The demonstration that electronically active transition metal species can be ordered in a chiral manner on this open framework indicates more complex ordering patterns, involving further ordering of Al^{3+} and Co^{2+}, should be attainable with more complex thermal treatments or substitution patterns.

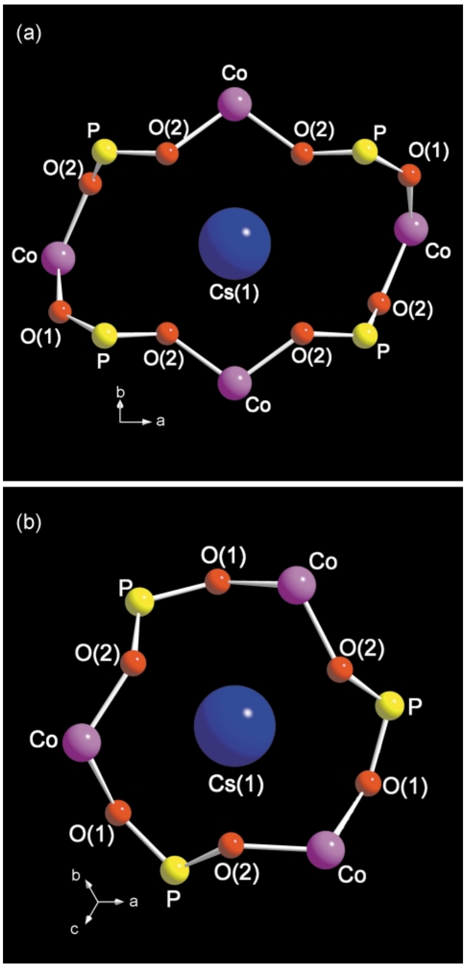

Fig. 3 The 12-coordinate site occupied by Cs1 viewed through (i) the 8-ring window (ii) the 6-ring window.

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Notes and references

† $Cs_2Co_2Al(PO_4)_3$ was prepared by the reaction of Cs_2CO_3, $AlPO_4$, $Co(PO_3)_2$ and Co_3O_4, which were ground under acetone to give a paste, dried at 80 °C and then re-ground before being transferred to an alumina crucible and heated for 16 h at 300 °C (heating ramp rate = $5\ \mathrm{C\ min^{-1}}$). The sample was then re-ground under acetone and pelleted, then heated for 24 h at 1000 °C (heating ramp rate = $1\ \mathrm{C\ min^{-1}}$). Laboratory X-ray powder diffraction data were collected on a Philips PW-1050 powder diffractometer with Fe-filtered Co $K\alpha$ radiation. Synchrotron powder X-ray diffraction data were collected at ambient temperature on station 9.1 of the Synchrotron Radiation Source at Daresbury Laboratory, at a wavelength of 0.803050 Å with the sample contained in a 0.5 mm capillary. Rietveld refinement was performed with the GSAS suite of programmes.[13]

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