DALTON
FULL PAPER

Hydrothermal synthesis and characterization of new aluminophosphates with $AlPO_4$-15 framework: $A_{1.5}[Al_2P_2O_{8.5}(OH)_{0.5}(H_2O)]\cdot xH_2O$ (A = K or Rb) †

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Two new isostructural aluminophosphates, $A_{1.5}[Al_2P_2O_{8.5}(OH)_{0.5}(H_2O)]\cdot xH_2O$ (A = K or Rb) have been synthesized hydrothermally and characterized by powder X-ray diffraction, infrared and solid state NMR spectroscopy and thermal analysis. The structure of the potassium compound has been determined by single crystal X-ray diffraction. The structure of its three-dimensional anionic framework is similar to that of $AlPO_4$-15 with intersecting tunnels occupied by A^+ ions and water of crystallization.

Introduction

We have recently synthesized, by solid state reactions, and structurally characterized by single crystal X-ray diffraction, three aluminophosphates, $A_3Al_2P_3O_{12}$ (A = K, Rb or Tl), with aluminium in tetrahedral and trigonal bipyramidal co-ordinations.[1] Their structures are three-dimensional in nature but quite different from those of NASICON, garnet, *etc.* of isomorphous compositions such as $Na_3Fe_2P_3O_{12}$ wherein the trivalent ion is octahedrally co-ordinated.[2–5] It is somewhat surprising that Al^{3+}, which is known to be stable in octahedral co-ordination as well in oxides, has lower co-ordination in these compounds. In fact there are hydrothermally synthesized, organically templated, layered aluminophosphates with $Al_2P_3O_{12}{}^{3-}$ stoichiometry known to have aluminium in four- and five-co-ordinations.[6–8] We have thus become interested in these aspects of co-ordination of aluminium and hence taken up a synthetic and structural study of $A_3Al_2P_3O_{12}$ compounds to examine the influence of different monovalent A ions and the method of preparation on the co-ordination of aluminium. It is in this context that we envisaged and attempted acid–base reactions of AH_2PO_4 (A = K or Rb) with $Al(OH)_3$ under hydrothermal conditions to synthesize $A_3Al_2P_3O_{12}$ compounds. These attempts have, however, resulted in aluminophosphates, $A_{1.5}[Al_2P_2O_{8.5}(OH)_{0.5}(H_2O)]\cdot xH_2O$ with AlPO-15 structure.[9,10] Synthesis and structural characterization of such three-dimensional framework structures with Al : P ratio of essentially 1 : 1 has been an active area in materials chemistry.[11–13] In this paper we report the hydrothermal synthesis, structural elucidation, spectroscopy and thermal analysis of these two new $A_{1.5}[Al_2P_2O_{8.5}(OH)_{0.5}(H_2O)]\cdot xH_2O$ (A = K or Rb) compounds.

Experimental

Synthesis

Both compounds $A_{1.5}[Al_2P_2O_{8.5}(OH)_{0.5}(H_2O)]\cdot xH_2O$ [A = K **1** or Rb **2**] were synthesized by hydrothermal reactions of KH_2PO_4/RbH_2PO_4 and $Al(OH)_3$ in 23 mL acid digestion bombs (Parr, US). The reaction mixture was heated for 4 d at a temperature of 200 °C for **1** and 225 °C for **2** and then cooled to 55 °C in 1.5 d. In both cases the final pH was 6–7 and the yields of polycrystalline compounds, based on $Al(OH)_3$, were as high as 98%. Compound **1** was synthesized in polycrystalline form from a mixture of 0.276 g (0.0031 mmol) of $Al(OH)_3$, 0.626 g (0.0046 mmol) of KH_2PO_4 and 4 mL of water. Small colorless block shaped crystals of **1** were isolated in a similar synthetic attempt with 0.075 g (0.000834 mmol) of $Al(OH)_3$ and 0.34 g (0.0023 mmol) of KH_2PO_4. Compound **2** was similarly prepared as a powder, from 0.25 g (0.002 mmol) of $Al(OH)_3$ and 0.761 g (0.0042 mmol) of RbH_2PO_4.

Characterization

Powder X-ray diffraction (XRD) patterns were recorded in a Shimadzu XD-D1 X-ray diffractometer using Ni-filtered Co-Kα (λ = 1.7902 Å) radiation. Thermogravimetric analysis was performed on a Netzsch Simultaneous Thermalanalyzer STA 409C under a nitrogen flow with a heating rate of 20 °C min^{-1}. Solid state nuclear magnetic resonance (NMR) experiments were performed with magic angle spinning (MAS) on a Bruker DSX 300 spectrometer operating at resonance frequencies of 78.2 and 121.5 MHz for ^{27}Al and ^{31}P respectively. Chemical shifts were referenced to an external standard of $Al(NO_3)_3$ for ^{27}Al and H_3PO_4 for ^{31}P. The spinning frequency was 6.8 kHz and recycle delay time 15 μs for both. The pulse length was 5.0 μs for ^{27}Al and 4.0 μs for ^{31}P. Infrared spectra were recorded on a Bruker 17S 66V FT-IR spectrometer. The samples were ground with dry KBr and pressed into transparent discs.

Single crystal X-ray diffraction analysis

X-Ray diffraction data collection was done at 293 ± 2 K on an Enraf Nonius CAD4 X-ray diffractometer by standard procedures for a colorless block shaped single crystal of $K_{1.5}[Al_2P_2O_{8.5}(OH)_{0.5}(H_2O)]\cdot 0.75H_2O$ of dimensions 0.09 × 0.15 × 0.3 mm. Crystal data: *M* 350.58; monoclinic, space group $P2_1/n$, *a* 9.495(2), *b* 9.5589(8), *c* 9.4384(2) Å; β 101.7400(3)°, *U* 838.8(2) Å^3, *Z* 4, μ 14.102 mm^{-1}, total reflections 1599, independent reflections 1514(R_{int} = 0.0946), *R*1 0.0476 and *wR*2 0.1242. The structure solution and refinement were done by the programs SHELXS 86 and SHELXL 93 respectively.[14] The equivalent isotropic displacement parameter, U_{eq} of O(11) was very large and indicated the possibility of partial site

† *Supplementary data available*: rotatable 3-D crystal structure diagram in CHIME format. See http://www.rsc.org/suppdata/dt/1999/3841/

Also available: powder X-ray diffraction data. For direct electronic access see http://www.rsc.org/suppdata/dt/1999/3841/, otherwise available from BLDSC (No. SUP 57641, 3 pp.) or the RSC Library. See Instructions for Authors, 1999. Issue 1 (http://www.rsc.org/dalton).

occupancy. Variation of its site occupancy in the subsequent refinements proceeded smoothly and led to a marked decrease of U_{eq} to 0.042(2) Å^2 with a concomitant decrease of the site occupancy factor to 0.739(19) from 1.00. There was only a marginal improvement in the $R1$ value from 0.0500 to 0.0476. The site occupancy factors of K(1) and K(2) were also refined in view of their slightly larger thermal parameters. These values settled down to 0.976 and 0.459 respectively, which are close to the ideal values of 1.0 and 0.5, without any significant improvement in thermal parameters and R values. Therefore, the composition, as determined from crystallography, is $K_{1.5}[Al_2P_2O_{8.5}(OH)_{0.5}(H_2O)]\cdot xH_2O$ ($x = 0.739$) and the water of crystallization is less than the ideal content of one. As the structure turned out to be related to that of the $AlPO_4$-15 anionic framework, the positional parameters and the data set of compound **1** were transformed to correspond to those reported by Pluth and Smith.[9] The graphic programs[15] ORTEP and ATOMS were used to draw the structures.

CCDC reference number 186/1643.

See http://www.rsc.org/suppdata/dt/1999/3841/ for crystallographic files in .cif format.

Results and discussion

Synthesis

The compound **1** could be synthesized, in pure form as single crystals or powder, hydrothermally at different temperatures such as 175, 200 and 225 °C from KH_2PO_4 and $Al(OH)_3$ taken in different (3:1, 3:4, 1:1, 3:2) ratios. Compound **2**, on the other hand, could be isolated as a pure polycrystalline sample from 3:2 or 3:1 reactant mixtures of RbH_2PO_4 and $Al(OH)_3$ at 225 °C. Chemical analysis of both **1** and **2**, by inductively coupled plasma atomic absorption spectroscopy, showed the compositions to be similar, with A:Al:P ratios of 1.4:2:2. Similar hydrothermal synthetic reactions of $Al(OH)_3$ with $NH_4H_2PO_4$ and NaH_2PO_4 have resulted in, as determined by powder X-ray diffraction (XRD) and thermogravimetry, $AlPO_4$-15 and a 1:1 aluminophosphate whose structure will be reported elsewhere.

X-Ray diffraction and crystal structure

The monophasic nature of the polycrystalline sample of compound **1** was established by comparing its powder XRD pattern (available as electronic supplementary information) with that simulated from the crystal data by the program LAZY PULVERIX.[16] The powder XRD of compound **2** (available as electronic supplementary information), refined by least squares fitting program AUTOX,[17] is similar to that of compound **1** establishing their isostructural nature. The bond lengths, selected bond angles and O···O non-bonding edges are given in Table 1.

The two compounds $A_{1.5}[Al_2P_2O_{8.5}(OH)_{0.5}(H_2O)]\cdot xH_2O$ (A = K or Rb) are isostructural and have, as determined from the single crystal XRD study of **1**, three-dimensional $[Al_2P_2O_{8.5}(OH)_{0.5}(H_2O)]^{1.5-}$ anionic frameworks with intersecting tunnels occupied by both A^+ counter ions and water of crystallization. These compounds are compositionally and structurally similar to $AlPO_4$-15, $[NH_4][Al_2P_2O_8(OH)(H_2O)]\cdot H_2O$ which is isostructural with leucophosphite,[18] $K[Fe_2P_2O_8(OH)(H_2O)]\cdot H_2O$. This point is evident from the similarity of not only compositions but also the space group, lattice parameters and positional parameters. The three-dimensional anion of the compounds **1** and **2** has the same structure and Al–P–O content as that of the $AlPO_4$-15 anion but with an additional negative charge of 0.5 due to partial substitution of OH^- by O^{2-}. The additional A^+ ions required for charge compensation are also found to reside in the tunnels. In view of this structural similarity, we followed, for the sake of uniformity and convenience, the labelling scheme of $AlPO_4$-15 for the sixteen non-hydrogen atoms and the additional K^+ ions are named K(2).

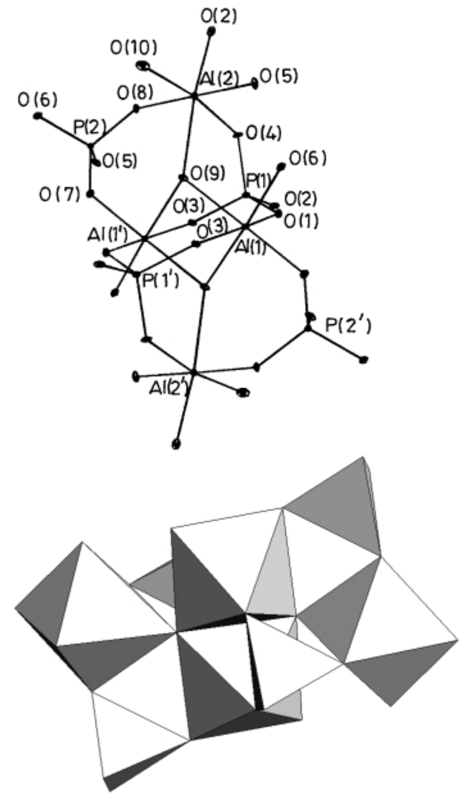

Fig. 1 The $Al_4P_4O_{23}(OH)(OH_2)_2$ moiety: top, ORTEP plot showing the atom labelling scheme (50% thermal ellipsoids) and bottom, polyhedral representation.

The $[Al_2P_2O_{8.5}(OH)_{0.5}(H_2O)]^{1.5-}$ anionic framework can be conceived as being built from centrosymmetric $Al_4P_4O_{23}(OH)(OH_2)_2$ blocks, which are, as shown in Fig.1, made of four AlO_6 octahedra and four PO_4 tetrahedra. First two $Al(1)O_6$ octahedra share an edge to form a dimer which further links at the shared corners to two $Al(2)O_6$ octahedra resulting in a centrosymmetric octahedral tetramer. Two $P(1)O_4$ tetrahedra are each connected, through three corners, to three octahedra of the tetramer. Two $P(2)O_4$ tetrahedra, on the other hand, are each connected, through two corners, to only two octahedra. These blocks are linked to one another such that the tetrahedra of one block are corner connected to octahedra of another, resulting in the three-dimensional anionic framework shown in Fig. 2. In other words, the symmetry-related octahedral tetramers could be described as being linked to one another through PO_4 tetrahedral corner-sharing.

The $Al(2)O_6$ octahedron has one unshared apical corner, O(10) oxygen atom of a water molecule. The O(9) oxygen atoms, constituting the shared edge of the $Al(1)O_6$ octahedra, are a 1:1 admixture of oxide and hydroxide ions. The eight oxygen atoms, O(1) to O(8), are all oxide ions representing the other corners of the tetramer. Atoms P(1) and P(2) are each tetrahedrally bonded to four oxygen atoms, O(1) to O(4) and O(5) to O(8) respectively. Atom O(11), with partial site occupancy, is water of crystallization, while cations K(1) and K(2) reside in the intersecting tunnels.

Both $Al(1)O_6$ and $Al(2)O_6$ octahedra are distorted with Al–O bond lengths spanning a wide range of 1.833(3)–2.249(4) Å and bond angles deviating, by as much as 10°, from the ideal values of 90 and 180°. Atom Al(1) is displaced by 0.013 Å from its best centre,[19] away from the shared O(9)···O(9′) non-bonding edge, towards edge O(6)···O(7). Similarly Al(2) is displaced from its best centre by 0.035 Å, away from O(9), towards O(2). The P–O bond lengths of the PO_4 tetrahedra range from 1.519(3) to 1.547(3) Å and the bond angles are close to the ideal

Table 1 Bond lengths (Å), selected bond angles (°) and O · · · O non-bonding distances in **1**

AlO_6 octahedra									
Al(1)	O(1)	O(3)	O(6)	O(7)	O(9)	O(9)			
O(1)	**1.904(3)**	—	2.793(5)	2.653(5)	2.679(5)	2.656(5)			
O(3)	167.9(2)	**1.884(3)**	2.692(5)	2.789(5)	2.652(5)	2.595(5)			
O(6)	96.7(2)	92.8(2)	**1.833(4)**	2.602(5)	2.778(5)	—			
O(7)	90.3(2)	97.1(2)	90.3(2)	**1.836(4)**	2.738(5)	—			
O(9)	86.31(14)	85.76(15)	92.4(2)	175.9(2)	**1.986(4)**	2.723(7)			
O(9′)	86.11(15)	84.17(15)	176.7(2)	91.5(2)	85.9(2)	**2.011(4)**			
Al(2)	O(2)	O(4)	O(5)	O(8)	O(9)	O(10)			
O(2)	**1.842(4)**	2.697(5)	2.576(5)	2.694(5)	—	2.777(5)			
O(4)	93.3(2)	**1.868(4)**	2.672(5)	2.632(5)	2.771(5)	—			
O(5)	88.1(2)	91.4(2)	**1.865(4)**	—	2.829(5)	2.670(5)			
O(8)	93.5(2)	89.9(2)	177.8(2)	**1.856(4)**	2.968(5)	2.591(5)			
O(9)	173.8(2)	84.04(14)	86.35(14)	92.11(14)	**2.249(4)**	2.855(5)			
O(10)	96.3(2)	170.2(2)	90.7(2)	87.6(2)	87.0(2)	**1.887(4)**			
PO_4 tetrahedra									
P(1)	O(1)	O(2)	O(3)	O(4)	P(2)	O(5)	O(6)	O(7)	O(8)
O(1)	**1.547(3)**	2.544(5)	2.528(5)	2.507(5)	O(5)	**1.525(3)**	2.496(5)	2.537(5)	2.467(5)
O(2)	112.2(2)	**1.519(3)**	2.475(4)	2.475(5)	O(6)	109.0(2)	**1.541(4)**	2.482(5)	2.475(4)
O(3)	110.4(2)	108.3(2)	**1.535(3)**	2.512(5)	O(7)	112.5(2)	108.0(2)	**1.526(3)**	2.520(5)
O(4)	108.5(2)	108.0(2)	109.5(2)	**1.541(4)**	O(8)	108.1(2)	107.7(2)	111.3(2)	**1.525(3)**
K(1)–O(3)	2.754(4)	K(1)–O(5)	3.276(4)	K(2)–O(1) × 2	2.817(3)				
K(1)–O(11)	2.850(8)	K(1)–O(6)	3.276(4)	K(2)–O(11) × 2	2.846(8)				
K(1)–O(4)	2.912(4)	K(1)–O(2)	3.289(4)	K(2)–O(8) × 2	2.873(3)				
K(1)–O(2)	2.973(4)	K(1)–O(1)	2.931(4)	K(2)–O(5) × 2	2.942(4)				
K(1)–O(10)	3.218(4)	K(1)–O(7)	2.789(4)	K(2)–O(6) × 2	3.181(3)				

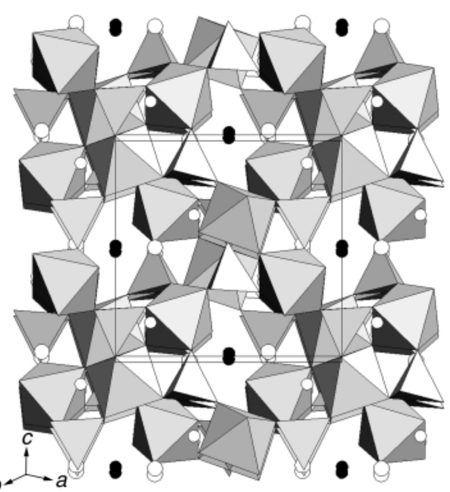

Fig. 2 Polyhedral representation of the unit cell of $K_{1.5}[Al_2P_2O_{8.5}(OH)_{0.5}(H_2O)]\cdot xH_2O$ viewed along the *c* axis: filled circles, K(2); empty small circles, K(1) and empty big circles, O(11).

value of 109.4°. While the $P(1)O_4$ tetrahedron has three long bonds and one short P(1)–O(2) bond, $P(2)O_4$ possess three short bonds and one long P(2)–O(6) bond. Atoms K(1) and K(2) are both ten-co-ordinated with K–O bond lengths ranging from 2.754 to 3.289 Å. Both KO_{10} polyhedra are of irregular shape and include not only some of the oxide ions but also water oxygen atoms, O(10) and O(11).

Bond valence sum calculations[20] for all the atoms, except O(11), of the asymmetric unit have been carried out based on the bonding distances between these non-hydrogen atoms. Values of 3.04, 2.97, 4.82, 4.90, 1.03 and 1.22 are obtained for Al(1), Al(2), P(1), P(2), K(1) and K(2) respectively confirming the presence of trivalent aluminium, pentavalent phosphorus and monovalent potassium. All the oxide ions, O(1) to O(8), have values ranging from 1.90 to 2.08, whereas O(9) and O(10), both bonded to hydrogen atoms also, have, as expected, lower values of 0.99 and 0.59 respectively.

We now refer to hydrogen bonding among these oxygen atoms by taking 3.0 Å as the cut off limit. A sphere of 3.0 Å radius around O(11) has O(10), O(7), O(4) and O(2) at distances of 2.907, 2.969, 2.991 and 2.681 Å which are indicative of hydrogen bonding interaction. A similar sphere around O(10) includes not only four atoms of non-bonding edges of octahedron $Al(2)O_6$ but also O(6), O(10) and O(11) at 2.818, 2.524 and 2.907 Å indicating its hydrogen bonding interaction with these three. On the other hand, a similar sphere around O(9) includes eleven atoms of only non-bonding edges of $Al(1)O_6$ and $Al(2)O_6$ octahedra. The short O(2) · · · O(11) and O(6) · · · O(10) distances suggest a qualitative difference between the two PO_4 tetrahedra in hydrogen bonding.

The presence of alkali metal ions in the interstitial channels of these compounds led us to try ion-exchange reactions by stirring and refluxing these samples in aqueous solutions of sodium and thallium(I) salts. However, these attempts turned out to be unsuccessful.

Solid state NMR spectroscopy

The ^{27}Al MAS NMR spectra of both compounds, as shown in Fig. 3, have single peak resonances around δ 0 and thus indicate, in corroboration with the crystal structure, octahedral co-ordination[21] for both the crystallographically distinct aluminium atoms, Al(1) and Al(2). In these ordinary NMR experiments the peaks are not sufficiently resolved to distinguish Al(1) and Al(2). The two resonances observed in ^{31}P NMR spectra of these compounds (Fig. 4) are attributed to tetrahedrally co-ordinated, crystallographically distinct phosphorus atoms,[22] P(1) and P(2). As noted earlier, the $P(1)O_4$ tetrahedron is more strongly hydrogen bonded, through O(2) to O(11), than is $P(2)O_4$, through O(6) to O(10). Thus P(1) with lesser electron density has a resonance at δ −7 while P(2) in **1** has at δ −14. However, in the case of **2**, the peak corresponding to P(2) is split,[23] probably due to further distinction in the water environment around $P(2)O_4$.

Infrared spectroscopy

The infrared spectra (Fig. 5) of these two compounds have a sharp absorption band around 3600 cm^{-1} due to stretching of the OH group attached to aluminium. Peaks in the 3485–3258 cm^{-1} region are due to stretching of both types of water, O(10) and O(11), whereas the sharp peak at 1632 cm^{-1} is due to the

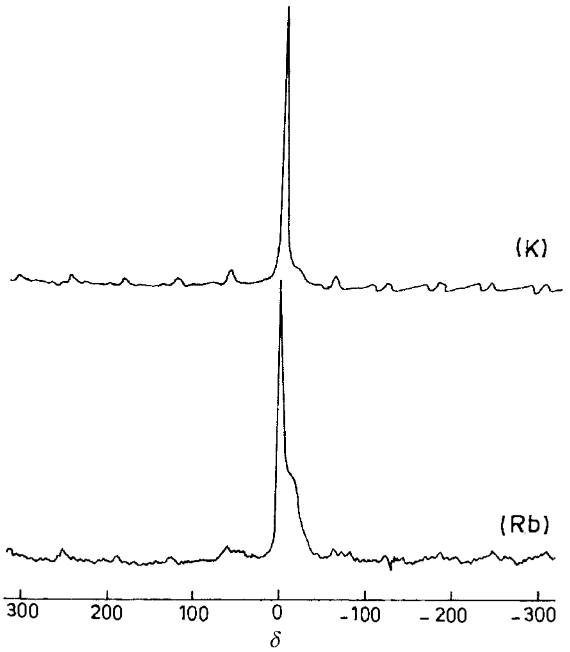

Fig. 3 The ^{27}Al MAS NMR spectra of $A_{1.5}[Al_2P_2O_{8.5}(OH)_{0.5}(H_2O)]\cdot xH_2O$ compounds (A = K or Rb).

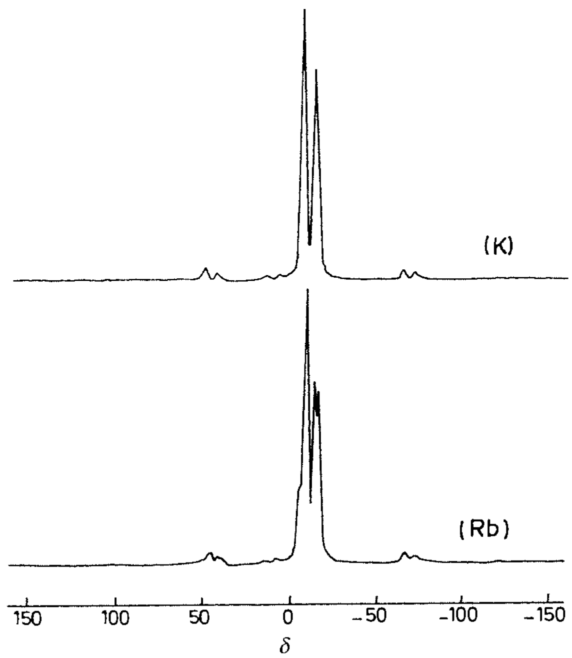

Fig. 4 The ^{31}P MAS NMR spectra of $A_{1.5}[Al_2P_2O_{8.5}(OH)_{0.5}(H_2O)]\cdot xH_2O$ compounds (A = K or Rb).

bending mode of vibration of free water only.[24] Both AlO_6 and PO_4 groups have their asymmetric and symmetric stretching vibrational frequencies in the range 950–1200 and 600–400 cm^{-1} and bending frequencies in the 400–550 cm^{-1} range respectively.[25] The bands in the range 1200–900 cm^{-1} may also contain bands due to Al–O–H bending modes of vibration.

Thermogravimetry

Thermogravimetric analysis of compound **1** (Fig. 6) showed that it undergoes weight loss in two stages, 9.63% at 291.8 °C and 1.4% at 455 °C. While the latter corresponds to the loss of 0.25 water molecule from 0.5 OH group of O(9), the former is due to loss of about 1.9 molecules of both water of crystallization and framework water. Compound **2** also behaves similarly with a weight loss of 8.85% indicating its water content as 1.82. Thus these weight losses compare with the crystallographic

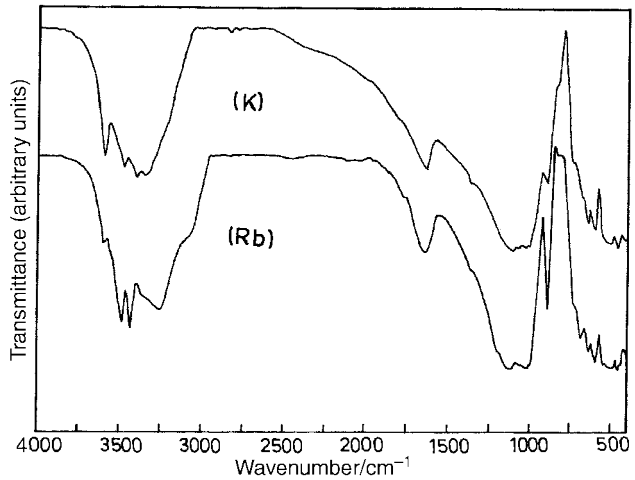

Fig. 5 The FT-IR spectra of $A_{1.5}[Al_2P_2O_{8.5}(OH)_{0.5}(H_2O)]\cdot xH_2O$ compounds (A = K or Rb).

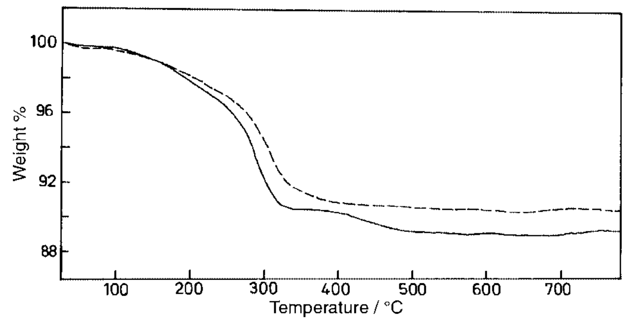

Fig. 6 Thermogravimetric profiles of $A_{1.5}[Al_2P_2O_{8.5}(OH)_{0.5}(H_2O)]\cdot xH_2O$ [A = K(——) or Rb(- - -)].

results for the water content with $x < 1$ and the total observed losses are in agreement with the values calculated for "$A_{1.5}Al_2P_2O_{8.75}$" as the final crystalline product residue of thermal decomposition.

Conclusion

The two new isostructural aluminophosphates, $A_{1.5}[Al_2P_2O_{8.5}(OH)_{0.5}(H_2O)]\cdot xH_2O$ (A = K or Rb), prepared under hydrothermal conditions, have three-dimensional anionic framework of $AlPO_4$-15 but with an additional negative charge of 0.5 due to partial substitution of OH^- by O^{2-}. The ^{31}P MAS NMR spectra reveal the difference in oxygen environment around the phosphorus atoms.

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References

1 R. Nandini Devi and K. Vidyasagar, unpublished work.
2 L. O. Hagman and P. Kierkegaard, *Acta Chem. Scand.*, 1968, **22**, 1822.
3 H. Y. Hong, *Mater. Res. Bull.*, 1976, **11**, 173.
4 W. Prandle, *Z. Krystallogr.*, 1966, **123**, 81.
5 F. d'Yvoire, M. Pintard-Screpel, E. Bretey and M. de la Rochere, *Solid State Ionics*, 1983, **9** & **10**, 851.
6 A. M. Chippindale, A. V. Powell, L. M. Bull, R. H. Jones, A. K. Cheetham, J. M. Thomas and R. Xu, *J. Solid State Chem.*, 1992, **96**, 199.
7 S. Oliver, A. Kuperman, A. Lough and G. A. Ozin, *Chem. Commun.*, 1996, 1761.

8 J. Yu, K. Sugiyama, K. Hiraga, N. Togashi, O. Terasaki, Y. Tanaka, S. Nakata, S. Qiu and R. Xu, *Chem. Mater.*, 1998, **10**, 3636.
9 J. J. Pluth and J. V. Smith, *Acta Crystallogr.*, *Sect. C*, 1984, **40**, 2008.
10 J. B. Parise, *Acta Crystallogr.*, *Sect. C*, 1984, **40**, 1641.
11 S. T. Wilson, B. M. Lok, C. A. Messina, T. R. Cannon and E. M. Flanigen, *J. Am. Chem. Soc.*, 1982, **104**, 1146.
12 M. E. Davis, C. Saldarriaga, C. Montes, J. Garces and C. Crowder, *Nature* (*London*), 1988, **331**, 698.
13 N. Simon, T. Loiseau and G. Ferey, *J. Chem. Soc.*, *Dalton Trans.*, 1999, 1147.
14 G. M. Sheldrick, SHELXS 86, University of Göttingen, 1986; SHELXL 93, University of Göttingen, 1993.
15 ORTEP, C. K. Johnson, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976; ATOMS, Eric Dowty, Kingsport, TN, 1989.
16 K. Yvon, W. Jeitschko and E. Parthe, *J. Appl. Crystallogr.*, 1977, **10**, 7.
17 V. B. Zlokazov, *J. Appl. Crystallogr.*, 1992, **25**, 69.
18 P. B. Moore, *Am. Mineral.*, 1972, **57**, 397.
19 T. B. Zunic and E. Markovicky, *Acta Crystallogr.*, *Sect. B*, 1996, **52**, 78.
20 N. Brese and M. O'Keeffe, *Acta Crystallogr.*, *Sect. B*, 1991, **47**, 192.
21 G. Engelhardt and D. Michel, *High-Resolution Solid-State NMR of Silicates and Zeolites*, Wiley, New York, 1987.
22 J. O. Perez, P. J. Chu and A. Clearfield, *J. Phys. Chem.*, 1991, **95**, 9994.
23 R. F. Mortlock, A. T. Bell and C. J. Radke, *J. Phys. Chem.*, 1993, **97**, 767.
24 S. Cheng, J.-N. Tzeng and B.-Y. Hsu, *Chem. Mater.*, 1997, **9**, 1788.
25 I. I. Boldog, A. M. Golub and A. M. Kalininichenko, *Russ. J. Inorg. Chem.*, 1976, **21**, 368.

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