Interwoven Pair of Open Frameworks in the Thiosphosphate $K_6Yb_3(PS_4)_5$

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The reactivity of rare earth elements in molten alkali metal chalcophosphate salts has been the subject of extensive investigations and has afforded a fascinating variety of complex materials.[1] There is a growing interest in these materials not only for their intriguing structural chemistry but also for their attractive physical properties.[2] Investigations in the A−RE−P−Q systems (where A = an alkali metal, RE = rare earth element, and Q = S, Se) have begun relatively recently,[3−10] while we focused our attention on the K−Yb−P−S system. We were curious to see if Yb would be found in the 2^+ oxidation state and form compounds with structures similar to the Eu^{2+}-containing chalcophosphates[3,5,8] or if Yb would mimic the chemistry of the Ln^{3+}-containing chalcophosphates.[4,6−10] In this context, the compound $NaYbP_2S_6$[10] is a known example with a structure resembling that of the $KREP_2Se_6$ phases.[6] In addition, Yb can give rise to mixed valency that can lead to unusual physical properties.[11] Here we describe $K_6Yb_3(PS_4)_5$ which presents an exceptional case of two identical interwoven networks that have unique framework topology. In this compound, Yb^{3+} centers exhibit a dual coordination property that plays a key role in the stabilization of the frameworks.

A few early transition metal-containing chalcophosphates feature networks with interpenetrating lattices;[12] however, such structures are not known for lanthanide metals. This kind of structural theme has been observed only recently for the actinide-containing thiophosphate UP_4S_{12}.[13] The phenomenon of interpenetration is of considerable interest in the field of porous materials.[14] Particularly interesting is the issue of how and what kind of structures assume interpenetrated motifs and whether it is possible to control the phenomenon.

$K_6Yb_3(PS_4)_5$ was prepared as orange polyhedra in a potassium thiophosphate flux.[15] The compound possesses an intricate, three-dimensional interlocked structure consisting of two identical, three-dimensional sublattices, which are related by an inversion center (see Figure 1a). Each $_\infty^3[Yb_3(PS_4)_5]^{6-}$ sublattice has a microporous structure and contains PS_4 tetrahedra and Yb atoms that adopt two different coordination geometries (see Figure 1b). There are three crystallographically unique Yb atoms, two with distorted octahedral coordination and one with a bicapped trigonal prismatic geometry (8 coordination). If the PS_4 tetrahedra are represented by sticks and the Yb atoms as balls, we can construct a simplified skeletal view of the sublattice (see Figure 2). In this perspective, each octahedral Yb has three nearest neighbors (trigonal planar), and the 8-coordinate Yb have four neighbors (tetrahedral). To the best of our knowledge, this architecture, composed of trigonal planar and tetrahedral centers, is unique for an open framework.

The octahedral Yb(2) and Yb(3) atoms connect to three PS_4 tetrahedra and have Yb−S distances ranging from 2.656(4) to 2.714(4) Å, while the bicapped trigonal prismatic Yb(1) atom connects to four PS_4 tetrahedra with Yb(1)−S distances ranging from 2.773(4) to 2.896(3) Å. The fact that Yb^{3+} adopts two different coordination geometries within the same structure is rare and noteworthy. The octahedral geometry for Yb(2) and Yb(3) is the
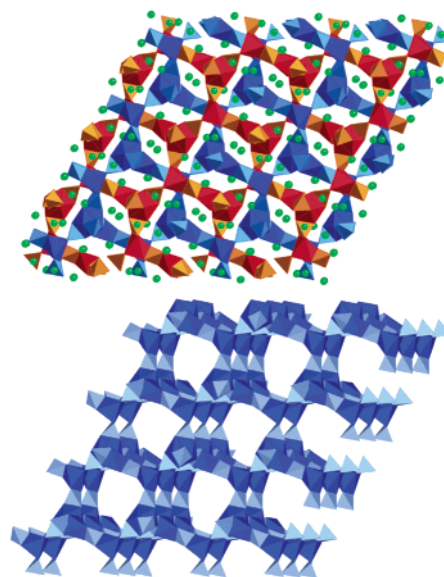
Figure 1. (a) Interlocked structure of $K_6Yb_3(PS_4)_5$ showing the two three-dimensional interpenetrating sublattices in red/orange and blue/light blue. K^+ are shown in green. (b) Structure of a single $_\infty^3[Yb_3(PS_4)_5]^{6-}$ sublattice showing the organization of its pore system.
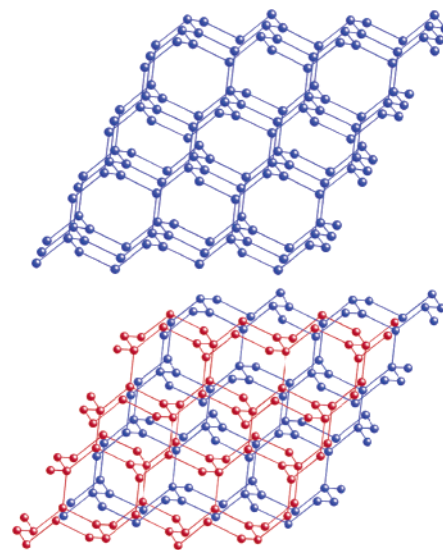
Figure 2. Framework topology: (a) a single $_\infty^3[Yb_3(PS_4)_5]^{6-}$ sublattice shown as a skeleton with PS_4 tetrahedra represented by straight lines and Yb^{3+} as spheres. This motif is assembled from trigonal planar and tetrahedral centers and (b) an interwoven pair of sublattice skeletons drawn in blue and red, respectively.

first example of octahedral lanthanide coordination in any chalcophosphate materials to date. In general, the lanthanides in these materials are found in trigonal prismatic (often capped) geometry. The octahedral geometry of Yb(2) in this compound is probably

due to the smaller atomic radius of Yb compared to the lanthanide metals that have been studied thus far in this chemistry. The bicapped trigonal prismatic Yb(1) center is responsible for the three-dimensional nature of each framework. All $[PS_4]^{3-}$ anions adopt the same binding mode by chelating two Yb^{3+} cations by using opposite edges. All K^+ cations have irregular geometries with coordination numbers ranging from six to eight.

$K_6Yb_3(PS_4)_5$ exhibits a sharp, well-defined energy gap, E_g, of $\sim$2.6 eV, consistent with its yellowish-orange color.[16] The electronic absorption responsible for the gap is likely an excitation from sulfur-based p-orbitals to vacant Yb d-orbitals. The Raman spectra, obtained on single crystals of $K_6Yb_3(PS_4)_5$,[17] show a very strong peak at 424 cm^{-1}, which is assigned to the $\nu_1(A_1)$ stretching mode of the $[PS_4]^{3-}$. This stretch exists at similar frequencies for other compounds containing $[PS_4]^{3-}$.[8a,18]

Magnetic measurements performed on polycrystalline samples of $K_6Yb_3(PS_4)_5$ clearly show Curie Weiss behavior from 50 to 300 K with a Weiss constant $\theta = -38.5$ K and a Curie constant $C = 2.77$. From the Curie constant, we obtain a $\mu_{eff} = 4.71$ μB, consistent with the theoretical value calculated for the Yb^{3+} free ion.[19] There was no difference between the field-cooled and zero-field-cooled data. The small negative Weiss constant indicates a possible weak antiferromagnetic exchange interaction. The absence of magnetic ordering is consistent with the fact that the shortest Yb–Yb distance in the structure is over 6 Å, and therefore the Yb^{3+} cations act as isolated magnetic ions. Field dependence data showed no evidence of saturation up to 5.4 kGauss.

Of all lanthanides, ytterbium seems to be special if not unique in its chemistry and reactivity. The surprising architecture of the frameworks in $K_6Yb_3(PS_4)_5$ and their interwoven nature are possible because of the distinctive combination of Yb^{3+} ions in both octahedral and bicapped trigonal prismatic coordination. All other lanthanides are larger and less likely to accommodate an octahedral environment. In addition, the three-dimensional framework motif is different from all other types reported for a framework structure. This architecture provides a new design to be targeted for synthesis of so-called isoreticular materials[20] by those involved in the construction of metal organic frameworks and coordination solids. This could be accomplished with judiciously chosen secondary building units (SBUs).

Supporting Information Available: Details of structural analysis in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Dhingra S.; Kanatzidis M. G. *Science* **1993**, *258*, 1769–1772. (b) Chung, D.-Y.; Hogan, T.; Brazis, P.; Rocci-Lane, M.; Kannewurf, C.; Bastea, M.; Uher, C.; Kanatzidis, M. G. *Science* **2000**, 287, 1024–1027. (c) Kanatzidis, M. G.; Sutorik A. *Progr. Inorg. Chem.* **1995**, *43*, 151–265.

(2) (a) Kumta, P. N.; Risbud, S. H. *J. Mater. Sci.* **1994**, *29*, 1135–1158. (b) Volodina, A. N.; Koubchinova, T. B.; Maximova, S. I. *Zh. Neorg. Khim. SSSR* **1987**, *32*, 2899–2901. (c) Rolland, B.; McMillan, P.; Molinié, P.; Colombet, P. *Eur. J. Solid State Inorg. Chem.* **1990**, *27*, 715–724.

(3) (a) Aitken, J. A.; Chondroudis, K.; Young, V. G., Jr.; Kanatzidis, M. G. *Inorg. Chem.* **2000**, *39*, 1525–1533. (b) Chondroudis, K.; McCarthy, T. J.; Kanatzidis, M. G. *Inorg. Chem.* **1996**, *35*, 840–844.

(4) (a) Chondroudis, K.; Kanatzidis, M. G. *Inorg. Chem. Commun.* **1998**, *1/2*, 55–57. (b) Chondroudis, K.; Kanatzidis, M. G. *Inorg. Chem.* **1998**, *37*, 3792–3797.

(5) Carrillo-Cabrera, W.; Peters, K.; von Schnering, H. G.; Menzel, F.; Brockner, W. *Z. Anorg. Allg. Chem.* **1995**, *621*, 557561.

(6) (a) Chen, J. H.; Dorhout, P. K. *Inorg. Chem.* **1995**, *34*, 5705–5706. (b) Chen, J. H.; Dorhout, P. K.; Ostenson, J. E. *Inorg. Chem.* **1996**, *35*, 5627–5633.

(7) Orgzall, I.; Lorenz, B.; Dorhout, P. K.; Van Calcar, P. M.; Brister, K.; Sander, T.; Hochheimer, H. D. *J. Phys. Chem. Solids* **2000**, *61*, 123–134.

(8) (a) Evenson, C. R., IV; Dorhout, P. K. *Inorg. Chem.* **2001**, *40*, 2884–2891. (b) Evenson, C. R., IV; Dorhout, P. K. *Inorg. Chem.* **2001**, *40*, 2875–2883.

(9) (a) Gauthier, G.; Jobic, S.; Brec, R.; Rouxel, J. *Inorg. Chem.* **1998**, *37*, 2332–2333. (b) Gauthier, G.; Jobic, S.; Danaire, V.; Brec, R.; Evain, M. *Acta Crystallogr.* **2000**, *C56*, E117.

(10) (a) Goh, E.-Y.; Kim, E.-J. Kim, S.-J. *J. Solid State Chem.* **2001**, *160*, 195–204. (b) Komm, T.; Schleid, T. *Z. Anorg. Allg. Chem.* **2004**, *630*, 712–716.

(11) Salvador, J. R.; Guo, F.; Hogan, T.; Kanatzidis, M. G. *Nature* **2003**, *425*, 702–705.

(12) (a) Cieren, X.; Angenault, J.; Couturier, J.-C.; Jaulmes, S.; Quarton, M.; Robert, F. *J. Solid State Chem.* **1996**, *121*, 230–235. (b) Angenault, J.; Cieren, X.; Wallez, G.; Quarton, M. *J. Solid State Chem.* **2000**, *153*, 55–65. (c) Evain, M.; Lee, S.; Queignec, M.; Brec, R. *J. Solid State Chem.* **1987**, *71*, 139–153. (d) Evain, M.; Queignec, M.; Brec, R.; Rouxel, J. *J. Solid State Chem.* **1985**, *56*, 148–157. (e) Evain, M.; Queignec, M.; Brec, R.; Sourisseau, C. *J. Solid State Chem.* **1988**, *75*, 413–431.

(13) Gieck, C.; Rocker, F.; Ksenofontov, V.; Gütlich, P.; Tremel, W. *Angew. Chem., Int. Ed.* **2001**, *40*, 908–911.

(14) (a) Chen, B. L.; Eddaoudi, M.; Hyde, S. T.; O'Keeffe, M.; Yaghi, O. M. *Science* **2001**, *291*, 1021–1023. (b) Rosi, N. L.; Eddaoudi, M.; Kim, J.; O'Keeffe, M.; Yaghi, O. M. *Angew. Chem., Int. Ed.* **2001**, *41*, 284–287.

(15) (a) In a nitrogen-filled glovebox, 0.25 mmol of Yb, 0.50 mmol of P_2S_5, 0.50 mmol of K_2S, and 2.0 mmol of S were loaded into a fused-silica tube that was flame-sealed under vacuum and inserted into a furnace. The temperature was raised from 50 to 700 °C in 24 h, kept at 700 °C for 96 h, and then cooled 2 °C/h to 250 °C followed by cooling to 50 °C in 3 h. Moisture-sensitive, orange polyhedral crystals of $K_6Yb_3(PS_4)_5$ (90%) were isolated by washing away the excess flux with *N,N*-dimethylformamide. Semiquantitative energy dispersive analysis (EDS) on a number of the orange polyhedra indicated the presence of K, Yb, P, and S in an approximate 6:3:5:20 molar ratio. (b) Crystal data at -100 °C: Bruker SMART diffractometer, Mo Kα radiation ($\lambda = 0.71073$ Å), $C2/c$, $a = 27.120(3)$, $b = 12.551(1)$, $c = 25.193(3)$ Å, $\beta = 118.940(1)$°, $V = 7504.3$-(13) Å^3, $Z = 8$, $D_c = 2.743$ g cm^{-3}, $0.2 \times 0.1 \times 0.1$ mm, $\mu = 9.412$ mm^{-1}, $\theta_{max} = 28.34$°, total reflections = 80 736, $R_1 = 0.0676$, w$R_2 = 0.1666$ for $I > 2\sigma(I)$. Attempts to find a single crystal were met with great difficulty, so a twinned specimen was selected for data collection. The collected reflections were processed with the program CELLNOW, which found three "twin" components. The second domain was rotated 180° about the 0, 1, -0.5 real axis of the major component. The third domain was rotated 180° about the 0, 1, 0.5 real axis of the major component. The data were integrated on all three components simultaneously using SAINT. TWINABS was used for the absorption correction. The structure was solved with direct methods. The ratio of the three crystal components refined to 78.26:15.19:6.55%. (c) *SMART, SAINT, CELLNOW, TWINABS, SHELXTL V-5*; Bruker Analytical X-ray Instruments, Inc., Madison, WI, and George Sheldrick.

(16) Energy gap was determined from optical diffuse reflectance spectra obtained at room temperature from ground polycrystalline samples over the range of 0.5–6 eV.

(17) Raman data (cm^{-1}) for $K_6Yb_3(PS_4)_5$: 594 w, 576 w, 565 w, 536 w, 512 vw, 423 vs, 329 w, 308 w, 265 wb, 202–180 wvb, 161 w (s = strong, w = weak, b = broad, v = very).

(18) Wibbelmann, C.; Brockner, W.; Eisenmann, B.; Schäfer, H. *Z. Naturforsch* **1983**, *39a*, 190–194.

(19) Kittel, C. *Introduction to Solid State Physics*; John Wiley & Sons: New York, 1996; p 425.

(20) Eddaoudi, M.; Kim, J.; Rosi, N.; Vodak, D.; Wachter, J.; O'Keefe, M.; Yaghi, O. M. *Science* **2002**, *295*, 469–472.

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