Synthesis, Crystal Structure and Characterization of a Novel Three-Dimensional Polymer: $[Cu_4V_2(OH)_2O_8]$

Chuan-De Wu,[a] Can-Zhong Lu,*[a] Hong-Hui Zhuang,[a] and Jin-Shun Huang[a]

Keywords: Hydrothermal synthesis / Oxo ligands / Vanadium / Copper / TGA

The three-dimensional polymeric compound $[Cu_4V_2(OH)_2O_8]$ (**1**) has been synthesized by the hydrothermal reaction of sodium vanadate and copper acetate in an aqueous solution basified with a 35% aqueous ammonia solution. Detailed experiments suggest that pH values within the range 8.5–11.3 are best for the formation of crystals of compound **1**. X-ray diffraction analysis reveals that the structure of **1** is a three-dimensional polymer constructed from wave-like polymeric oxocuprate layers linked by vanadate tetrahedra, of which the sub-layer is formed by joining the zigzag ribbons together in *cis* zigzag way. Thermogravimetric analysis (TGA) suggests that the structure of compound **1** is quite stable in the temperature range 40–440 °C.

(© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2003)

Introduction

As oxygen is the most abundant and highly reactive terrestrial element, the transition metal oxides represent an expanding class of materials, which are ubiquitous as both naturally existing and synthetic materials.[1−3] Because of their stability, diversity of chemical composition and variety of topological architectures, they exhibit a vast range of solid-state properties giving rise to wide applications in areas as diverse as catalysis, sorption, ion-exchange, molecular electronics, energy storage, optical materials and ceramics, heavy construction and biomineralization. The synthesis and characterization of metal oxide-based solids has provoked significant contemporary interest.[4−11]

Since the discovery of the high-temperature oxide superconductors, oxocuprates have been a focus of interest,[12] particularly the study of the relationship between crystal structures and physical properties. It has been found that the coordination environments of copper atoms and the linkages of these coordination polyhedra seem to be crucial. Inorganic chemists have devised many approaches to synthesize such kinds of materials. One very important way is the hydrothermal synthesis method, which operates at a relatively low temperature (110−220 °C) under autogenous pressure and provides a suitable technique to bring suitable metal-oxide building units together to generate polymeric oxometallic materials.[13−16]

The ability of vanadium in its higher oxidation states to form various polynuclear anionic metal-oxygen clusters is well known, and many polyvanadates with an extraordinary variety of relevant topological and electronic structures have been reported.[17−21] On the other hand, copper(II) cations tend to form various oxygen- and/or hydroxyl-bridged polymers under different reaction conditions.[12] There have been a large number of copper vanadates and related compounds reported in the past decades.[22−48] Neutral copper vanadates were first described by solid-state chemists (and later found to occur naturally; for example Blossite,[22,23] Stoiberite,[24] Ziesite,[25] McBimeyite,[26] Volborthite,[27,28] Vesignieite,[29] Calciovolborthite,[30] Mottramite,[31] Averievite,[32] Sengierite,[33] Fingerite,[34] Lyonsite,[35] Howardevansite,[36] etc.), and $Cu_3(VO_4)_2$, for instance, exists in two allotropic forms, one with the spinel structure[41] and the other[26] being isotypic with $Cu_3(PO_4)_2$.[49] Based upon the inherent properties of vanadium and copper atoms, we report here the hydrothermal synthesis, X-ray crystal structure and characterization of a three-dimensional polymeric compound $[Cu_4V_2(OH)_2O_8]$ (**1**).

Results and Discussion

Dark-blue crystals of compound **1** were synthesized by the hydrothermal reaction of sodium vanadate and copper acetate in an aqueous solution basified with 35% aqueous ammonia solution. Detailed experiments suggest that pH values within the range 8.5−11.3 are best for the formation of crystals of compound **1**. When the pH value is below 8.5, only green sediments are obtained instead of crystals. It is very interesting that the crystal size increases with the pH value of the reaction solutions. However, no product was obtained at pH values above 11.3. The aqueous ammonia solution plays a significant role in the formation of

[a] The State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, the Chinese Academy of Sciences,
Fuzhou, Fujian, 350002, China
Fax: (internat.) +86-591/371-4946
E-mail: czlu@ms.fjirsm.ac.cn

compound **1**, which might help the formation of polyoxocuprate fragments and monomeric vanadate. However, if the concentration of NH_3 is above the value where the $[Cu(NH_3)_4]^{2+}$ cation is stabilzed, the formation of polyoxocuprate is prevented. A bond-valence sum calculation[50] reveals that two oxygen atoms are protonated, of which each hydroxyl group bridges three copper centers. Multiple bands from $\tilde{\nu}$ = 947 to 559 cm^{-1} in the IR spectrum of **1** are attributed to the V−O stretching or the bridging [Cu−O−V(Cu)] group absorptions, while the band at 1620 cm^{-1} is attributed to the O−H bending.[51]

The X-ray diffraction analysis reveals that the structure of **1** is a neutral three-dimensional polymeric compound constructed from wave-like polymeric oxocuprate layers linked by vanadate tetrahedra. The asymmetric unit in **1** consists of two $\{VO_4\}$ tetrahedra, two $\{CuO_5\}$ square pyramids and one $\{CuO_6\}$ octahedron (Figure 1). The oxocuprate layer is built up from three crystallographically independent copper(II) atoms, of which two copper centers exhibit a square-pyramidal geometry with Cu−O distances in the 1.881(10)−2.213(9) Å range; the other copper center has an octahedral geometry with Cu−O distances in the 1.914(7)−2.318(8) Å range. These copper atoms form a ribbon through edge sharing in a zigzag arrangement with all copper atoms coplanar (Figure 2). Adjacent ribbons are further joined together by bridging oxygen atoms also through edge sharing. Interestingly, as shown in Figure 3, these ribbons turn by an angle of 47.3(1)° and shift one polyhedral length at the "step" junction. Consequently, the adjacent ribbons are joined together in a *cis* zigzag manner to form a wave-like layered sub-framework. The wave-like oxocuprate sub-layer can also be seen as being constructed from twelve-membered copper rings, which are formed by edge sharing copper square-pyramids or octahedra. These chair-shaped rings are further attached into wave-like layers through edge-sharing copper square-pyramids or octahedra (Figure 4).

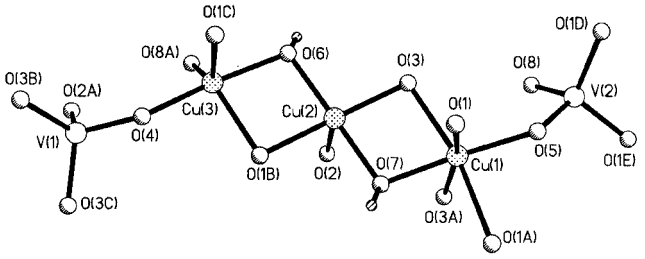

Figure 1. The symmetry-expanded unit in **1**, showing the atom connectivities and the coordination environments (the small right-hatched rings represent hydrogen atoms)

Two crystallographically independent vanadium atoms are both coordinated by four oxygen atoms in tetrahedral geometries. The V−O distances range from 1.638(8) to 1.775(9) Å, with O−V−O angles in the range 107.9(4)−111.4(5)°. The tetrahedrally coordinated vanadium(V) centers link the wave-like sub-layers together to form a three-dimensional polymeric framework (Figure 5) where each vanadate is coordinated to seven or eight $\{CuO_6\}$ octahedra and $\{CuO_5\}$square pyramids by corner sharing.

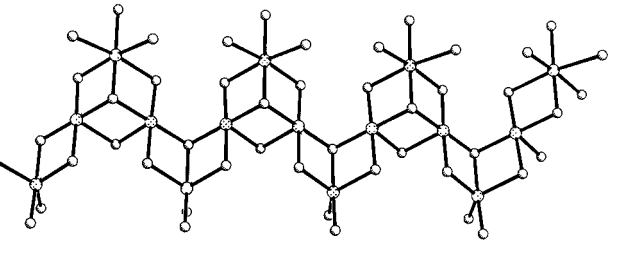

Figure 2. The one-dimensional zigzag ribbon in **1** constructed by linking $\{CuO_6\}$ octahedra and $\{CuO_5\}$ square pyramids

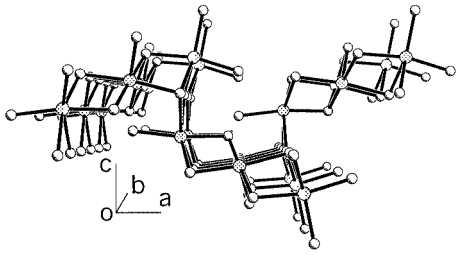

Figure 3. Side view of the linkages between the coplanar chains achieved through bridging oxygen atoms along the *b* axis (the adjacent angle between two planes is 47.3°)

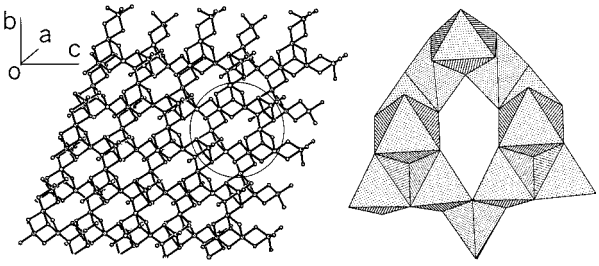

Figure 4. The layered sub-framework of **1** viewed down the *a* axis (right: polyhedral representation of a twelve-membered copper ring in **1**, which is outlined on the left-hand side)

The overall structure of **1** suggests that it should be very stable, and this was confirmed by the thermogravimetric analysis (TGA). The TGA data, recorded from 40 to 1000 °C under inflowing N_2, show that the weight of **1** is almost unchanged from 40 to 440 °C (Figure 6). Above 440 °C, compound **1** began to decompose gradually. The observed weight loss (3.32%) is slightly lower than that of losing one water molecule per empirical formula unit (3.47%). This fact suggests that the hydroxyl groups are changed into H_2O after a complicated reaction process and released from

 © 2003 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

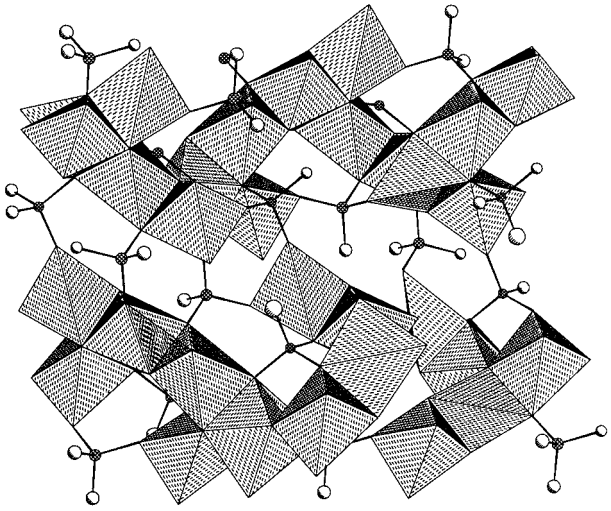

Figure 5. Polyhedral representation of the $\{CuO_6\}$ octahedra and $\{CuO_5\}$ square pyramids as well as a ball-and-stick representation of the $\{VO_4\}$ tetrahedra, showing the three-dimensional polymeric framework of **1**

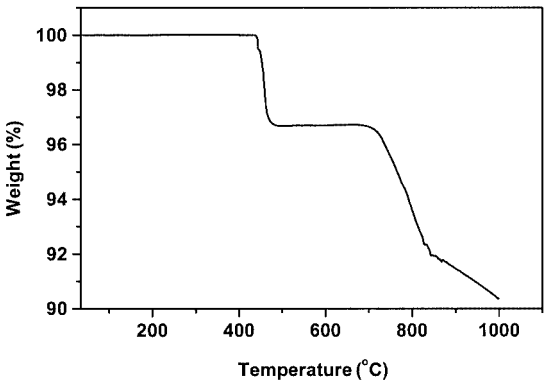

Figure 6. Thermogravimetric (TGA) analysis of **1** between 40 and 1000 °C

the sample above 440 °C. The TGA chart shows that the weight is almost unchanged in the next stage (490−700 °C). Above 700 °C, the product begins to decompose completely.

Conclusion

In conclusion, we have synthesized a three-dimensional polymeric compound under hydrothermal reaction conditions. This result shows that basic reaction conditions can help the formation of polymeric oxocuprate building blocks and monomeric vanadate, and that the pH value of the reaction conditions is a very important impact factor for the formation of novel target materials. The thermogravimetric

Table 1. Selected bond lengths (Å) and angles (°) for compound **1**[a]

Cu(1)−O(7)	1.914(7)	O(7)−Cu(1)−O(5)	172.4(4)	O(2)^{vi}−V(1)−O(4)	110.1(5)
Cu(1)−O(5)	1.943(10)	O(7)−Cu(1)−O(3)	78.8(2)	O(2)^{vi}−V(1)−O(3)^{vii}	109.3(3)
Cu(1)−O(3)	2.154(9)	O(5)−Cu(1)−O(3)	106.1(3)	O(4)−V(1)−O(3)^{vii}	108.8(3)
Cu(1)−O(1)	2.318(8)	O(3)^{i}−Cu(1)−O(3)	96.0(5)	O(3)^{vii}−V(1)−O(3)^{viii}	110.6(6)
Cu(2)−O(7)	1.939(5)	O(7)−Cu(1)−O(1)	88.0(2)	O(8)−V(2)−O(5)	107.9(4)
Cu(2)−O(3)	1.963(7)	O(5)−Cu(1)−O(1)	86.5(3)	O(8)−V(2)−O(1)^{ix}	109.1(3)
Cu(2)−O(6)	1.966(7)	O(3)−Cu(1)−O(1)	87.9(3)	O(5)−V(2)−O(1)^{ix}	109.6(3)
Cu(2)−O(1)^{ii}	2.020(6)	O(3)−Cu(1)−O(1)^{i}	165.1(3)	O(1)^{ix}−V(2)−O(1)^{x}	111.4(5)
Cu(2)−O(2)	2.213(9)	O(1)−Cu(1)−O(1)^{i}	84.9(4)	V(2)^{ii}−O(1)−Cu(2)^{ix}	120.7(5)
Cu(3)−O(4)	1.881(10)	O(7)−Cu(2)−O(3)	83.1(3)	V(2)^{ii}−O(1)−Cu(3)^{ix}	112.3(3)
Cu(3)−O(8)^{iii}	1.930(8)	O(7)−Cu(2)−O(6)	178.7(4)	Cu(2)^{ix}−O(1)−Cu(3)^{ix}	91.8(3)
Cu(3)−O(6)	1.937(10)	O(3)−Cu(2)−O(6)	97.8(4)	V(2)^{ii}−O(1)−Cu(1)	132.1(4)
Cu(3)−O(1)^{ii}	2.206(9)	O(7)−Cu(2)−O(1)^{ii}	94.4(3)	Cu(2)^{ix}−O(1)−Cu(1)	98.3(3)
V(1)−O(2)^{vi}	1.674(12)	O(3)−Cu(2)−O(1)^{ii}	172.8(3)	Cu(3)^{ix}−O(1)−Cu(1)	91.3(4)
V(1)−O(4)	1.679(10)	O(6)−Cu(2)−O(1)^{ii}	84.7(4)	V(1)^{vi}−O(2)−Cu(2)	136.6(2)
V(1)−O(3)^{vii}	1.739(9)	O(7)−Cu(2)−O(2)	86.7(3)	Cu(2)−O(2)−Cu(2)^{i}	85.1(4)
V(2)−O(8)	1.638(8)	O(3)−Cu(2)−O(2)	96.8(4)	V(1)^{xi}−O(3)−Cu(2)	121.7(5)
V(2)−O(5)	1.704(10)	O(6)−Cu(2)−O(2)	94.2(3)	V(1)^{xi}−O(3)−Cu(1)	138.9(4)
V(2)−O(1)^{ix}	1.775(9)	O(1)^{ii}−Cu(2)−O(2)	89.7(4)	Cu(2)−O(3)−Cu(1)	94.5(3)
		O(4)−Cu(3)−O(8)^{iii}	96.3(4)	V(1)−O(4)−Cu(3)	146.5(7)
		O(4)−Cu(3)−O(6)	166.6(5)	V(2)−O(5)−Cu(1)	133.2(6)
		O(8)^{iii}−Cu(3)−O(6)	97.1(4)	Cu(3)−O(6)−Cu(2)	102.2(4)
		O(4)−Cu(3)−O(1)^{ii}	90.1(3)	Cu(2)^{v}−O(6)−Cu(2)	102.6(5)
		O(8)^{iii}−Cu(3)−O(1)^{ii}	134.5(2)	Cu(1)−O(7)−Cu(2)	103.5(3)
		O(6)−Cu(3)−O(1)^{ii}	80.5(3)	Cu(2)^{i}−O(7)−Cu(2)	101.0(4)
		O(1)^{iv}−Cu(3)−O(1)^{ii}	90.3(4)	V(2)−O(8)−Cu(3)^{iii}	169.3(5)

[a] Symmetry transformations used to generate equivalent atoms: i): $x, -y + 1/2, z$; ii): $-x + 1/2, -y, z + 1/2$; iii) $-x + 1, -y, -z + 1$; iv): $-x + 1/2, y - 1/2, z + 1/2$; v): $x, -y - 1/2, z$; vi): $-x + 1, -y, -z + 2$; vii): $x, y, z + 1$; viii): $x, -y - 1/2, z + 1$; ix): $-x + 1/2, -y, z - 1/2$; x): $-x + 1/2, y + 1/2, z - 1/2$; xi): $x, y, z - 1$.

 © 2003 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

analysis suggests that the framework of compound **1** is stable up to 440 °C.

Experimental Section

General Remarks: All chemicals were of reagent grade and were used as received. Infrared spectra were recorded on a FTS-40 spectrophotometer using pressed KBr pellets. Thermogravimetric analysis (TGA), using a universal V2.4F TA Instrument, was performed on a powdered sample of **1** under inflowing N_2 with heating rate of 10 °C·min^{-1} in the temperature range 40−1000 °C.

$[Cu_4V_2(OH)_2O_8]$ (1): $NaVO_4 2H_2O$ (0.079 g, 0.5 mmol) and $Cu(CH_3COO)_2{\cdot}H_2O$ (0.10 g, 0.5 mmol) were dissolved in H_2O (16 mL) at room temperature. The pH value of the solution was adjusted to 8.67 by adding 35% aqueous ammonia solution dropwise, resulting in a deep-blue solution. The solution was transferred into a 30 mL polytetrafluoroethylene-lined Parr acid digestion vessel. The vessel was then sealed and heated at 195 °C for five days under autogenous pressure. After cooling, dark blue crystals were filtered off and washed with water and ethanol. Yield: about 76% (based on Cu). IR (KBr pellet): $\tilde{\nu}$ = 1620 m cm^{-1}, 947 m, 877 s, 822 m, 769 s, 559 m.

X-ray Crystallographic Study: $Cu_4H_2O_{10}V_2$, M = 518.06, orthogonal, space group *Pnma*, a = 14.9251(1), b = 6.0607(1), c = 8.5460(1) Å, V = 773.04(2) Å^3, Z = 4, D_c = 4.451 g·cm^{-3}, μ = 13.167 mm^{-1}, $F(000)$ = 976, crystal size = 0.32 × 0.26 × 0.12 mm^3. The determination of the unit cell and the data collection for a dark-blue crystal of compound **1** were performed on an Enraf−Nonius CAD4 diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) in the ω-2θ range 2.73 < θ < 30.03°. Lorentz-polarization corrections and an empirical absorption were applied to the data. The structure was solved by direct methods and refined by full-matrix least-squares, leading to a convergence with final $R1$ = 0.0734, $wR2$ = 0.1279 and S = 1.089 for 705 reflections with $F_o > 4\sigma(F_o)$ and 87 parameters. The structure analysis and refinement were carried out using the SHELXL-97 software package.[52] Selected bond lengths and angles are listed in Table 1.

Further details of the crystal-structure investigation may be obtained from the Fachinformationzentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository number CSD-412990.

Acknowledgments

We are grateful to the 973 Program of the MOST (001CB108906), the National Natural Science Foundation of China (90206040, 20073048), the NSF of Fujian (2002F015) and the Chinese Academy of Sciences for financial supports.

[1] L. L. Hench, *Inorganic Biomaterials in Materials Chemistry, An Emerging Discipline* (Eds.: L. V. Interrante, L. A. Caspar, A. B. Ellis), ACS Series 245, **1995**, ch. 21, pp. 523−547.
[2] B. Mason, *Principles of Geochemistry, 3rd ed.,* Wiley, New York, **1966**.
[3] D. W. Bruce, D. O'Hare, *Inorganic Materials*, Wiley, Chichester, **1992**.
[4] A. K. Cheetham, *Science* **1994**, *264*, 794 and references therein.
[5] A. Müller, H. Reuter, S. Dillinger, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2328.
[6] M. T. Pope, A. Müller, *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 34.
[7] P. A. Cox, *Transition Metal Oxides*, Clarendon Press, Oxford, **1995**.
[8] M. T. Pope, *Heteropoly and Isopoly Oxometalates*, Springer, New York, **1983**.
[9] A. Müller, F. Peters, M. T. Pope, D. Gatteschi, *Chem. Rev.* **1998**, *98*, 239.
[10] A. Clearfield, *Chem. Rev.* **1988**, *88*, 125.
[11] P. J. Hagrman, D. Hagrman, J. Zubieta, *Angew. Chem. Int. Ed.* **1999**, *38*, 2638.
[12] H. Müller-Buschbaum, *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 723.
[13] J. Gopalakrishnan, *Chem. Mater.* **1975**, *7*, 1265.
[14] A. Rabenau, *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 1026.
[15] R. A. Ludise, *Chem. Eng. News* **1987**, *65*, 30.
[16] J. Y. Lu, M. L. Lawandy, J. Li, T. Yuen, C. L. Lin, *Inorg. Chem.* **1999**, *38*, 2695.
[17] W. G. Klemperer, T. A. Marquart, O. M. Yaghi, *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 49.
[18] Y.-J. Liu, J. L. Schindler, D. C. DeGroot, C. R. Kannewurf, W. Hirpo, M. G. Kanatzidis, *Chem. Mater.* **1996**, *8*, 525.
[19] C.-G. Wu, D. C. DeGroot, H. O. Marcy, J. L. Schindler, C. R. Kannewurf, Y.-J. Liu, W. Hirpo, M. G. Kanatzidis, *Chem. Mater.* **1996**, *8*, 1992.
[20] Y. Zhang, J. R. D. DeBord, C. J. O'Connor, R. C. Haushalter, A. Clearfield, J. Zubieta, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 989.
[21] M. I. Khan, E. Yohannes, R. J. Doedens, *Angew. Chem. Int. Ed.* **1999**, *38*, 1292.
[22] C. Calvo, R. Faggiani, *Acta Crystallogr., Sect. B* **1975**, *31*, 603.
[23] P. D. Robinson, J. M. Hughes, M. L. Malinconico, *Am. Mineralogist* **1987**, *72*, 397.
[24] R. D. Shannon, C. Calvo, *Acta Crystallogr., Sect. B* **1973**, *29*, 1338.
[25] D. Mercurio-Lavaud, B. Frit, *Comptes Rendus Hebdomadaires des Seances de l' Academie des Sciences, Serie C, Sciences Chimiques* **1973**, *277*, 1101.
[26] J. Coing-Boyat, *Acta Crystallogr., Sect. B* **1982**, *38*, 1546.
[27] R. Basso, A. Palenzona, L. Zefiro, *Neues Jahrbuch fuer Mineralogie. Monatshefte* **1988**, 385.
[28] M. A. Lafontaine, A. LeBail, G. Ferey, *J. Solid State Chem.* **1990**, *85*, 220.
[29] Z. Ma, R. He, X. Zhu, *Dizhi Xuebao* **1990**, *4*, 302.
[30] R. Basso, A. Palenzona, L. Zefiro, *Neues Jahrbuch fuer Mineralogie. Monatshefte* **1989**, 300.
[31] M. A. Cooper, F. C. Hawthorne, *Canad. Mineralogist.* **1995**, *33*, 1119.
[32] G. L. Starova, S. V. Krivovichev, V. S. Fundamenskii, S. K. Filatov, *Mineralogical Magazine* **1997**, *61*, 441.
[33] P. Piret, J. P. Declercq, D. Wauters-Stoop, *Bulletin de Mineralogie* **1980**, *103*, 176.
[34] L. W. Finger, *Am. Mineralogist* **1985**, *70*, 197.
[35] J. M. Hughes, S. J. Starkey, M. L. Malinconico, L. L. Malinconico, *Am. Mineralogist* **1987**, *72*, 1000.
[36] J. M. Hughes, J. W. Drexler, C. F. Campana, M. L. Malinconico, *Am. Mineralogist* **1988**, *73*, 181.
[37] J. Galy, D. Lavaud, *Acta Crystallogr., Sect. B* **1971**, *27*, 1005.
[38] M.-L. Ha-Eierdanz, U. Müller, *Z. Anorg. Allg. Chem.* **1993**, *619*, 287.
[39] D. Mercurio-Lavaud, B. Frit, *Acta Crystallogr., Sect. B* **1973**, *29*, 2737.
[40] C. Calvo, D. Manolescu, *Acta Crystallogr., Sect. B* **1973**, *29*, 1743.
[41] R. D. Shannon, C. Calvo, *Canad. J. Chem.* **1972**, *50*, 3944.
[42] J. R. Rea, E. Kostiner, *J. Solid State Chem.* **1973**, *7*, 163.

 © 2003 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

[43] J. R. Rea, E. Kostiner, *J. Solid State Chem.* **1973**, *7*, 17.
[44] J. Galy, D. Lavaud, A. Casalot, P. Hagenmuller, *J. Solid State Chem.* **1970**, *2*, 531.
[45] J. R. Rea, P. W. Bless, E. Kostiner, *J. Solid State Chem.* **1972**, *5*, 446.
[46] S. Aschwanden, H. W. Schmalle, A. Reller, H. R. Oswald, *Mater. Res. Bull.* **1993**, *28*, 45.
[47] J. Galy, D. Lavaud, A. Casalot, P. Hagenmuller, *J. Solid State Chem.* **1970**, *2*, 531.
[48] M. Blanc, G. Ferey, *Acta Crystallogr., Sect. C* **1990**, *46*, 15.
[49] G. L. Shoemaker, J. B. Anderson, E. Kostiner, *Acta Crystallogr.* **1977**, *33*, 2969.
[50] N. E. Brease, M. O'Keeffe, *Acta Crystallogr., Sect. B* **1991**, *47*, 192.
[51] M. I. Khan, T. Hope, S. Cevik, C. Zheng, D. Powell, *J. Cluster Sci.* **2000**, *11*, 433.
[52] G. M. Sheldrick, Universität Göttingen, Germany, **1997**.
Received February 12, 2003

 © 2003 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim