

**HIGH LITHIUM-ION CYCLABILITY IN A NOVEL NANOPOROUS HYBRID-CHANNEL HOST**K. Lin

National Chung-Hsing University Department of Chemistry TAICHUNG 402 TAIWAN

Well-ordered crystalline solids with both large and hybrid pores are exceedingly rare or lacking. We report the synthesis and structure of a novel nanoporous organo-phosphonate involving mixed vanadium-gallium metals. It adopts intersecting hydrophobic large pores, chinese vase-like cage with dimensions of 11 - 14 Å, with thermally stable up to 550 oC. Two fascinating intercalation methodologies were conducted. First, conducting polyaniline filaments have been encapsulated in the hybrid channels. Second, it reveals a highly reversible lithium-ion intercalation and de-intercalation cycling between the applied potential limits +3 and +5 volts; such preliminary cyclability is thought to be a key aspect of rechargeable lithium battery cathode materials.

**Keywords:** MICROPOROUS, HYBRID, LITHIUM INSERION**STRUCTURE OF A NOVEL NANOPOROUS CRYSTAL OF Rb<sub>3</sub>Ta<sub>5</sub>O<sub>14</sub> AND CHARACTERISATION OF RELATED Rb-Ta-O AND Cs-Ta-O COMPOUNDS**A. Oono<sup>1</sup> D. J. du Boulay<sup>1</sup> N. Ishizawa<sup>1</sup> S. Oishi<sup>2</sup><sup>1</sup>Tokyo Institute of Technology Interdisciplinary Graduate School of Science and Engineering 4259 Nagatsuta Midori YOKOHAMA 2268503 JAPAN  
<sup>2</sup>Sinshu University

Single crystals of Rb<sub>3</sub>Ta<sub>5</sub>O<sub>14</sub> were grown by the flux method and the structure was determined by the synchrotron X-ray single crystal diffraction. The compound crystallises in an orthorhombic *Pnma* symmetry with  $a = 7.3677(3)$ ,  $b = 14.7904(19)$ ,  $c = 25.379(3)$  Å, and has a three dimensional framework comprised of edge or corner-shared TaO<sub>6</sub> and TaO<sub>5</sub> polyhedra. The structure includes nanometer-sized cavities which act as the Rb reservoirs. The cavities are interconnected with each other through the subnanometer-sized openings. The structural features suggest that the Rb-exchanged products would behave as an excellent ionic conductor of Li and H. The Rb:Ta ratio of the present system is 3:5 which is close to 4:6 of the well-known photocatalytic compounds A<sub>4</sub>B<sub>6</sub>O<sub>17</sub> (A = K, Rb, B = Nb, Ta). However, the 3:5 compound is structurally different from the 4:6 compounds which are characterised by the layered BO<sub>6</sub> octahedral sheets. A powder diffractogram of the product obtained by the flux growth experiment of Rb<sub>3</sub>Ta<sub>5</sub>O<sub>14</sub> (Rb/Ta ratio = 0.600) suggested an existence of additional minor phase ascribed to Rb<sub>4</sub>Ta<sub>6</sub>O<sub>17</sub> (Rb/Ta ratio = 0.667). Powder diffractograms of the compounds fired at 1473 K with various Rb/Ta ratios in the range 0.567 -- 0.733 showed that the major component was Rb<sub>3</sub>Ta<sub>5</sub>O<sub>14</sub> for all products, while Rb<sub>4</sub>Ta<sub>6</sub>O<sub>17</sub> was detected only in the products with Rb/Ta ratio above 0.700 inclusive.

**Keywords:** NANOPOROUS FRAMEWORK RUBIDIUM TANTALATE SYNCHROTRON X-RAY SINGLE CRYSTAL DIFFRACTION**CRYSTAL STRUCTURE OF A NEW ZINC GALLOPHOSPHATE WITH AN OPEN-FRAMEWORK**M. Mrak U. Kolitsch V. Kaucic E. Tillmanns

National Institute of Chemistry Inorganic Chemistry and Technology Hajdrihova 19 LJUBLJANA SLOVENIA SI-1000 SLOVENIA

The synthesis of open-framework metal phosphates has attracted much attention for their rich structural chemistry, zeolitic properties and potential application as molecular sieves, catalysts and ion exchangers. The new zinc gallophosphate, NH<sub>4</sub>(Ga,Zn)(PO<sub>4</sub>)<sub>2</sub>, has been synthesized under hydrothermal conditions at 443 K and the structure determined using 150 K single-crystal X-ray diffraction data (monoclinic, space group *C2/c*;  $a = 13.370(03)$ ,  $b = 13.190(3)$ ,  $c = 8.998(2)$  Å,  $\beta = 100.46(3)^\circ$ ,  $V = 1560.4(6)$  Å<sup>3</sup>,  $Z = 8$ ,  $R1 = 0.0232$  and  $wR2 = 0.0592$ ). The compound has a three-dimensional anionic framework assembled from corner sharing (Ga,Zn)O<sub>4</sub> and PO<sub>4</sub> tetrahedra. The tetrahedra form eight-membered rings with channels occupied by disordered NH<sub>4</sub><sup>+</sup> cations counterbalancing the charge on the framework. The structure is isostructural with that of K(Co,Al)<sub>2</sub>(PO<sub>4</sub>)<sub>2</sub> and [(NH<sub>4</sub>)<sub>x</sub>(NH<sub>3</sub>)<sub>0.5-x</sub>]Al<sub>1-x</sub>Co<sub>x</sub>PO<sub>4</sub>, where  $x$  is less or equal 0.4. The presence of NH<sub>3</sub> groups in the latter was based on the observation that the refinement gave an occupancy ratio of Co:Al = 0.38:0.63. In our case the atomic ratio of Zn to Ga determined from single-crystal structure refinement 1: 1 was further confirmed by electron probe microanalysis data 1.07: 1.00.

**Keywords:** MICROPOROUS INORGANIC MATERIALS**POWDER DIFFRACTION STUDY OF FE AND GA SILICALITES**D. Viterbo<sup>1</sup> M. Milanese<sup>1</sup> L. Palin<sup>2</sup> C. Lamberti<sup>3</sup> G. Marra<sup>4</sup> R. Aiello<sup>5</sup> F. Testa<sup>7</sup><sup>1</sup>universita Del Piemonte Orientale Dista Corso T. Borsalino 54 Alessandria I-15100 Italy <sup>2</sup>European Synchrotron Radiation Facility, B.P. 220, F38043 Grenoble Cedex, France <sup>3</sup>dipartimento Di Chimica Ifm, Universita, Via P. Giuria 7, I-10125 Torino, Italy <sup>4</sup>polimeri Europa S.R.L., Istituto Guido Donegani, Via Fauser 4, I-28100 Novara, Italy <sup>5</sup>dipartimento Di Ingegneria Chimica E Dei Materiali, Universita Della Calabria, I-87030 Rende (Cs), Italy

High resolution XRD powder profiles were collected at room temperature on a variety of Ga and Fe silicalite samples, synthesized from fluoride media [Testa et al, in Porous Materials in Environmentally Friendly Processes, Stud.Surf.Sci.Cat, 125, 165 (1999)] from a gel composition: 10SiO<sub>2-x</sub>·Het(FeNO<sub>3</sub>)<sub>3.9</sub>H<sub>2</sub>O + yMF + 1.25TPABr + 300H<sub>2</sub>O, where Het = Fe and Ga and M = NH<sub>4</sub><sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Cs<sup>+</sup>. Both as made and calcined samples were investigated. At first, the same Na-Fe-silicalite sample employed for the single crystal analysis [Milanese et al., J.Phys.Chem. B,104, 9951 (2000)] was measured, after grinding, to make sure that the results obtained from single crystal are not biased by twinning. In particular, after Rietveld refinement, the extra-framework peak near T9 was located in the difference Fourier map in the same position obtained from single crystal analysis. NH<sub>4</sub><sup>+</sup> and Cs<sup>+</sup> derivatives have a relatively high framework heteroatom content as revealed by the significant increase in cell volume with respect to pure silicalite, and do not give single crystals, but just spherical aggregates of 1 micron crystallites. The volume increase is smaller for Ga-silicalites than for Fe-silicalites in agreement with the smaller ionic radius of Ga<sup>3+</sup> with respect to Fe<sup>3+</sup>. The high brilliance of the synchrotron source permitted to find the presence of traces of impurities (NaFe, Na<sub>3</sub>F<sub>6</sub>, K<sub>2</sub>SiF<sub>6</sub>, Cs<sub>2</sub>SiF<sub>6</sub>), yielding a better understanding of the destiny of the M<sup>+</sup> and F<sup>-</sup> ions. For a Ga derivative data were collected just before and on the Ga absorption edge in order to exploit the resonant scattering effect to locate the Ga atoms in the MFI framework.

**Keywords:** ZEOLITES, FE-SILICALITE, GA-SILICALITE