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Room-Temperature Synthesis and Characterization of New ZnPO and ZnAsO Sodalite Open Frameworks

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We report the room-temperature syntheses and crystal structures of two new anionic frameworks of zinc phosphate and zinc arsenate, containing three-dimensional cages occupied by sodium cations and water molecules. These materials are isostructural with the prototype hydrated sodium aluminosilicate sodalite phase, $Na_6(AlSiO_4)_6{\cdot}8H_2O$.[1-3] Room-temperature reactions produce highly crystalline materials.

Recent reports have revealed a variety of novel phases in the zinc–phosphorus–oxygen system, including layered organophosphonates[4] and channel-containing zinc phosphite phases.[5] Here, we consider the zinc–phosphate and zinc–arsenate systems in relation to zeolitic, aluminosilicate frameworks. Notably, these ions all coordinate tetrahedrally to oxygen, have similar ionic radius ratios to aluminum and silicon, and form a framework "anion" ($ZnXO_4^-$) equivalent to that found in aluminosilicates ($AlSiO_4^-$), which is easily charge balanced by monovalent cations.

The sodalite analogue, ZnPO, was synthesized hydrothermally:[9] a mixture of ZnO, H_3PO_4, NaOH, and water was sealed in a Teflon bottle and heated to 50 °C for 12 h. The reaction mixture was allowed to cool to room temperature and filtered, and a white crystalline powder, suitable for Rietveld analysis, was obtained. The same product can also be made when the starting materials are allowed to react at room temperature for 24 h. A room-temperature powder X-ray pattern of this material showed a primitive cubic framework (a = 8.828 05 (12) Å) consistent with the absence conditions for space group $P\bar{4}3n$, suggesting that the material was isostructural with sodium aluminosilicate sodalite $Na_6(AlSiO_4)_6{\cdot}8H_2O$ (a = 8.86 Å). Thermogravimetric analysis data (calculated weight loss 11.5%, found 11.5%) confirmed a material of stoichiometry $Na_6(ZnPO_4)_6{\cdot}8H_2O$, which loses all eight water molecules upon dehydration at 142 °C to give a new hexagonal phase.

The sodalite-type ZnAsO is similar to ZnPO in many of its synthetic and structural characteristics. Hydrothermally prepared,[9] the mixture contained $Na_2HAsO_4{\cdot}7H_2O$, NaOH, $Zn(NO_3)_2$, and water, all placed in a Teflon bottle and heated to 70 °C for 12 h. The same results were obtained upon reaction at room temperature for 72 h. Both samples were filtered and a highly crystalline white powder, suitable for X-ray Rietveld analysis, with a cubic (a = 9.02729 (7) Å) unit cell was recovered. TGA (calculated weight loss 9.5%, found 9.5%) shows that $Na_6(ZnAsO_4)_6{\cdot}8H_2O$ loses all eight water molecules upon dehydration at approximately 175 °C and transforms to a hexagonal phase, similar to that found in the phosphate system.

The crystal structures of these materials were established by X-ray Rietveld refinement, using the starting sodium aluminosilicate model of Felsche et al. in space group $P\bar{4}3n$.[3,6,7] The final cycle of least squares converged to give residuals of R_{wp} = 9.09% and R_p = 7.38% for the ZnPO structure and R_{wp} = 6.32% and R_p = 5.26% for the ZnAsO. Final observed, calculated, and difference profile plots for the ZnAsO are illustrated in Figure 1. Atomic positional and thermal parameters are available as supplementary material.

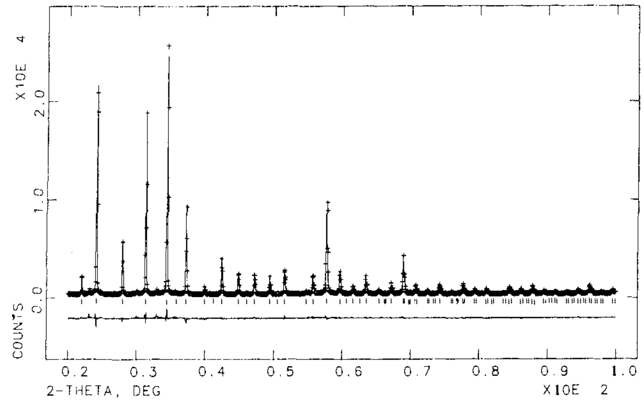

Figure 1. Final observed (crosses), calculated (line) and difference profiles for the X-ray Rietveld refinement of $Na_6(ZnAsO_4)_6{\cdot}8H_2O$. Reflection positions are indicated by tick marks.

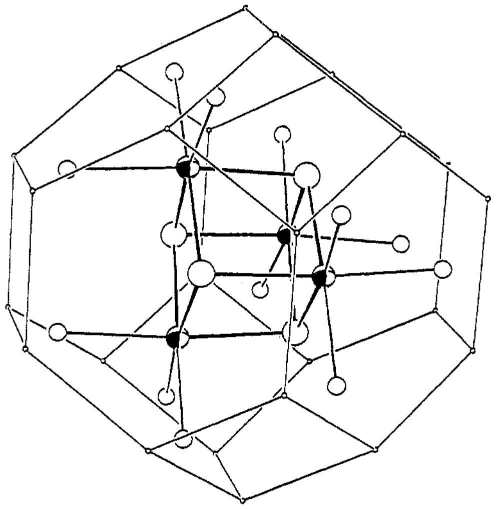

Figure 2. ORTEP view of the "cubane" geometry of the $Na_3(H_2O)_4$ cluster occupying the sodalite β cage, outlined as schematic Zn–As links, with Zn–O–As bonds omitted for clarity. On average, each cage contains only three sodium ions, statistically disordered over four of the cube vertices. The sodium ions are shaded; framework oxygens are small spheres; water oxygens are large spheres.

These new modifications of the sodalite structure[2] consist of face-sharing truncated octahedra, built up from ZnO_4 and XO_4 (X = P, As) tetrahedral units. The Zn to X ratio is unity and the ZnO_4 and XO_4 units alternate throughout the structure. This topology results in spherical cavities (β cages) of approximate diameter 6.5 Å, interconnected via six rings of approximate diameter 2.2 Å.[1] The negative charge of the $ZnXO_4$ framework is compensated by the positive charge of the sodium cations, which reside in the β cages. The sodium cations, which have a crystallographic site occupancy of 0.75, are 3-fold coordinated by framework oxygens and 3-coordinated by guest water molecules, resulting in approximate octahedral geometry. The waters are pyramidally coordinated by three sodium atoms and probably also make H-bond contacts with framework oxygens atoms,[3] although no protons were located in these powder studies. The β-cage contents are thus $Na_3(H_2O)_4$, and a cubane-like geometry results, as illustrated in Figure 2, although on average only three sodiums

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(2) As well as aluminosilicates, many sodalite-type analogues are known, such as $AlPO_4$, $BeSiO_4$, and $BeGeO_4$ as the framework atoms. For more details, see: Meier, W. M.; Olson, D. H. *Atlas of Zeolite Structure Types*; Polycrystal Book Service: Pittsburgh, PA, 1978.

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(6) Room-temperature (25 (1) °C), high-resolution powder X-ray data were collected on a Scintag PAD-X automated diffractometer operating in θ–θ geometry (λ = 1.54178 Å), between 2θ = 20 and 100° in 0.02° steps for a total of 4000 data. Rietveld refinement was carried out using the program GSAS.[7] Harrison, W. T. A.; Eddy, M. M.; Keder, N. L.; Stucky, G. D. In preparation.

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are found per sodalite cage. There was no evidence suggesting any sodium ordering, such as supercell reflections. Models based on the "basic" sodalite structure[3,8] $Na_{8-\delta}(AlSiO_4)_6(OH)_{2-\delta}\cdot 4H_2O$ ($\delta > 0$) gave substantially poorer profile fits. Selected bond length data, with esd's in parentheses, for these phases are as follows: in the ZnPO system the Zn(1)–O(1), P(1)–O(1), Na(1)–O(1), and Na(1)–O_ω(1) contacts are 1.946 (6), 1.531 (3), 2.414 (8), and 2.397 (8) Å, respectively; in the ZnAsO system the Zn(1)–O(1), As(O)–O(1), Na(1)–O(1), and Na(1)–O_ω(1) bond lengths are 1.946 (6), 1.670 (6), 2.424 (11), and 2.431 (8) Å, respectively. O_ω(1) is the water molecule in each case. The Zn–O–X bond angle is 126.1 (3)° for ZnPO and 123.8 (3)° for ZnAsO, much smaller than the 136.2 (3)° found for the Al–O–Si bond angle in $Na_6(AlSiO_4)_6\cdot 8H_2O$.[3] The closest sodium–sodium contacts are 3.53 (3) Å for ZnPO and 3.56 (3) Å for ZnAsO (3.764 (8) Å for the sodium aluminosilicate[3]). The ZnAsO represents the largest cage size dimension observed to date in hydrated sodalite-type phases.

The results obtained to date have demonstrated that an extensive chemistry exists with respect to the room-temperature synthesis of novel non-aluminosilicate zeolitic-type materials. Synthetic and structural studies on other phases will be reported in subsequent publications.[9,10]

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Supplementary Material Available: Table of atomic positional and thermal parameters for $Na_6(ZnPO_4)_6\cdot 8H_2O$ and $Na_6(ZnAsO_4)_6\cdot 8H_2O$ (1 page). Ordering information is given on any current masthead page.

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Solid-State Electrochemistry: Voltammetric Monitoring of Redox Transitions in Single Crystals of Silicotungstic Acid

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Recently there has been considerable interest in extending electrochemical methods to the study of solid-state redox transitions in thin polymeric films containing fixed redox sites,[1,2b] as well as in bulk mixed-valence and porous inorganic materials.[2] The eligible systems are ionically conducting solids having various accessible oxidation states and remaining capable of fast electron transfer between redox sites. A direct extension of normal electrochemical methods to the solid state would involve such crystalline molecular materials as heteropolyacids[3,4] and infinite colloidal oxides of tungsten,[3b,5] which possess distinct multiple valence states within their structures,[6] high protonic conductivities,[7] and semiconducting or semimetallic electronic properties.[3b–d,5e,6] They host mobile charged species, especially protons, at fairly large concentrations; and these can serve the same purpose as supporting electrolytes in conventional electrochemistry. Thus, the migration effects and electric fields within the material can become negligible.

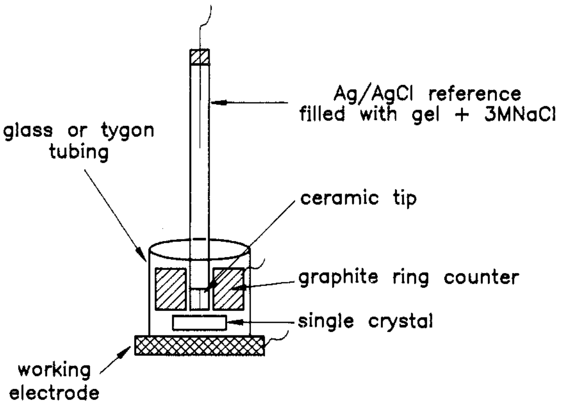

Figure 1. Illustration of a three-electrode cell arrangement for use in solid-state electrochemistry.

Of particular interest are single crystals of tetragonal silicotungstic acid, $H_4SiW_{12}O_{40}\cdot 31H_2O$.[3f] They have a structure in which the rigid Keggin-type, molecular heteropolyanion[3b–d] $SiW_{12}O_{40}{}^{4-}$ is surrounded by a hydrated three-dimensional "pseudoliquid",[3c,8] which also hosts the protons[7] required for charge balance. These protons are known to be transported, virtually as fast as in aqueous solutions.[7a,c] Reduction of the rigid (het-

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