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New Low Temperature Synthetic Route to an Ammonium Zinc Arsenate Zeolite Analogue with an ABW-Type Structure

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The synthesis and stability of zeolite analogues are of potential interest to the waste management community as waste metals may be used in the framework of these materials. A new synthetic route to an ABW-type ammonium zinc arsenate is proposed. The stability of this material is then examined in an aqueous environment by quantitative X-ray diffraction and leach testing.

Interest in new zeolite analogues has produced a substantial quantity of research. Of potential interest to the waste management community are zeolite analogues with metal arsenate frameworks. Because of the chemical similarities between arsenic and phosphorus, a number of arsenate analogues of metal phosphates with open-framework structures have been identified. These materials include zinc,[1−4] aluminum,[4,5] and gallium[4,6] arsenates, with various topological types. Many potential uses of these materials rely on the stability of the phase formed. Unstable phases are of little practical value.

During a study on the potential of various zinc arsenate zeolite analogues for toxic waste immobilization, by incorporation of waste metals in the framework, a new low temperature, high yield, route to an ABW-type ammonium zinc arsenate zeolite was found, and the stability of this phase was assessed.

The structure (Figure 1) of this material was determined by Reitveld refinement of the powder X-ray diffraction pattern using an analogous phosphate[7,8] as a template. This structure, determined by single crystal X-ray diffraction by Feng, Zhang, and Bu who used a different synthetic procedure, has subsequently been published.[4]

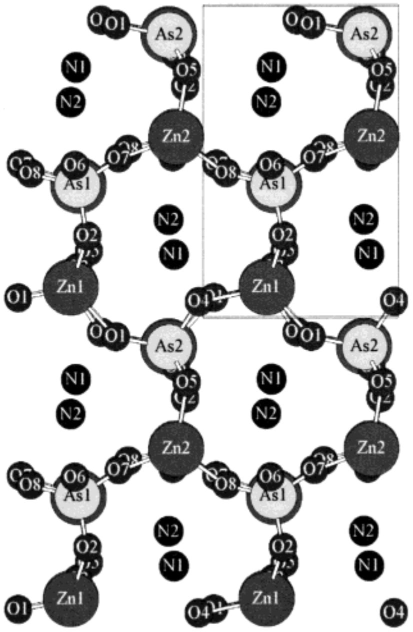

Figure 1. Structure of ABW-type NH_4ZnAsO_4, orientated a = vertical, c = horizontal. Monoclinic crystal, space group $P2_1$, a = 8.9454 Å, b = 5.6241 Å, c = 9.1197 Å, β = 90.374°. Box outlines unit cell.

Our synthesis of this ammonium zinc arsenate was by the following method. A 6.5 mL portion of 4 M H_3AsO_4 was mixed with 12 mL of 2 M $Zn(NO_3)_2$. An ammonia solution (2 M) was added until the pH was 8. The mixture was heated in a sealed HDPE bottle to 70 °C for 70 h. A fine white powder was produced and separated by vacuum filtration.

Analyses for arsenic and zinc were carried out by ICP-OES. Ammonia concentrations were obtained by spectrophotometry using the indophenol method.[9] Quantitative powder X-ray diffraction (QXRD) was carried out, using a corundum internal standard, to quantify the crystallinity of the sample. The sample was also dispersed in water four

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(1) Harrison, W. T. A.; Broach, R. W.; Bedard, R. A.; Gier, T. E.; Stucky, G. D. *Chem. Mater.* **1996**, *8*, 691−700.
(2) Bu, X.; Feng, P.; Gier, T. E.; Stucky, G. *J. Solid State Chem.* **1998**, *136*, 210−215.
(3) Jenson, T. R.; Norby, P.; Norlund, C. A.; Hanson, J. *Microporous Mesoporous Mater.* **1998**, *26*, 77−87.
(4) Feng, P.; Zhang, T.; Bu, X. *J. Am. Chem. Soc.* **2001**, *123*, 8608−8609.
(5) Harrison, W. T. A. *Acta Crystallogr., Sect. C* **2001**, *C56*, e421.
(6) Bu, X.; Gier, T. E.; Feng, P.; Stucky, G. D. *Microporous Mesoporous Mater.* **1998**, *20* (4−6), 371−379.
(7) Bu, X.; Feng, P.; Gier, T. E.; Stucky, G. *Zeolites* **1997**, *19*, 200−208.
(8) Fletcher, D. A.; McMeeking, R. F.; Parkin, D. J. *J. Chem. Inf. Comput. Sci.* **1996**, *36*, 746−749.
(9) Marczenko, Z. *Separation and spectrophotometric determination of elements*; Ellis Horwood Limited: Chichester, U.K., 1986.

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Table 1. Results of Elemental Analysis of Precipitated Solid

analyte:	NH_4^+	AsO_4^{3-}	Zn^{2+}
wt %	5.7	55.7	29.6

Table 2. Sample Composition and Initial Immobilization after Precipitation of NH_4ZnAsO_4

formula	ideal Zn:As	sample Zn:As	% AsO_4 removed
NH_4ZnAsO_4	1:1	1.135:1	81.5%

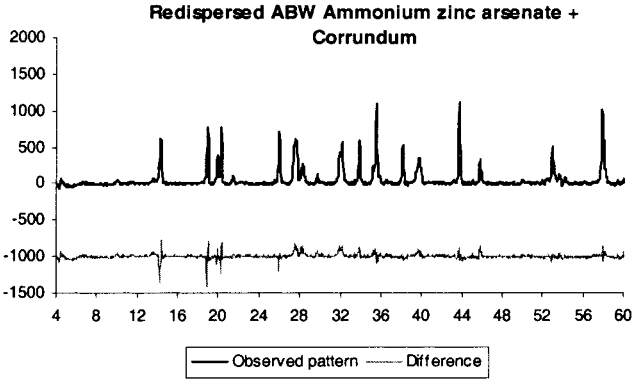

Figure 2. QXRD trace of ABW-type ammonium zinc arsenate mixed with 50% corundum with difference plot.

times and examined to determine the solid stability in the presence of water.

When synthesized by Feng et al.,[10] crystals of this material were found as part of a mixture of different phases; 0.85 g of arsenic acid ($H_5As_3O_{10}$) was mixed with 0.49 g of $Zn(NO_3)_2 \cdot 6H_2O$, 0.93 g of $Ga(NO_3)_3$ hydrate, and 11.15 g of H_2O. The mixture was stirred for several hours after which 4.48 g of ethylene glycol was added, with stirring. A 0.80 g portion of 3,3′-diaminodipropylamine was added slowly until pH reached 8.02. The mixture was stirred for 1 h and transferred into an autoclave at 170 °C for 8 days.

The solid composition was analyzed by dissolving 0.0161 g of the solid in 10% nitric acid. The results of the elemental analysis are given in Table 1. This shows that the analytes make up 91% of the solid sample mass. Analysis of the mother liquor from which the material was precipitated allowed us to calculate the recovery of arsenic from solution. Table 2 gives ideal solid compositions, measured solid compositions, and the percentage of arsenate removed from solution. This indicates that the final solid is slightly zinc rich in comparison to the ideal and that the amorphous material has more zinc than the crystalline phase. This is most likely due to the local precipitation of zinc hydroxide as the ammonia solution is poured into the mixture. This hydroxide would account for a significant proportion of the unaccounted for mass.

QXRD analysis of the white powder obtained after 70 h by our procedure showed that 60.3 wt % of the powder was the ABW-type ammonium zinc arsenate. The rest of the mass was nondiffracting material. Figure 2 shows the QXRD pattern with difference plot for the fitted ABW-type material and corundum.

Table 3. Compositions from QXRD Data before and after Redispersion

	before redispersion		after redispersion	
formula	target	amorphous	target	amorphous
NH_4ZnAsO_4	60 ± 1%	40 ± 1%	30 ± 1%	70 ± 1%

Table 4. Dissolution of Arsenic During Redispersion

	concentration mg L^{-1}	mass of arsenate in 50 mL
redispersion 1	425	21.2
redispersion 2	1226	61.3
redispersion 3	1445	72.2
	total	154.7 mg

After redispersion in water, QXRD was again carried out on the solid sample to asses its stability. The results show that there is a decrease in the crystalline proportion of the solid. There are no crystalline degradation products, just an increase in the amount of amorphous material present. Table 3 shows the solid composition before and after redispersion. Leaching of arsenate into the solution in which the solid was dispersed shows a very high solubility for this material. Arsenate concentrations were in excess of 400 ppm. Two grams of solid were redispersed in 50 mL of water so the proportion of arsenic released over the three redispersions can be calculated. These results are shown in Table 4. This loss suggests dissolution of 20% of the crystalline arsenate content. Very low corresponding zinc concentrations lead us to believe that the zinc portion in the crystalline material is becoming part of the amorphous component of the sample. With this taken into account, these arsenic concentrations are not high enough to account for the release of all the arsenate in the missing crystalline phase suggesting that a secondary noncrystalline phase is forming.

These results show that for the immobilization of arsenate this material is too unstable. Although the zeolite analogue reported in this communication is not a practical route for immobilization and storage of arsenic waste in an aqueous environment, it is important for new zeolite analogues to be tested in this way. With a large number of different zeolite analogues being produced, the potential of this method is wide ranging. The syntheses of zeolite analogues containing many different waste materials are possible.

The stability of the zinc ammonium arsenate phase described here rules out its use in aqueous environments. We have demonstrated that this zeolite analogue is formed under relatively mild conditions and is produced as the only crystalline phase present. It is possible to further increase the yield of crystalline product by slow release of zinc[11] and by using a more arsenic rich environment during the synthesis.

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(10) Feng, P. Private communication, 2001.

(11) Harrison, W. T. A.; Phillips, M. L. F.; Bu, X. *Microporous Mesoporous Mater.* **2000**, *39*, 359−365.