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LETTERS TO THE EDITOR

Syntheses and Characterization of Two Novel Inclusion Compounds: $AlAsO_4 \cdot 0.2(CH_3)_4NOH \cdot 0.3H_2O$ and $GaAsO_4 \cdot 0.2(CH_3)_4NOH \cdot 0.1H_2O$

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Two novel inclusion compounds similar to $AlPO_4^{n-}$ or $GaPO_4^{n-}$ were synthesized hydrothermally and characterized with X-ray powder diffraction, IR spectra, and thermal analyses. The chemical compositions were $AlAsO_4 \cdot 0.2(CH_3)_4NOH \cdot 0.3H_2O$ and $GaAsO_4 \cdot 0.2(CH_3)_4NOH \cdot 0.1H_2O$, respectively. © 1989 Academic Press, Inc.

Introduction

As molecular sieves, organic-amine-occluding $AlPO_4^{n-}$ compounds (*1*) with open frameworks have been investigated widely. Recently, a new family of $GaPO_4^{n-}$ (*2–4*) similar to $AlPO_4^{n-}$ has proved very interesting. It is of considerable significance to clarify whether $AlAsO_4^{n-}$ or $GaAsO_4^{n-}$ inclusion compounds with open frameworks can be prepared since Al and Ga belong to Group IIIA and P and As belong to Group VA in the periodic table. Earlier, we reported a novel aluminoarsenate denoted $AlAsO_4^{1-}$) occluding ethanolamine (*5*). In this letter, we describe the formation and characterization of two novel compounds (denoted $AlAsO_4^{2-}$ and $GaAsO_4^{1-}$ occluding tetramethylammonium hydroxide (TMAOH). $GaAsO_4^{1-}$ is the first organic-amine-occluding galloarsenate reported so far.

Experimental

Preparation of $AlAsO_4^{2-}$. Pyroarsenic acid, aluminum isopropylate, tetramethylammonium hydroxide, and water were mixed in the molar ratio 1.2 TMAOH : Al_2O_3 : 1.2 As_2O_5 : 40 H_2O. The mixture was stirred until homogeneous, sealed in a Teflon-lined autoclave, and heated at 200°C for 5 days. The crystalline product was separated from amorphous materials by an ultrasonic wave, washed with water, and dried at 100°C in air.

Preparation of $GaAsO_4^{1-}$. Metallic gallium was dissolved in nitric acid, precipitated as $Ga(OH)_3$ with $NH_3 \cdot H_2O$, filtered, washed with water, and dried in air. $Ga(OH)_3$ as prepared above, TMAOH, pyroarsenic acid, and water were mixed in the molar ratio 1.2 TMAOH : Ga_2O_3 : As_2O_5 : 36.0 H_2O. The subsequent procedure was the same as that described for $AlAsO_4^{2-}$ except that the reaction temperature was 180°C.

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Elemental analyses were performed on a P-240C element analyser, X-ray powder diffraction on a Rigaku 3DX diffractometer, IR spectra on a Nic-Nicolet 5DX spectrometer, and thermal analyses on a Rigaku thermobalance.

Results and Discussion

Under an optical microscope both $AlAsO_4^{2-}$ and $GaAsO_4^{1-}$ appear to be pure phases. The powder diffraction patterns (Fig. 1) reveal that they are new compounds with novel structures. The mole ratios of Al/As in $AlAsO_4^{2-}$ and Ga/As in $GaAsO_4^{1-}$ were measured by chemical analyses to be unity. Elemental analyses indicated that in $AlAsO_4^{2-}$, $C = 5.36\%$, $H = 1.79\%$, $N = 1.79\%$, and in $GaAsO_4^{1-}$, $C = 3.83\%$, $H = 1.08\%$, $N = 1.51\%$. The empirical formulae of $AlAsO_4^{2-}$ and $GaAsO_4^{1-}$ derived from these analyses were $AlAsO_4 \cdot 0.2(CH_3)_4NOH \cdot 0.3H_2O$ and $GaAsO_4 \cdot 0.2(CH_3)_4NOH \cdot 0.1H_2O$, respectively. For synthesis of $AlAsO_4^{2-}$, the favorable molar ratios were $As_2O_5/Al_2O_3 = 1.0–1.3$, $TMAOH/Al_2O_3 = 1.0–1.5$, $H_2O/Al_2O_3 = 35–50$. As_2O_5/Al_2O_3 larger than 1.5 readily resulted in dense phases of $AlAsO_4$. The ranges suitable for synthesis of $GaAsO_4^{1-}$ were $As_2O_5/Ga_2O_3 = 1.0–1.2$, $TMAOH/Ga_2O_3 = 1.2–1.6$, and $H_2O/Ga_2O_3 = 30–45$. Reaction temperatures higher than 200°C led to formation of α-quartz-type $GaAsO_4$. We have also tried, but failed, to synthesize $AlAsO_4$ and $GaAsO_4$ inclusion compounds using other larger quaternary ammonium hydroxides such as tetraethylammonium, tetrapropylammonium, and tetrabutylammonium hydroxides.

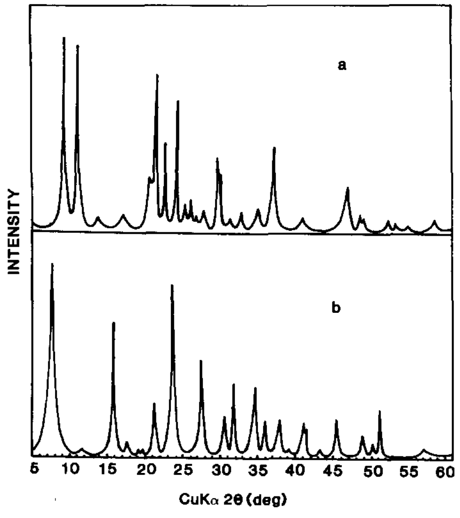

FIG. 1. X-ray powder diffraction patterns of $AlAsO_4^{2-}$ (a) and $GaAsO_4^{1-}$ (b).

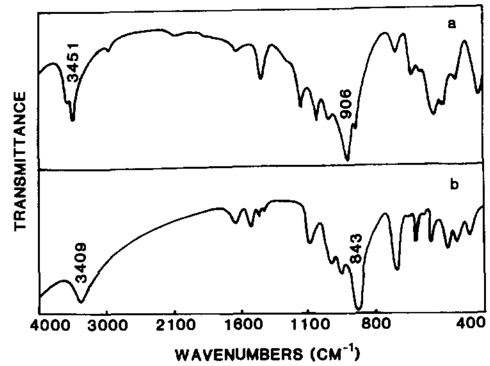

FIG. 2. IR spectra of $AlAsO_4^{2-}$ (a) and $GaAsO_4^{1-}$ (b).

The IR spectrum of $AlAsO_4^{2-}$ (Fig. 2) shows a main absorption at 906 cm^{-1} corresponding to asymmetric stretching vibrations of TO_n (T = Al or As, n = 4–6) coordination polyhedra (*6*). The wavenumber is 45 cm^{-1} smaller than that of α-quartz-type $AlAsO_4$. The absorption at 3451 cm^{-1} is assigned to the vibrations of O–H bonds. The DTA curve of $AlAsO_4^{2-}$ (Fig. 3) has small endothermic peaks between 400 and 460°C and pronounced exothermic peaks between 600 and 650°C. In these two temperature ranges the TGA curve shows corresponding weight losses. On the basis of other work (*7*), the low-temperature thermal effect is assigned to the pyrolysis of occluded TMAOH and the high-temperature one to its oxidative decomposition.

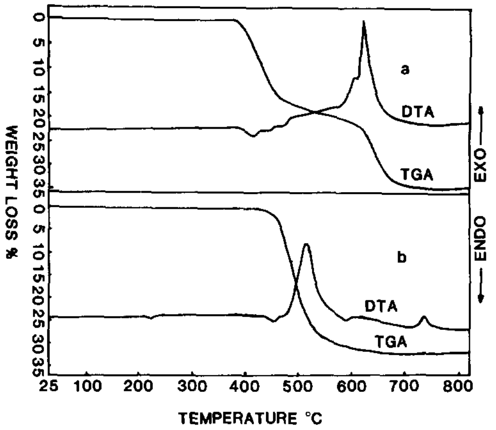

FIG. 3. TGA-DTA in air of AlAsO$_4^{2-}$ (a) and GaAsO$_4^{1-}$ (b).

The TO_n (T = Ga or As, n = 4–6) IR absorption of GaAsO$_4^{-1}$ (Fig. 2) is at 843 cm^{-1}, 42 cm^{-1} smaller than that of α-quartz-type GaAsO$_4$. The O–H absorption is around 3409 cm^{-1}. Differing from that of AlAsO$_4^{-2}$, the TGA curve of GaAsO$_4^{-1}$ (Fig. 3) shows only one evident weight loss from 420 to 600°C. However, its DTA curve shows a small endothermic effect near 450°C in addition to a pronounced exothermic effect around 510°C. This phenomenon suggests that the oxidative decomposition of TMAOH begins before the end of its pyrolysis.

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