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BRIEF COMMUNICATION

Low-Temperature Synthesis of ZrW_2O_8 and Mo-Substituted ZrW_2O_8

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A low-temperature synthesis of ZrW_2O_8 and HfW_2O_8 has been developed which yields the normal crystalline forms of these compounds at a temperature where they are presumably not thermodynamically stable. This same synthesis approach has allowed for the first time the synthesis of cubic $ZrW_{2-x}Mo_xO_8$ phases up to $x = 1.5$. © 1998 Academic Press

INTRODUCTION

Cubic ZrW_2O_8 has been shown to display unique thermal expansion characteristics (1, 2) suggesting several possible applications. Over a temperature range from 10 to 1050 K, it displays strong negative thermal expansion. Although it undergoes a phase transition at near 430 K, it is cubic above and below this transition, thus maintaining isotropic thermal expansion throughout this entire temperature range. Because its potential uses include electronics, optics, fuel cells, oxygen sensors, thermostats, and dental filling products, there is much incentive to produce it easily and efficiently.

According to the phase diagram for the ZrO_2–WO_3 system (3), ZrW_2O_8 is thermodynamically stable only between 1380 and 1530 K. Therefore, successful syntheses of ZrW_2O_8 were generally restricted to this temperature range. There was, however, an indication that ZrW_2O_8 could be prepared at temperatures below 1380 K where it presumably is not thermodynamically stable (1, 4).

For $ZrMo_2O_8$, only a hexagonal layered structure is known (5). Our previous attempts to prepare Mo-substituted ZrW_2O_8 by our standard high-temperature synthesis route were unsuccessful. We have now perfected a low-temperature synthesis of ZrW_2O_8 and find that Mo can be substituted into ZrW_2O_8 under the conditions of this synthesis. This low-temperature route is based on modifications of a synthesis reported for hydrated zirconium molybdate (6). One difference is that our source of tungsten is ammonium tungstate instead of sodium tungstate.

EXPERIMENTAL

Reactants to prepare ZrW_2O_8 were ammonium metatungstate and zirconium oxychloride. Although the formulae of these compounds are generally given as $(NH_4)_6H_2W_{12}O_{40}$ and $ZrOCl_2 \cdot 8H_2O$, neither formula is reliable. Therefore, weighed amounts of each were heated to 1173 K for conversion to WO_3 and ZrO_2. The observed weight losses were then used to calculate amounts of ammonium metatungstate and zirconium oxychloride to be used to prepare aqueous solutions containing known amounts of W or Zr. These solutions were 1 M with respect to W and 0.5 M with respect to Zr. Fifty ml of each of these solutions was added to 25 ml of water simultaneously by dropwise addition with continuous stirring. A white precipitate formed immediately. This mixture was stirred continuously for 10 h. Then 125 ml of 6 M HCl was added, and the mixture was refluxed for 48 h. After this mixture had cooled to room temperature, most of the liquid was eliminated by decanting. The remaining liquid was removed by filtration. The product was then aged at room temperature for 7 days before calcination. X-ray diffraction showed that the precipitate produced was amorphous before and after the 7-day aging. This aged precipitate was then heated for 10 h in air at various

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temperatures from 273 to 973 K. HfW_2O_8 was synthesized using a method identical to that for ZrW_2O_8, except that hafnium oxychloride was used instead of zirconium oxychloride.

Many attempts were made to simplify and shorten this synthesis procedure. Shortening the reflux time to 24 h or shortening the aging time to 5 days, as well as elimination of the HCl addition, led to final products that were not single phase regardless of calcination temperature. One modification was, however, found to shorten the synthesis time. The initial product formed on mixing the tungsten and zirconium solutions was placed in a Parr bomb and heated at 473 K for 4 h. The reflux and aging steps were eliminated, and a single phase crystalline product was produced after heating the filtered product at 873 K for 10 h.

Phases of the type $ZrW_{2-x}Mo_xO_8$ were prepared in an analogous manner substituting some of the ammonium tungstate solution with an ammonium molybdate solution. Appropriate amounts of the tungstate and molybdate solutions were mixed before the dropwise addition to water. The X-ray patterns of the Mo containing products all showed a crystalline pattern of $Zr(Mo,W)_2O_7(OH)_2(H_2O)_2$ before calcination (6).

X-ray diffraction patterns were obtained with a Siemens D5000 diffractometer using Cu$K\alpha$ radiation. A Si internal standard was used for those samples where cell edges were refined by least squares. Particle size was determined by the sedimentation technique using a Horiba Model CAPA-700 particle size analyzer. Chemical analysis by ICP confirmed the absence of significant quantities of Zr, W, or Mo in decanted liquid or filtrate and also confirmed the intended Mo-to-W ratios in the solid solutions.

RESULTS AND DISCUSSION

In the zirconium tungstate system, calcination for 10 h gave X-ray amorphous products when the calcination temperature was 823 K or lower. Calcination at 873 K gave a crystalline product showing X-ray diffraction peaks of only cubic ZrW_2O_8. When calcined at 973 K, the X-ray diffraction patterns of the products showed peaks of WO_3 and ZrO_2 in addition to those of ZrW_2O_8. In the case of the synthesis of HfW_2O_8, X-ray patterns of products calcined at both 873 and 973 K showed only the peaks of the cubic ZrW_2O_8 type structure. This suggests that HfW_2O_8 is somewhat more thermally stable than ZrW_2O_8.

Samples in the $ZrW_{2-x}Mo_xO_8$ system were prepared for x values of 0.4, 0.6, 0.7, 1.0, 1.2, 1.4, and 1.5. For the $x = 0.4$ and 0.6 samples, calcination at 873 K gave products with X-ray diffraction patterns showing only peaks of an α-ZrW_2O_8 type pattern (space group $P2_13$). As with ZrW_2O_8, calcination at 973 K resulted in the presence of extra phases. When x was in the range 0.7–1.5, distinctly different results were obtained. Calcinations at temperatures as low as 723 K gave products with X-ray diffraction patterns showing only peaks of cubic ZrW_2O_8. However, the pattern (Fig. 1) was that of β-ZrW_2O_8 (space group $Pa\bar{3}$), not α-ZrW_2O_8 (space group $P2_13$). This is easily determined because peaks due to the 530, 510, and 310 reflections are allowed for space group $P2_13$ but not for $Pa\bar{3}$. The cubic cell edge was also distinctly smaller. This cell edge was 9.16 to 9.15 Å for the $x = 0.0$ to 0.6 range but was 9.05 to 9.03 Å for the $x = 0.7$ to 1.5 range. This cell edge decrease on substitution of Mo may be partly due to the smaller size of Mo^{6+} relative to W^{6+}. However, a more significant factor appears

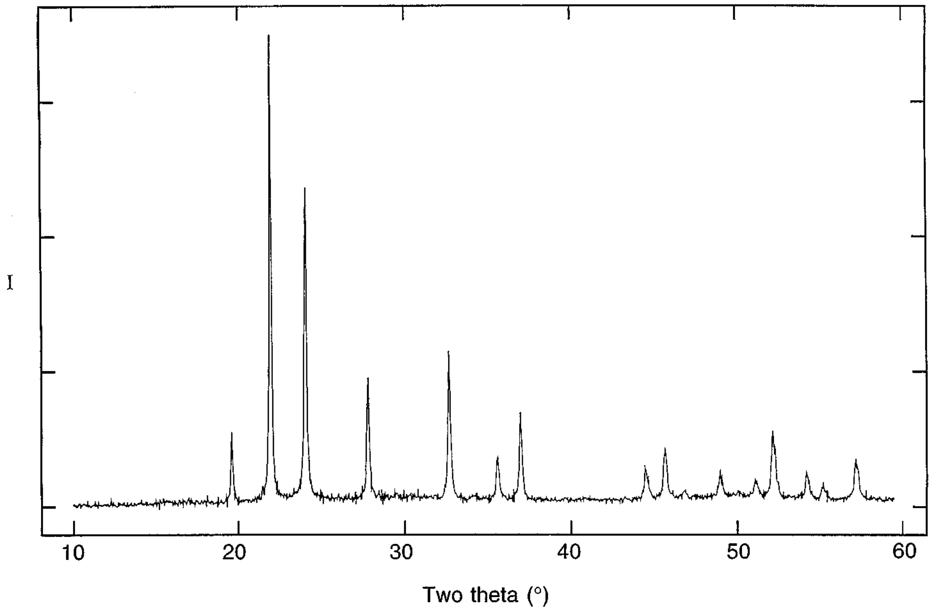

FIG. 1. X-ray diffraction pattern for $ZrW_{0.8}Mo_{1.2}O_8$.

to be related to the α-to-β phase transition which causes considerable shrinkage in ZrW_2O_8 (1, 2).

The effect of substitution of Mo for W is apparently to lower the α-to-β phase transition. To further confirm this conclusion, a sample of $ZrW_{1.6}Mo_{0.4}O_8$ was examined by high-temperature X-ray diffraction. The α-to-β transition was found to commence at about 373 K with decreasing intensity of peaks such as that due to the 310 reflection. The transition appeared complete by 393 K. For ZrW_2O_8, this transition occurs at about 423 K. On the basis of our X-ray diffraction data above room temperature, the thermal expansion coefficient for $ZrW_{1.6}Mo_{0.4}O_8$ was found to be $-11.8 \times 10^{-6}\ K^{-1}$ between room temperature and 273 K and $-7.4 \times 10^{-6}\ K^{-1}$ from 383 to 473 K. The higher value is somewhat more negative than for ZrW_2O_8, which has a thermal expansion coefficient of $-8.7 \times 10^{-6}\ K^{-1}$ (1, 2).

As might be expected, this low-temperature synthesis method yields a product with decreased particle size. We find an average particle size very close to 1 μm, whereas the same materials prepared in the high-temperature, thermodynamic equilibrium range have an average particle size just over 10 μm.

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