Autohydration of Nanosized Cubic Zirconium Tungstate

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Negative thermal expansion (NTE) materials have attracted widespread interest due to their potential applications as fillers in controlled thermal expansion composites and coatings.1-11 High quality composites require small, homogeneous particles that are stable in their environment. To date, cubic zirconium tungstate (ZrW2O8) has been considered one of the most promising NTE materials. Here we report that nanosized ZrW2O8 absorbs atmospheric moisture under ambient conditions, resulting in formation of a hydrated material and loss of NTE character.

Micron sized cubic ZrW2O8 has been incorporated into ceramic composites for optical fiber coatings and grating supports to minimize spectral shifts caused by thermal expansion.12,13 This NTE material possesses a number of desirable properties, including a wide temperature range of isotropic expansion with α values of −8.8 × 10−6 K−1 from 0.3 to 430 K and −4.9 × 10−6 K−1 from 430 to 1050 K.1,2 ZrW2O8 is part of the AM2O8 (A = Zr, Hf; M = Mo, W) family of materials,2,14,15 in which the oxygens in the linear M−O−M bonds undergo transverse vibrations, causing a decrease in unit cell volume.16,17

The preparation of high quality composites requires a homogeneous distribution of filler particles, making small particles with uniform particle morphology favorable for such applications. The first reported synthesis of ZrW2O8 used sintering of WO3 and ZrO2 at 1473 K for 15 min, followed by rapid quenching in water.18 The quenching step is necessary to avoid decomposition into binary oxides, as ZrW2O8 is only thermodynamically stable between 1380 and 1530 K and metastable below 1050 K.1 It was later shown that ZrW2O8 is accessible at low temperatures by dehydrolysis of a precursor, ZrW2O7(OH)2·2H2O, followed by topotactic recrystallization. This hydroxide hydrate was originally obtained by reflux for 24 h.19 The synthesis can also be carried out in other acids, however, the crystallization kinetics depend strongly on hydronium and chloride ion concentration.21 Changes in solution composition can be used to influence the final particle size through controlled variation of nucleation and growth rates. Small particles could be obtained by substituting HClO4 for HCl and adding NaCl as a chloride source,22 but the particles were highly agglomerated. It was necessary to overcome this agglomeration problem, as it interferes with the preparation of high quality homogeneous composites. It was found that reactions in alcohol/HCl mixtures significantly reduced agglomeration while maintaining small particle sizes. Optimized particles were obtained from 2.7 M 1-butanol/7 M HCl mixtures, resulting in rods that were 15−50 nm wide by 200−500 nm long, and formed agglomerates of 50−100 nm by 300−600 nm.

In an attempt to further reduce agglomeration additional alcohols were investigated. Small particles with reasonable agglomeration were obtained for alcohol chain lengths of 3−5 carbons. To our surprise, nanoparticles of cubic ZrW2O8 prepared in these acid/alcohol mixtures were significantly less stable than those prepared in the absence of alcohols. In this paper, we report that nanosized ZrW2O8 particles show autohydration under ambient conditions.
with a lattice constant of 9.14 Å was observed (Figure 1a). The width of the peaks corresponded to an average crystallite size of 25–30 nm.

Hydrated cubic ZrW2O8·xH2O was first prepared by Duan et al. by hydrothermal treatment.23 Full hydration of zirconium tungstate results in a linear decrease in lattice constant from 9.14 Å in ZrW2O8 to 8.84 Å in ZrW2O8·1H2O. Hydration results in an increase in the tungsten coordination number from 4 to 5 and a change in space group from P213 to Pn3. This higher coordination number leads to rotations of the WO6 and ZrO6 units, causing further contraction of the unit cell. The extent of autohydration of nano-ZrW2O8 can be estimated using the lattice constant relationship found by Duan et al. The lattice constant of a sample exposed to the atmosphere for 1 year, 8.91 Å, should correspond to a hydration level of ZrW2O8·0.75H2O. TG-DTA analysis showed a steep mass loss between 100 and 140 °C and a non-negligible mass loss between room temperature and 100 °C. The total mass loss of 2.20% corresponds to a composition of ZrW2O8·0.73H2O, which is in good agreement with the water content suggested by the lattice constant.

The particles of corresponding hydroxide hydrate and cubic phases were imaged in an electron microscope. It was previously reported that the particle size and shape of the precursor are preserved during the conversion to cubic ZrW2O8. Surprisingly, significant changes in particle morphology were observed for some of the heat treated samples in this study (Figure 2). The individual rods of the hydroxide hydrate appear to fuse together, forming larger entities without distinct particle boundaries in the cubic phase. This suggests that the particles of the precursor contain a significant number of defects, which present high energy sites that facilitate the fusion process. These defects may also play an important role in the observed autohydration behavior. Micron sized ZrW2O8 particles with low defect concentrations do not react with atmospheric moisture, while autohydration has been reported for micrometer sized mixed cation ZrW2−xMoO6 compositions, which are likely to contain more defects than pure ZrW2O8 or ZrMoO6. The kinetics of autohydration are related to the surface area of the particles. Micron sized ZrW2O8 as well as nanoparticles prepared in the absence and presence of alcohols showed BET surface areas of 4.75, 6.46, and 18.99 m2/g, respectively. The fact that no hydration was observed in the micrometer sized particles, while slow autohydration occurred in the nanoparticles prepared without alcohols, suggests that defects determine whether autohydration occurs while the surface areas dictate the kinetics. Samples prepared in the presence of alcohols showed considerable hydration after a period of a few weeks, while samples with similar particle sizes prepared in the absence of alcohols only reached a comparable degree of hydration after several months.

The autohydration of nanosized cubic ZrW2O8 imposes serious limitations on the potential use of this compound as a filler in controlled thermal expansion composites. Further studies are underway to gain a detailed understanding of the effect of defects on this behavior and to optimize processing conditions to minimize or prevent autohydration.

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