Communication

o-ZrW$_{1.6}$Mo$_{0.4}$O$_8$ A Novel Orthorhombic Intermediate Phase Formed During the Synthesis of the Negative Thermal Expansion Cubic ZrW$_{1.6}$Mo$_{0.4}$O$_8$ Material by the Precursor Dehydration Route

ZHAO Xin-Hua[* a]   HUANG Ling[a]   LIU Peng-Hui[a]   MA Hui[b]

[a] *Department of Chemistry Beijing Normal University Beijing 100875 China*
[b] *Analyzing and Testing Center Beijing Normal University Beijing 100875 China*

The mechanism of the precursor dehydration route was revealed for the synthesis of NTE c-ZrW$_{1.6}$Mo$_{0.4}$O$_8$. The hydrate precursor was dehydrated at 473 K and transformed to a NTE cubic compound above 800 K. A novel intermediate phase o-ZrW$_{1.6}$Mo$_{0.4}$O$_8$ occurs between the temperature range of 573—800 K. The XRD pattern of novel intermediate was refined with the structural model of LT-ZrMo$_2$O$_8$ by using Rietveld method. The residuals are R_{wp} = 7.80% and R_p = 5.79%. The space group is $Pmn2_1$ and the lattice parameters are a = 0.5917 4 nm b = 0.7273 4 nm c = 0.9148 6 nm and Z = 2.

Keywords   precursor dehydration route negative thermal expansion NTE materials ZrW$_{2-x}$Mo$_x$O$_8$

Negative thermal expansion NTE materials have received considerable attention in recent years [1-6] especially the cubic phases ZrW$_2$O$_8$ c-ZrW$_2$O$_8$ and ZrMo$_2$O$_8$ c-ZrMo$_2$O$_8$. These particular materials undergo isotropic NTE behavior over a wide temperature range 0.3 K to 1050 K and 1378 K to 1530 K for ZrW$_2$O$_8$[1 2] and 0 to 660 K for ZrMo$_2$O$_8$ respectively.[7] c-ZrMo$_2$O$_8$ possesses beneficial intrinsic properties[7-9] over ZrW$_2$O$_8$ such as lower density and lower phase transition temperature but its temperature range for NTE is narrower than that of ZrW$_2$O$_8$. For this reason solid solutions between ZrMo$_2$O$_8$ and ZrW$_2$O$_8$ system Zr W Mo $_2$O$_8$ should compensate the disadvantages of the two end members.[8] Furthermore the stability and the NTE critical temperature of ZrWMoO$_8$ increase up to 1473 K.[10]

Several preparation methods are used to synthesize c-ZrW$_2$O$_8$ c-ZrMo$_2$O$_8$ and their solid solutions.[10-12] The strict preparation conditions[13] make the pure phase c-ZrMo$_2$O$_8$ non-facile. The best synthetic route to obtain c-ZrMo$_2$O$_8$[7 13 14] and the solid solutions Zr W Mo $_2$O$_8$[8 11 15] involve the sol-gel route to form precursors Zr Mo W $_2$O$_7$ OH $_2$ 2H$_2$O then the precursor is dehydrated at medium temperatures. Mo-substituted zirconium tungstates Zr W Mo $_2$O$_7$ OH $_2$ 2H$_2$O have been prepared as crystalline samples in an analogous manner to that of basic zirconium molybdate.[16] The particular steps of the sol-gel synthesis and heat-treatment are very important to obtain pure phase products as discussed by Closmann[15] and Lind.[13] Many attempts to simplify and shorten the synthesis procedure for zirconium tungstate failed resulting in the formation of multi-phase products. In our investigations we found that the heat-treatment is not a simple procedure for obtaining pure phase NTE materials. A novel orthorhombic intermediate formed during the dehydration procedure.

Prior to the synthesis of the precursor ZrW$_{1.6}$Mo$_{0.4}$O$_7$ OH $_2$ H$_2$O 2 H$_2$O content in the starting reagents Na$_2$WO$_4$ 2H$_2$O A.R. Na$_2$MoO$_4$ 2H$_2$O A.R. and ZrOCl$_2$ 8H$_2$O A.R.   was determined accurately by using gravimetric methods in order to prepare the starting solutions with precise concentrations which are formed 0.5 mol L^{-1} for Zr^{4+} and 1.0 mol L^{-1} for W^{6+} + Mo^{6+} respectively. The synthetic procedure followed the reported method.[16] The precipitated was dried at 378 K to form the precursor ZrW$_{1.6}$Mo$_{0.4}$O$_7$ OH $_2$ H$_2$O 2. The absence of significant quantities of Zr W and Mo in the mother liquor determined by using the ICP-AES JY VLTIMA France   confirmed that the ratios of the metals in the precursor as well as in the title compound were Zr∶W∶Mo = 1∶1.6∶0.4.

The powder X-ray diffraction XRD of the hydrated compound ZrW$_{1.6}$Mo$_{0.4}$O$_7$ OH $_2$ H$_2$O 2 was performed on a Rigaku Dmax-3A diffractometer Cu Kα radiation and Ni filter . The structure of the hydrated precursor was refined using powder XRD data collected in the range of 10°—120° 2θ by the Rietveld method as embodied in the GSAS program.[17] ZrMo$_2$O$_7$ OH $_2$ H$_2$O 2[16] was used as the starting structural model for ZrW$_{1.6}$Mo$_{0.4}$O$_7$ OH $_2$ H$_2$O 2 with the appropriate proportion of the Mo atoms replaced by W atoms. The final refinement plot is displayed in Fig. 1 and the refinement results are R_p =

7.12% R_{wp} = 8.79% a = 1.14245 5 nm c = 1.24619 7 nm. The occupancy of W/Mo is 0.83 2 / 0.17 2 . The coordinate of Mo/W site S. G. $I4_1cd$ 16b x y z was refined to be 0.0167 2 0.1638 2 and 0.2223 3 and the coordinate of Zr site 8a 0 0 z was refined to be 0 0 − 0.014 2 .
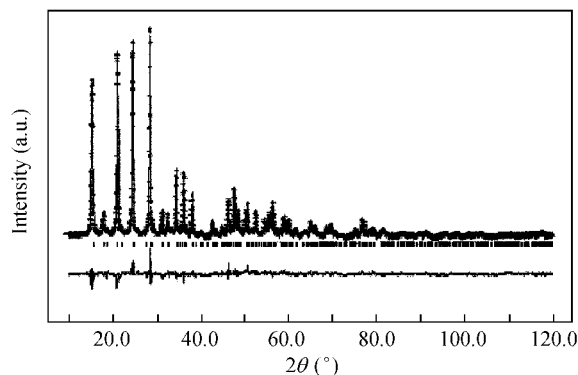

Fig. 1 XRD patterns of the observed + and calculated − plots and their difference lower for $ZrW_{1.6}Mo_{0.4}O_7$ OH $_2$ H_2O $_2$. Bragg reflection positions are indicated by tick marks.

The FT-IR spectrum was taken for hydrated precursor using the Nicolet Avatar 360 instrument with the sample incorporated in a KBr wafer. The IR pattern of $ZrW_{1.6}$-$Mo_{0.4}O_7$ OH $_2$ H_2O $_2$ is similar to that of $ZrMo_2O_7$ OH $_2$ H_2O $_2$ [16] in which the 3239 cm^{-1} and 1654 cm^{-1} bands analogy with 3320 cm^{-1} and 1665 cm^{-1} [16] were assigned to the vibrations of H_2O and the 3333 cm^{-1} band analogy with 3340 cm^{-1} [16] was assigned to the vibrations of the OH group.

The heat treatment program to process the hydrated precursor was determined by thermogravimetric analysis using a TGA-DSC Netch Sta 409C heating the sample from 303 to 973 K with a rate of 20 K/min and an Ar carrier gas. The TGA-DSC curves displayed in Fig. 2 indicate that at 476 K a weight loss of 8.92% occurs that is attributable to the weight loss of three H_2O molecules from the precursor calcd 8.92% according to the reaction $ZrW_{1.6}Mo_{0.4}O_7$ OH $_2$ H_2O $_2$ = $ZrW_{1.6}Mo_{0.4}O_8$ + 3H_2O g .

The DSC curve in Fig. 2 indicates that there is an intermediate phase o-$ZrW_{1.6}Mo_{0.4}O_8$ which exists between 573 K and 800 K during the conversion of the hydrated precursor to the final cubic c-$ZrW_{1.6}Mo_{0.4}O_8$. The only exothermic peak in the DSC curve corresponds to the phase transition of the intermediate phase of o-$ZrW_{1.6}Mo_{0.4}O_8$ to cubic phase which was reported in reference. [11]

The intermediate phase o-$ZrW_{1.6}Mo_{0.4}O_8$ was obtained upon annealing the hydrated compound at *ca*. 725 K in a muffle furnace for 24 h and then quenching the sample in air. The sample was kept in a desiccator to prevent absorption of moisture from the atmosphere. The XRD data over the range of 3°—90° 2θ for the novel intermediate phase o-$ZrW_{1.6}Mo_{0.4}O_8$ were collected on the

diffractometer MAC MXP21VAHF M21 Japan equipped with high temperature furnace. Prior to data collection the sample was annealed in nitrogen atmosphere at 473 K for 1 h and then cooled to room temperature in N_2 atmosphere. The positions of the strong diffraction peaks were searched automatically from 3° to 70° 2θ using the PowderX software.[18] The data were corrected by line pairs method[19] and the pattern was indexed successfully using the TREOR method[20] contained within the PowderX program. The best solution gives an orthorhombic cell with lattice parameters a = 0.9093 nm b = 0.7219 nm c = 0.5587 nm V = 0.3667 nm^3 M 20 = 13 F 20 = 15 . The density for this phase measured at 308 K by using Pyconometric method is 4.776 5 g/cm^3 and the content number Z in a unit cell was deduced to be 2.
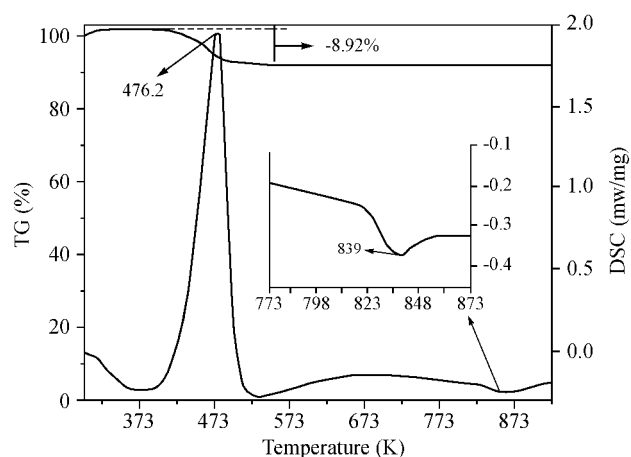

Fig. 2 TG-DSC curve of heating $ZrW_{1.6}Mo_{0.4}O_7$ OH $_2$ H_2O $_2$ to c-$ZrW_{1.6}Mo_{0.4}O_8$.

Recently Evans and his coworkers[21] reported a novel type of structure of LT-$ZrMo_2O_8$. Both o-$ZrW_{1.6}Mo_{0.4}O_8$ and LT-$ZrMo_2O_8$ have the similar cell volume as well as the formula and the same Z. Therefore we characterized the crystal structure of o-$ZrW_{1.6}Mo_{0.4}O_8$ by using LT-Zr-Mo_2O_8 as the structural model. The powder XRD pattern was fitted using the Rietveld method. The starting model which has the space group of $Pmn2_1$ was modified by replacing Mo atoms with W atoms randomly. The occupancy of Mo crystal sites was adjusted according to the composition of the compound. For final cycles of the refinement eight background terms five pseudo-Voigt peak shape parameters three microstrain broadening factors three lattice parameters one scale factor and Zero point were refined. Nine structural coordinates of atoms were refined in which the coordinates of W and Mo in the same crystal site and all O atoms were constrained respectively. A final refinement factors of R_{wp} = 7.80% and R_p = 5.79% were obtained. The refinement results of structural parameters were a = 0.5917 4 nm b = 0.7273 4 nm c = 0.9148 6 nm V = 0.3936 7 nm^3 and d_x = 4.655 g/cm^3. The fitted pattern from 3° to 90° 2θ was displayed in Fig. 3.

We note that by application of the microstrain broadening correction terms the peak shapes were matched better than before between observed and calculated patterns. This is the evidence that the microstrain occurred within the intermediate phase during the phase transition.
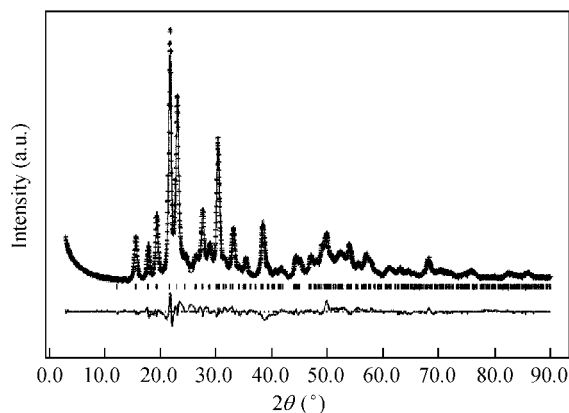

Fig. 3 Final refinement result of XRD pattern of the o-ZrW$_{1.6}$-Mo$_{0.4}$O$_8$ refined by using LT-ZrMo$_2$O$_8$ as the structural model.

We have found that the preparation of the cubic NTE material ZrW$_{1.6}$Mo$_{0.4}$O$_8$ by this method involves the formation of a novel orthorhombic intermediate phase. This is different from the pure phase c-ZrW$_2$O$_8$ by the same route. In that route the hydrated precursor ZrW$_2$O$_7$(OH)$_2$·(H$_2$O)$_2$ transforms to the cubic phase via the formation of an amorphous phase.[15] This method is suitable for preparing the NTE c-ZrW$_{1.6}$Mo$_{0.4}$O$_8$ as well as c-ZrW$_{2-x}$Mo$_x$O$_8$ and c-ZrMo$_2$O$_8$ materials. The novel isomorph is different from γ-ZrW$_2$O$_8$[3] model obviously whose unit cell are a = 0.9067 nm, b = 2.07035 nm, c = 0.8921 nm. Further investigations showed that the orthorhombic ZrW$_{1.6}$Mo$_{0.4}$O$_8$ intermediate phase is metastable phase as it absorbs moisture from the air to form another orthorhombic phase ZrW$_{1.6}$Mo$_{0.4}$O$_8$·H$_2$O which was denoted as δ'-ZrW$_{1.6}$Mo$_{0.4}$O$_8$ phase.[22]

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