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Preparation of $\text{Zr}(\text{Mo},\text{W})_2\text{O}_8$ with a larger negative thermal expansion by controlling the thermal decomposition of $\text{Zr}(\text{Mo},\text{W})_2(\text{OH},\text{Cl})_2 \cdot 2\text{H}_2\text{O}$

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Solid solutions of $\text{Zr}(\text{Mo},\text{W})_2\text{O}_7(\text{OH},\text{Cl})_2 \cdot 2\text{H}_2\text{O}$ with a preset ratio of components were prepared by a hydrothermal method. The chemical composition of the solutions was determined by energy dispersive X-ray spectroscopy (EDX). For all the samples of $\text{ZrMo}_x\text{W}_{2-x}\text{O}_7(\text{OH},\text{Cl})_2 \cdot 2\text{H}_2\text{O}$ ($x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8$, and 2.0), TGA and *in situ* powder X-ray diffraction (PXRD) studies (300–1100 K) were conducted. For each case, the boundaries of the transformations were determined: $\text{Zr}(\text{Mo},\text{W})_2\text{O}_7(\text{OH},\text{Cl})_2 \cdot 2\text{H}_2\text{O} \rightarrow$ orthorhombic- $\text{ZrMo}_x\text{W}_{2-x}\text{O}_8$ (425–525 K), orthorhombic- $\text{ZrMo}_x\text{W}_{2-x}\text{O}_8 \rightarrow$ cubic- $\text{ZrMo}_x\text{W}_{2-x}\text{O}_8$ (700–850 K), cubic- $\text{ZrMo}_x\text{W}_{2-x}\text{O}_8 \rightarrow$ trigonal- $\text{ZrMo}_x\text{W}_{2-x}\text{O}_8$ (800–1050 K for $x > 1$) and cubic- $\text{ZrMo}_x\text{W}_{2-x}\text{O}_8 \rightarrow$ oxides (1000–1075 K for $x \leq 1$). The cell parameters of the disordered cubic- $\text{ZrMo}_x\text{W}_{2-x}\text{O}_8$ (space group Pa-3) were measured within 300–900 K, and the thermal expansion coefficients were calculated: $-3.5 \cdot 10^{-6} - -4.5 \cdot 10^{-6} \text{ K}^{-1}$. For the ordered $\text{ZrMo}_{1.8}\text{W}_{0.2}\text{O}_8$ (space group P2₁3), a negative thermal expansion (NTE) coefficient $-9.6 \cdot 10^{-6} \text{ K}^{-1}$ (300–400 K) was calculated. Orthorhombic- ZrW_2O_8 is formed upon the decomposition of $\text{ZrW}_2\text{O}_7(\text{OH},\text{Cl})_2 \cdot 2\text{H}_2\text{O}$ within 500–800 K.

Both applied material science and academic research fields are interested in substances with negative thermal expansion (NTE)^{1–4}. Due to its unique behaviour, $\text{ZrMo}_x\text{W}_{2-x}\text{O}_8$ is an advanced filler material used to produce composites with controlled expansion. The main advantage of the family of cubic- $\text{ZrMo}_x\text{W}_{2-x}\text{O}_8$ materials over other materials is their large isotropic NTE over a wide temperature range. The most famous and well-studied ZrW_2O_8 has an NTE coefficient of $-8.8 \cdot 10^{-6} \text{ K}^{-1}$ for oxygen-ordered cubic α - ZrW_2O_8 from 0.3 K to 430 K and $-4.8 \cdot 10^{-6} \text{ K}^{-1}$ for dynamically disordered cubic β - ZrW_2O_8 from 430 K to 1050 K⁵. Cubic γ - ZrMo_2O_8 is isostructural to cubic β - ZrW_2O_8 , and it has an NTE coefficient of $-5.0 \cdot 10^{-6} \text{ K}^{-1}$ from 11 to 573 K, as reported in ref.⁶. Simon Allen and J.S.O. Evans made precise measurements of the NTE coefficient of γ - ZrMo_2O_8 : $-6.9 \cdot 10^{-6} \text{ K}^{-1}$ from 2 to 200 K and $-5.0 \cdot 10^{-6} \text{ K}^{-1}$ from 250 to 502 K⁷.

This material can be obtained by dehydration and topotactic recrystallization from a hydrated precursor, $\text{ZrMo}_x\text{W}_{2-x}(\text{OH},\text{Cl})_2 \cdot 2\text{H}_2\text{O}$ ⁸. According to the thermogravimetric results presented by us in a previous paper⁹, the thermal decomposition of the precursor $\text{ZrW}_2\text{O}_7(\text{OH},\text{Cl})_2 \cdot 2\text{H}_2\text{O}$ starts at 500 K and results in the appearance

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Figure 1. A comparison of the PXRD diffraction pattern (red dots) for $ZrMo_xW_{2-x}O_7(OH,Cl)_2 \cdot 2H_2O$ ($x = 1.8$) with that calculated by the Rietveld refinement model (green solid line). The corresponding crystal structure is shown in the inset (pink octahedra – $\{W(Mo)O_6\}$, brown pentagonal bipyramids – $\{Zr(Cl,O)_7\}$).

of an amorphous intermediate, which crystallizes as cubic β - ZrW_2O_8 above 850 K. The strong exothermic effect at 1100 K is related to the decomposition of cubic β - ZrW_2O_8 into oxides. The transformation of cubic α - ZrW_2O_8 into cubic β - ZrW_2O_8 is not registered by differential thermal analysis (DTA).

The DTA curve for $ZrMo_xW_{2-x}O_7(OH,Cl)_2 \cdot 2H_2O$ showed the expected endothermic peak, corresponding to the weight loss and formation of the orthorhombic phase of β - $ZrMo_2O_8$, while the two exothermic peaks at 700 and 800 K can be assigned to the crystallization of the cubic γ - $ZrMo_2O_8$ and trigonal α - $ZrMo_2O_8$ phases, respectively¹⁰.

The solid solutions of $ZrW_{2-x}Mo_xO_8$ (with different values of “x”) have been prepared by a number of scientific groups^{7,8,11–14}. A significant number of solid solutions of the precursor $ZrMo_xW_{2-x}O_7(OH)_2 \cdot 2H_2O$ was prepared by Ling Huang and co-authors¹². Cubic phases were obtained for $x = 0.2, 0.4, 0.6, 0.7$ and 0.8 , but the NTE coefficients were not measured. Accurate measurement of the NTE coefficient for $ZrMo_xW_{2-x}O_8$ ($x = 1.0$) was reported in work⁶. For the cubic, ordered phase, the NTE was $-9.0 \cdot 10^{-6} \text{ K}^{-1}$ from 2 to 200 K, and $-5.5 \cdot 10^{-6} \text{ K}^{-1}$ from 250 to 502 K for the disordered phase. Solid solutions of $ZrMo_xW_{2-x}O_8$ ($x = 0.4, 0.6, 0.7, 1.0, 1.2, 1.4$ and 1.5) were prepared by C. Closmann⁸. The phase composition was determined for all the samples after heating them to 723, 823, and 923 K and quenching. For one of these solutions ($ZrMo_{0.4}W_{1.6}O_8$), the NTE coefficient was $-11.8 \cdot 10^{-6} \text{ K}^{-1}$ (273–298 K) and $-7.4 \cdot 10^{-6} \text{ K}^{-1}$ (383–473 K). The NTE coefficient $-11.8 \cdot 10^{-6} \text{ K}^{-1}$ is the largest known (in absolute value).

We assumed that one of the cubic- $ZrMo_xW_{2-x}O_8$ solutions may have a larger coefficient than that previously determined. We carefully investigated the conditions for obtaining cubic- $ZrMo_xW_{2-x}O_8$ ($x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8$, and 2.0) from precursors and measured their NTE coefficients.

Results and Discussion

Synthesis of the precursors and their characterization. We synthesized $ZrMo_xW_{2-x}O_7(OH,Cl)_2 \cdot 2H_2O$ by a hydrothermal method¹⁰. Stoichiometric amounts of $Na_2WO_4 \cdot 2H_2O$, Na_2MoO_4 and $ZrOCl_2 \cdot 8H_2O$ were placed in a flask with 2.3 M HCl (solid: liquid $\sim 1:10$) and stirred for 30 minutes. The obtained reaction mixture was placed in an autoclave with a Teflon liner and heated at 450 K for 48 hours. After cooling, $ZrMo_xW_{2-x}O_7(OH,Cl)_2 \cdot 2H_2O$ was filtered, washed with water and dried at 380 K for 24 hours. Eleven samples were obtained. The colours of the powders of $ZrMo_xW_{2-x}O_7(OH,Cl)_2 \cdot 2H_2O$ changed from white to bluish as a function of the value of “x”.

The powders of $ZrMo_xW_{2-x}O_7(OH,Cl)_2 \cdot 2H_2O$ were examined by powder X-ray diffraction (Fig. 1) on a DRON-RM4 diffractometer (CuK_α source, graphite monochromator at the diffracted beam, room temperature, 2θ range $5\text{--}60^\circ$). The experimental data were processed with the PowderCell program v.2.4¹⁵, and the data from the powder structural database powder diffraction file (PDF) were used as the reference¹⁶. The EDX spectral analysis was performed using a Hitachi TM3030 desktop scanning electron microscope and the Quantax70 microanalysis system.

The PXRD data showed that all the samples were single phase. We performed an EDX investigation for all the prepared samples and found that the preset stoichiometry was retained in the products of the reaction within the experimental uncertainty. Determining the content of molybdenum and tungsten in $ZrMo_xW_{2-x}O_7(OH,Cl)_2 \cdot 2H_2O$ by the Zen-Retgers rule is extremely difficult because of the extreme similarity of the unit cell volumes (Table 1).

DTA and high-temperature PXRD of $ZrMo_xW_{2-x}O_7(OH,Cl)_2 \cdot 2H_2O$. A thermal analysis was performed on an “STA 449 F1 Jupiter” in a platinum crucible under an oxygen–argon atmosphere (20% O_2) in the temperature range 298–1073 K.

x, set value	x, found	a, Å	c	V/Z (Z = 8)
0	0.00	11.461(2)*	12.509(2)*	205.39(4)*
0.2	0.24(2)	11.417(1)	12.454 (1)	202.92(3)
0.4	0.42(2)	11.218 (1)	12.235(1)	192.47(3)
0.6	0.58(2)	11.390(1)	12.414(2)	201.30(5)
0.8	0.80(2)	11.244(1)	12.276(1)	194.01(3)
1.0	1.00(2)	11.439(1)	12.498(1)	204.42(3)
1.2	1.20(2)	11.393(1)	12.429 (1)	201.68(4)
1.4	1.40(2)	11.404 (1)	12.450 (2)	202.37(3)
1.6	1.54(2)	11.384(1)	12.427(2)	201.29(4)
1.8	1.74(2)	11.429(1)	12.471(1)	203.61(4)
2	2.00	11.447(1)	12.495 (1)	204.67(3)

Table 1. Data for the EDX experiment for $\text{ZrMo}_x\text{W}_{2-x}\text{O}_7(\text{OH},\text{Cl})_2 \cdot 2\text{H}_2\text{O}$ and the calculated cell parameters (space group $I4_1cd$). *ICSD #157755.

Figure 2. Data on the temperatures of the thermal effect maxima for the thermal degradation of solid solution $\text{ZrMo}_x\text{W}_{2-x}\text{O}_7(\text{OH},\text{Cl})_2 \cdot 2\text{H}_2\text{O}$ obtained by DTA (a) and the phases detected by high-temperature PXRD (b).

High-temperature experiments were carried with time-resolved diffractometry at channel 5b of the Siberian Synchrotron and Therahertz Radiation Centre^{17,18}. The wavelength used was 1.516 Å. The diffraction patterns were recorded by a one-coordinate detector (OD-3) developed in Budker Institute of Nuclear Physics of Siberian Branch Russian Academy of Sciences¹⁹. The exposure time for a frame was set to 1 minute. The samples were heated in air up to 1123 K at a rate of 10 K/min.

The behaviours of the $\text{ZrMo}_x\text{W}_{2-x}\text{O}_7(\text{OH},\text{Cl})_2 \cdot 2\text{H}_2\text{O}$ samples upon thermal decomposition are similar (Fig. 2a), but some features depend on the value of “x”. The decomposition of $\text{ZrMo}_x\text{W}_{2-x}\text{O}_7(\text{OH},\text{Cl})_2 \cdot 2\text{H}_2\text{O}$ begins at 450 K for $x = 2$ and increases linearly up to 500 K for $x = 0$. The first stage is accompanied by an endothermic effect and a weight loss (Fig. 3). The data from the high-temperature PXRD confirmed the following reaction:

We calculated the molar ratio of the chloride ion to the hydroxide ion (In all the samples, the ratio was approximately 1:3.) based on the loss of the mass, which was measured by DTA, as described in article⁹.

Figure 3. A typical thermogram for $\text{ZrMo}_x\text{W}_{2-x}\text{O}_8$ ($x = 1.2$).

The diffraction peaks of $\text{ZrMo}_x\text{W}_{2-x}\text{O}_7(\text{OH}, \text{Cl})_2 \cdot 2\text{H}_2\text{O}$ decreased to zero, and the diffraction pattern of orthorhombic- $\text{ZrMo}_x\text{W}_{2-x}\text{O}_8$ appeared. The peaks of the formed orthorhombic- $\text{ZrMo}_x\text{W}_{2-x}\text{O}_8$ had large widths, and the crystallite size was small, approximately 10–15 nm (The Scherer equation was used to calculate the crystallite sizes).

The crystallite sizes did not increase with the temperature in our experiments. Allen²⁰ used a long heat treatment (8 hours at 573 K) to prepare good crystalline samples of orthorhombic- $\text{ZrMo}_x\text{W}_{2-x}\text{O}_8$.

The second transformation did not have a weight loss and was accompanied by an exothermal effect. The temperatures of the transformation (650–800 K) had a complex dependence on the parameter “ x ” (Fig. 2a). We observed the appearance of the peaks of a nicely crystalline cubic-phase $\text{ZrMo}_x\text{W}_{2-x}\text{O}_8$ in the powder pattern. The width of the synthetic “window” for single-phase, cubic $\text{ZrMo}_x\text{W}_{2-x}\text{O}_8$ was not large: 70–200 K ($x = 0$ –1.4) and 30–50 K ($x = 1.4$ –2.0). Preparation of pure cubic, single-phase samples required accurate work. The precursor had to be heated to the minimal possible temperature (blue line on Fig. 2b) and held for 10–60 minutes (60 minutes for $x = 0$ and 10 minutes for $x = 2$).

Further heating led to the formation of trigonal $\text{ZrMo}_x\text{W}_{2-x}\text{O}_8$ at 500–700 K ($x = 1.2$ –2.0) or decomposition of the material into constituent oxides at 1050 K ($x = 0$ –1.0) (Fig. 2b). In study¹⁴, it was found that the resulting products with $x \leq 0.5$ would decompose to WO_3/MoO_3 and ZrO_2 upon a temperature increase, while for $x > 0.5$, the cubic phase would transform into the trigonal phase. Shi Yongfang¹¹ noted that the appearance of the trigonal phase occurs at relatively low temperatures, i.e., 861 K ($x = 0.73$) and 889 K ($x = 0.53$). This fact was confirmed in our work. Trace amounts of the trigonal phase were often present in all the PXRD patterns, while the cubic compound was the main phase. However, we did not observe the exothermal effect for the cubic-to-trigonal transformation for $x = 0.2$ –0.8, 1.6, and 1.8 in the DTA experiments.

Trigonal $\text{ZrMo}_x\text{W}_{2-x}\text{O}_8$ ($x = 1.2$ –1.8) had a good thermal stability, and we found no evidence of its decomposition for $x = 1.4$, 1.6 and 1.8 under the conditions in our experiment. Trigonal $\text{ZrMo}_x\text{W}_{2-x}\text{O}_8$ ($x = 1.2$) decomposed at 1150 K. However, trigonal ZrMo_2O_8 decayed into oxides with an exo-effect at 925 K.

We should note that all the transformations of orthorhombic-cubic-trigonal-oxides are exothermic. This can be explained if all those phases (with the exception of the oxides) are metastable in our experimental temperature ranges. The transformations were accompanied by a decrease in the volume of the formula unit (V/Z), e.g., for $x = 1.2$ (Fig. 4):

Our data directly indicated the formation of a poorly crystalline orthorhombic phase ($\text{Pmn}2_1$) of zirconium tungstate (ZrW_2O_8) in the temperature range 550–825 K (Fig. 2).

NTE coefficient of cubic- $\text{ZrMo}_x\text{W}_{2-x}\text{O}_8$. The thermal expansion of cubic- $\text{ZrMo}_x\text{W}_{2-x}\text{O}_8$ was investigated using variable temperature PXRD. Diffraction data were measured using a Bruker D8 Advance diffractometer ($\text{CuK}\alpha$ radiation) with a parallel-beam geometry with Göbel Mirrors. *In situ* experiments were carried out using an Anton Paar XRD900 reaction chamber. The patterns were measured in the 2θ range from 10 to 70° with a step of 0.05° and a collection time of 3 s per point. The heating rate was 12 K/min. The acquisition of the X-ray patterns was started when the given temperature was reached. Sample cooling was immediately performed. The profile analysis and structural refinement by the LeBail method were performed using the TOPAS v.4.3 program²¹, and the data from the powder structural database PDF were used as the standards¹⁶. The lengths of the coherent

Figure 4. Conversions for the $\text{ZrMo}_x\text{W}_{2-x}\text{O}_7(\text{OH,Cl})_2 \cdot 2\text{H}_2\text{O}$ and $\text{ZrMo}_x\text{W}_{2-x}\text{O}_8$ compounds. The inset presents typical data of a high-temperature PXR; in this case, $x = 1.2$.

x	Temperature of ($\alpha \rightarrow \beta$) transformations, K	NTE coefficient, $\cdot 10^6, \text{K}^{-1}$		D, nm
		Ordered phase	Disordered phase	
0 ⁵	430	−8.8	−4.8	
0 ⁹	400	−6.9	−4.5	
0.2	398*	—	−3.5	34(2)
0.3 ¹⁴	380*	−6.61	−6.61	
0.4 ⁸	373–393	−11.8	−7.4	
0.4	364*	—	−3.5	28(2)
0.6	331*	—	−3.5	31(1)
0.8	297*	—	−3.6	58(1)
1.0	263*	—	−4.5	70(2)
1.0 ⁶	250	−9.0	−5.5	
1.2	230*	—	−4.5	56(1)
1.4	196*	—	−4.0	60(2)
1.6	162*	—	−4.6	75(4)
1.8	470 (129*)	−9.6	−4.0	114(1)
2.0 ⁷	200 (95*)	−6.9	−5.0	

Table 2. Data for cubic $\text{ZrMo}_x\text{W}_{2-x}\text{O}_8$: temperature of the ordered to disordered transition, calculated NTE coefficients, crystallite size for the disordered phase. *Calculated using formula¹³ $T (\text{K}) = 432 - 168.45 \cdot x$.

scattering domain were calculated using LVol-IB values (i.e., volume weighted mean column height based on the integral breadth).

When measuring the NTE coefficient, it is important to realize which form of cubic $\text{ZrMo}_x\text{W}_{2-x}\text{O}_8$ is being measured, i.e., ordered or disordered. For ZrW_2O_8 , this transition is called $\alpha \rightarrow \beta$. In article¹³, the thermal effects for the transition (ordered $\rightarrow$ disordered) were measured, and a formula describing the temperature of the $\alpha \rightarrow \beta$ transitions for cubic- $\text{ZrMo}_x\text{W}_{2-x}\text{O}_8$ was proposed: $T (\text{K}) = 432 - 168.45 \cdot x$. We used it in our work to estimate whether the NTE coefficient belongs to the corresponding ordered or disordered form (Table 2). Of course, the dependence is not linear for $x > 1$; this is clearly visible when comparing the calculated and experimental values for $x = 1.8$ and 2.0 (Table 2).

We were able to obtain reliable data for the NTE coefficients for only the disordered phase, except for $x = 1.8$. The calculated coefficients have similar values (from $-3.5 \cdot 10^{-6} \text{K}^{-1}$ to $-4.5 \cdot 10^{-6} \text{K}^{-1}$) and almost did not differ from those of the “pure components”. Our value of the NTE coefficient, $3.5 \cdot 10^{-6} \text{K}^{-1}$, for $x = 0.4$ did not coincide with the value⁸ obtained earlier, $-7.4 \cdot 10^{-6} \text{K}^{-1}$. Only for cubic $\text{ZrMo}_{1.8}\text{W}_{0.2}\text{O}_8$ could the calculated NTE coefficient, $-9.6 \cdot 10^{-6} \text{K}^{-1}$ (300–400 K), be attributed to the ordered cubic $\text{ZrMo}_x\text{W}_{2-x}\text{O}_8$ (space group $\text{P}2_13$).

Conclusion

All the investigated phases of $\text{ZrMo}_x\text{W}_{2-x}\text{O}_7(\text{OH},\text{Cl})_2 \cdot 2\text{H}_2\text{O}$ and $\text{ZrMo}_x\text{W}_{2-x}\text{O}_8$ are metastable at $T < 1200\text{ K}$ and $P(\text{air}) = 1\text{ bar}$. All transformations that occur during heating are irreversible.

The precursors $\text{ZrMo}_x\text{W}_{2-x}\text{O}_7(\text{OH},\text{Cl})_2 \cdot 2\text{H}_2\text{O}$ (average size of individual particles 50 nm) with pre-determined chemical compositions can be obtained by a hydrothermal method.

Heating of the precursors up to $T = 525\text{--}50 \cdot x\text{ K}$ affords crystals of orthorhombic $\text{ZrMo}_x\text{W}_{2-x}\text{O}_8$ (10–15 nm).

Cubic $\text{ZrMo}_x\text{W}_{2-x}\text{O}_8$ solid solutions with a small crystal grain size (30–100 nm) can be obtained by thermal decomposition of the corresponding precursor or orthorhombic $\text{ZrMo}_x\text{W}_{2-x}\text{O}_8$ at a temperature up to 850–900 K at $x \leq 1.8$ and $T = 2200\text{--}750 \cdot x\text{ K}$ at $x > 1.8$.

Trigonal $\text{ZrMo}_x\text{W}_{2-x}\text{O}_8$ (only for $x > 1$) can be prepared by heating the precursor or cubic $\text{ZrMo}_x\text{W}_{2-x}\text{O}_8$ or orthorhombic $\text{ZrMo}_x\text{W}_{2-x}\text{O}_8$ up to 850–1050 K, depending on the exact composition.

Solid solutions of cubic $\text{ZrMo}_x\text{W}_{2-x}\text{O}_8$ in the ordered form have a higher coefficient of thermal expansion (CTE) in comparison to that of other materials, but they exist in a very limited and relatively low-temperature range, which limits their possible applications.

The disordered form of cubic $\text{ZrMo}_x\text{W}_{2-x}\text{O}_8$ solid solutions does not have an advantage over that of the “pure components” in the value of CTE. The use of solid solutions is justified in the case when it is necessary to have a uniform CTE material for a certain temperature range (e.g., 250–800 K for $x = 1.0$).

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Author Contributions

M.Y.P., E.S.D. and G.A.I. synthesized all samples; M.Y.P. and E.S.D. performed EDX experiments; M.Y.P., E.Y.F. and E.A.Z. performed PXRD experiments; P.E.P. performed DTA experiments; M.Y.P. and M.R.S. performed high-temperature PXRD experiments; M.Y.P., S.V.K., S.N.K., E.A.D. and G.A.I. analysed the data; M.Y.P., S.V.K., S.N.K. and G.A.I. designed the experiments; G.A.I. supervised the project; and all authors wrote the paper.

Additional Information

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