W- rich mixed oxide solid solutions under pressure

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Abstract. We report high-pressure synchrotron X-ray powder diffraction data for the W-rich cubic $ZrW_{2-x}Mo_xO_8$ (x=0.4) up to 10 GPa with open decompression. This study shows that cubic- $ZrW_{1.6}Mo_{0.4}O_8$ transforms to orthorhombic phase at the 5.04 GPa. Pressure-induced reversable amorphization of material was observed at 8.13 GPa. The obtained data suggest that W-rich cubic $ZrW_{2-x}Mo_xO_8$ (x=0.4) solid solutions are more attractive for creating products working under extreme conditions and mechanic stress.

1. Introduction

Most materials show a positive coefficient of thermal expansion, which may be explained by the increase in average bond lengths with increasing thermal energy [1]. There is, however, a few phenomena which give an opposing effect and contribute to contraction on heating. In some cases, these effects outweigh the general increase in bond lengths, and lead to a net negative thermal expansion (NTE) [2-5]. Much of the recent interest in NTE has been based on the system $ZrW_{2-x}Mo_xO_8$ ($0 \leq x \leq 2$) shows a significantly large thermal compression with α = -11.8×10^{-6} K^{-1} (for x=1.6) [6]. The $ZrW_{2-x}Mo_xO_8$ ($0 \leq x \leq 2$) system is used in the production of composite materials with controllable coefficient thermal expansion (CTE), where several materials, including ceramics, metal and polymers, can act as a matrix [7-10]. The precision products with an adjusted coefficient of thermal expansion are widely used in various fields such as aerospace engineering, high-precision optics, electronics, oil and gas industry. Thus, the study of $ZrW_{2-x}Mo_xO_8$ ($0 \leq x \leq 2$) phase transitions under the influence of temperature and pressure is of great importance. ZrW_2O_8 and $ZrMo_2O_8$ phase transitions depending on the applied pressure have been studied intensively [11, 12]. A pressure-induced phase transition γ-$ZrMo_2O_8$ (cubic, $P2_13$) occurs at pressures of 0.7-2.0 GPa, compared to 0.21 GPa for the similar transition from cubic ZrW_2O_8 ($P2_13$) to orthorhombic phase with $P2_12_12_1$ symmetry [13-15]. Carlson and Andersen [16] has shown that at room temperature α-$ZrMo_2O_8$

(trigonal, $P\bar{3}c$) turns into β-$ZrMo_2O_8$ (monoclinic, $C2/m$) at about 1.1 GPa, and another phase transition from β-$ZrMo_2O_8$ to the triclinic phase with P_1 space group symmetry occurs in the pressure range from 2 to 2.5 GPa.

The effect of pressure on $ZrW_{2-x}Mo_xO_8$ (with x=1 and x=1.6) was reported previously by the authors [17]. This study shows that disordered cubic- $ZrWMoO_8$ (space group $Pa\bar{3}$) transforms to ordered cubic- $ZrWMoO_8$ (space group $P2_13$) at low pressure. A further high-pressure influence leads followed by amorphization of the sample at 2.2 GPa. All transformations are irreversible. Pressure-induced changes from cubic to orthorhombic $ZrW_{2-x}Mo_xO_8$ (x=1.6) phase at 1.38 GPa are observed. The sample amorphization is irreversible during decompression. The aim of this article is to synthesize W-rich $ZrW_{2-x}Mo_xO_8$ (x=0.4) using the hydrothermal method and to study properties under the pressure for comparison with previously obtained data.

2. Experimental procedure

The precursor $ZrW_{1.6}Mo_{0.4}O_7(OH,Cl)_2 \cdot 2H_2O$ was obtained by the most effective hydrothermal method described in [18,19]. $Na_2WO_4 \cdot 2H_2O$ (1.648 g), Na_2MoO_4 (0.247 g) and $ZrOCl_2 \cdot 8H_2O$ (1.035) in the required stoichiometric ratio were dissolved in H_2O (5 ml). The resulting solutions were mixed and 15 ml of 8M hydrochloric acid solution was added and mixed again. The hydrothermal reaction was carried out in a steel autoclave (volume 70 ml) with a Teflon insert at a temperature of 450 K for 48 hours. The resulting product was washed several times with distilled water. The filtration was carried out and dried in an oven at a temperature of 380 K for 24 hours. The powder of $ZrW_{1.6}Mo_{0.4}O_7(OH,Cl)_2 \cdot 2H_2O$ was examined by powder X-ray diffraction on a DRON-RM4 diffractometer (CuK_α source, graphite monochromator at the diffracted beam, room temperature, 2θ range 5–60°). The EDX spectral analysis was performed using a Hitachi TM3030 desktop scanning electron microscope and the Quantax70 microanalysis system.

The cubic-$ZrW_{1.6}Mo_{0.4}O_8$ was synthesized at 800 K. The powders of $ZrW_{1.6}Mo_{0.4}O_8$ have been examined with powder X-ray diffraction on a DRON-RM4 diffractometer (CuK_α source, graphite monochromator at the diffracted beam, room temperature, 2θ range 5–50°). The experimental data were processed with Topas Academic software.

Pressure powder X-ray diffraction experiments were carried out at the European Synchrotron Radiation Facility (ESRF) ID15B High Pressure Beamline up to 10 GPa with open decompression. Determination of high-pressure phases of the $ZrW_{1.6}Mo_{0.4}O_8$ using angular dispersive diffraction on cells with a membrane-controlled diamond anvil with ditches of 600 μm. As pressure transmitting medium was used ethanol-water medium with a small ruby crystal. Pressure was measured using the ruby luminescence method. X-ray diffraction patterns were integrated using Dioptas and Topas academic software.

3. Result and discussion

We performed an EDX investigation for the prepared sample of $ZrW_{1.6}Mo_{0.4}O_7(OH,Cl)_2 \cdot 2H_2O$ and found that the preset stoichiometry was retained in the product of the reaction within the experimental uncertainty.

Rietveld refinement of the powder X-ray diffraction data for $ZrW_{1.6}Mo_{0.4}O_8$ was carried out in Topas Academic and structural model consisting of the $P2_13$ structure of $ZrW_{1.6}Mo_{0.4}O_8$ without additional phases were identified. The Rietveld fit is shown in Figure 1.

The research data of $ZrW_{2-x}Mo_xO_8$ (x=1.6) sample under the influence of pressure are presented in Figure 2. It was found that under an applied pressure of 5.04 GPa the cubic $ZrW_{1.6}Mo_{0.4}O_8$ undergoes a phase transition to orthorhombic phase. As can be seen from Figure 2 at a pressure of an 8.13 GPa (black line) structure becomes X-ray amorphous. The onset of amorphization was determined by the broadening of the peaks and the disappearance of orthorhombic reflections from the diffraction data. It is interesting to note that, in comparison with Mo-rich $ZrW_{2-x}Mo_xO_8$ ($0 \le x \le 2$) solid solutions for W-rich materials, a reversible amorphization is observed, which is expressed in the appearance of additional peaks in the X-ray diffraction patterns.
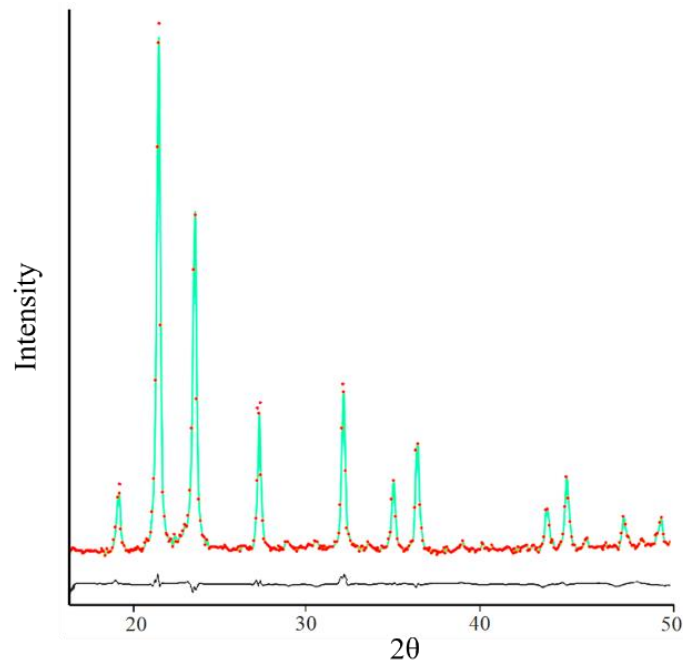
Figure 1. Rietveld refinement plot for $ZrW_{2-x}Mo_xO_8$ (x=0.4): observed powder pattern (green); calculated diffraction pattern (red); difference plot (black).

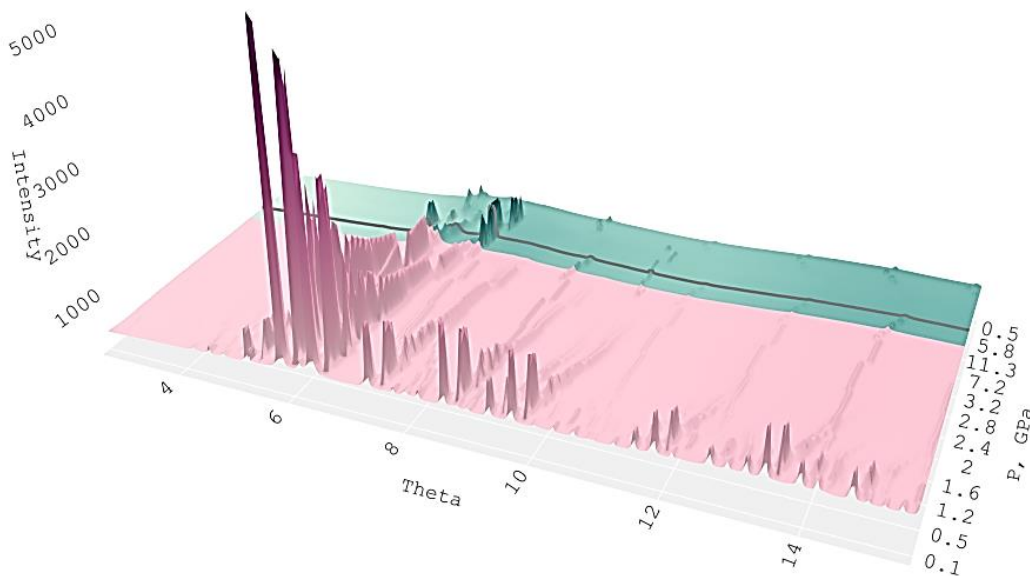**Figure 2.** Pressure-induced changes in $ZrW_{2-x}Mo_xO_8$ (x=0.4).

4. Conclusion

The behavior of cubic $ZrW_{1.6}Mo_{0.4}O_8$ on compression up to 10 GPa with open decompression was examined by a synchrotron X-ray diffraction at the European Synchrotron Radiation Facility (ESRF) ID15B High Pressure Beamline. The diffraction data show the complete formation of orthorhombic ZrW_2O_8 at high pressure (5.04 GPa) and amorphization onset at 8.13 GPa. The phase transition pressure is much higher than for the pure cubic phase of zirconium tungstate and Mo-rich $ZrW_{2-x}Mo_xO_8$ ($0 \leq x \leq 2$) solid solutions. The obtained data describe the W-rich $ZrW_{2-x}Mo_xO_8$ ($0 \leq x \leq 2$)

solid solutions as the most attractive for creating composites that will work under extreme pressures in many industries.

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