W- rich mixed oxide solid solutions under pressure

M Yu Petrushina1,2, E.S. Dedova3,4, K V Yusenko5, A S Portnyagin6, E K Papynov6, E Yu Filatov1, S V Korenev1 and A I Gubanov1

1Nikolaev Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences, 3, Academician Lavrentiev Ave., 630090 Novosibirsk, Russia
2Novosibirsk State University, Pirogova str. 2, 630090 Novosibirsk, Russia
3Institute of Strength Physics and Materials Science, Siberian Branch of the Russian Academy of Sciences, 2/4, Academicicheskii Ave., 634021 Tomsk, Russia
4Tomsk Polytechnic University, 30, Lenin Ave. 634050 Tomsk, Russia
5Federal Institute of Materials Research and Testing, 11, Richard-Willstätter Str. D-12489 Berlin, Germany
6Institute of Chemistry of Far Eastern Branch of the Russian Academy of Sciences, 159, Prospect 100-letiya Vladivostoka, 690022 Vladivostok, Russia

E-mail: mapet1003@mail.ru

Abstract. We report high-pressure synchrotron X-ray powder diffraction data for the W-rich cubic ZrW_{2.8}Mo_{0.2}O_{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 reversible amorphization of material was observed at 8.13 GPa. The obtained data suggest that W-rich cubic ZrW_{2.8}Mo_{0.2}O_{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_{x}O_{8} (0≤x≤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_{x}O_{8} (0≤x≤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_{x}O_{8} (0≤x≤2) phase transitions under the influence of temperature and pressure is of great importance. ZrW_{2}O_{8} and ZrMo_{2}O_{8} phase transitions depending on the applied pressure have been studied intensively [11, 12]. A pressure-induced phase transition γ-ZrMo_{2}O_{8} (cubic, P2_3) occurs at pressures of 0.7-2.0 GPa, compared to 0.21 GPa for the similar transition from cubic ZrW_{2}O_{8} (P2_3) to orthorhombic phase with P2_12_12_1 symmetry [13-15]. Carlson and Andersen [16] has shown that at room temperature α-ZrMo_{2}O_{8}...
trigonal, $P\overline{3}c$) turns into $\beta$-ZrMo$_2$O$_8$ (monoclinic, $C2/m$) at about 1.1 GPa, and another phase transition from $\beta$-ZrMo$_2$O$_8$ 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$_{2.8}$Mo$_{0.2}$O$_8$ (with $x=1$ and $x=1.6$) was reported previously by the authors [17]. This study shows that disordered cubic-ZrWMoO$_8$ (space group Pa3) transforms to ordered cubic-ZrWMoO$_8$ (space group P2$_1$$3$) at low pressure. A further high-pressure influence leads by amorphization of the sample at 2.2 GPa. All transformations are irreversible. Pressure-induced changes from cubic to orthorhombic ZrW$_{2.8}$Mo$_{0.2}$O$_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$_{2.8}$Mo$_{0.2}$O$_8$ (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)$_2$·2H$_2$O was obtained by the most effective hydrothermal method described in [18,19]. Na$_2$WO$_4$·2H$_2$O (1.648 g), Na$_2$MoO$_4$ (0.247 g) and ZrOCl$_2$·8H$_2$O (1.035) in the required stoichiometric ratio were dissolved in H$_2$O (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)$_2$·2H$_2$O was examined by powder X-ray diffraction on a DRON-RM4 diffractometer (CuK$_\alpha$ source, graphite monochromator at the diffracted beam, room temperature, 20 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$_\alpha$ source, graphite monochromator at the diffracted beam, room temperature, 20 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)$_2$·2H$_2$O 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_1$$3$ 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$_{2.8}$Mo$_{0.2}$O$_8$ (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$_{2.8}$Mo$_{0.2}$O$_8$ (0≤x≤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$_x$O$_8$ (x=0.4): observed powder pattern (green); calculated diffraction pattern (red); difference plot (black).

Figure 2. Pressure-induced changes in ZrW$_{2.4}$Mo$_{0.4}$O$_8$ (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$_2$O$_8$ 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$_x$O$_8$ (0≤x≤2) solid solutions. The obtained data describe the W-rich ZrW$_{2.4}$Mo$_{0.4}$O$_8$ (0≤x≤2)
solid solutions as the most attractive for creating composites that will work under extreme pressures in many industries.

Acknowledgements

We thank the European Synchrotron Radiation Facility for the provision of synchrotron radiation facilities, and we would like to thank I. Collings for assistance during the beamtime and for the loading of diamond-anvil cells (MA 4315 experiment). The authors are grateful to the Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences. The reported study was funded by RFBR according to the research project № 19-33-90041.

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