High-pressure structural transformations of PbCrO_4 up to 51.2 GPa:

An angle-dispersive synchrotron x-ray diffraction study

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Abstract

We report on high-pressure x-ray diffraction measurements up to 51.2 GPa in PbCrO_4 at room temperature. Three high-pressure phases with structures different than the ambient-pressure monazite-type ($P2_1/n$) are reported. One phase transition was found at 3.8 GPa to an isomorphic structure to monazite. A second transition occurs at 11.1 GPa. After this transition, the coexistence of tetragonal ($I4_1/a$) and monoclinic ($P2_1$) structures is detected up to 21.1 GPa. Beyond this pressure and up to 51.2 GPa, only the high-pressure monoclinic phase is observed. Upon decompression all structural changes are reversible. Finally, the axial compressibilities for the different phases have been determined as well as the equations of state.

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I. Introduction

PbCrO_4 (the mineral crocoite) crystallizes in the monoclinic monazite structure (space group $P2_1/n$, $Z = 4$) at ambient conditions. This structure is characterized by isolated CrO_4 tetrahedra separated by polyhedral units in which Pb is in enneadic coordination. Monazite-type oxides form an extended family of compounds. Several applications for them are already reported or under development [1]. They include photoconductive dielectric materials, humidity sensing resistors, yellow pigments, effective solid lubricants, coating and diffusion barriers, ion conductors, and geochronology among others. Monazites exist in nature. They easily incorporate rare-earth elements and thus they can effectively control the rare-earths distribution in igneous rocks [2, 3]. In addition, monazites are common accessory minerals in plutonic and metamorphic rocks. Therefore, the knowledge of the high-pressure (HP) behavior of monazites is very relevant not only for technological applications, but also for mineral physics, chemistry, and petrology [4].

Because of the broad interest in monazite-type oxides, they have been extensively studied, in particular under compression [3, 5 - 11]. These studies reported the occurrence of phase transitions. In the case of PbCrO_4 , two pressure-induced transitions have been found around 3-5 and 9-12 GPa [5, 11]. The first transition has been proposed to be to a structure isomorphic to monazite, however, the crystal structure of it has not been fully solved yet. The crystal structure of the second HP remains unknown. In order to improve the knowledge of the HP structural behavior of PbCrO_4 , here we report x-ray diffraction (XRD) measurements performed under quasi-hydrostatic conditions up to 51.2 GPa. Details on the crystal structure of the different phases are reported. The pressure evolution of unit-parameters and room-temperature (RT) equations of state (EOS) are also presented.

II. Experimental details

Experiments were performed on natural crocoite minerals collected at the Red Lead Mine, Dundas, Tasmania, Australia. Electron microprobe analysis was performed to determine the impurities present in the natural crystals. The only detected impurity was Fe (0.06%). The crystals were then grounded with a mortar and a pestle into a fine powder. XRD measurements confirmed the monazite crystal structure. In order to perform HP studies, pre-pressed pellets were prepared using the finely ground powder. Synchrotron powder XRD experiments were performed at room temperature (RT) up to 51.2 GPa using a diamond-anvil cell with diamond-culets of 300 μm . The pellets were loaded into a 100- μm hole of a rhenium gasket pre-indented to 30 μm . Ruby fluorescence was used for pressure determination [12] and Ne as pressure-transmitting medium. At pressures exceeding 5 GPa Bragg peaks of Ne were detected and used as pressure scale too [13]. Differences between both methods were within 0.2 GPa. Angle-dispersive XRD experiments were carried out at HPCAT, sector 16-IDB, of the Advanced Photon Source (APS) with an incident wavelength of 0.3977 Å. The monochromatic x-ray beam was focused down to $10 \times 10 \mu\text{m}^2$ using Kirkpatrick–Baez mirrors. The detector was a MAR345 image plate located 350.7 mm away from the sample. Images were integrated and corrected for distortions using FIT2D [14]. Structural solution and refinements were performed using GSAS [15] and POWDERCELL [16].

III Results

Fig. 1 shows a selection of XRD patterns measured at different pressures. The patterns collected below 3.8 GPa can be assigned to the ambient pressure monazite structure. At 3.8 GPa, subtle changes occur in the diffraction pattern. In particular, some Bragg peaks shift under compression towards larger angles more than the others (see

inset of Fig. 2). As we will show below, these changes are associated to an isomorphic transformation [5] to a structure that we will name as monazite-II. Additionally, more notorious changes are detected at 11.1 GPa in the XRD spectra indicating the onset of a second phase transition. Upon further compression new changes are detected at 21.1 GPa suggesting a third structural change. The possible structures of these HP phases, which we will denote as phase III and IV, will be discussed below. Upon decompression all changes were found to be reversible. In particular, phase IV remained as a single phase up to 19.8 GPa, phase III reappeared at 14 GPa, and phase II and monazite were recovered at 9.4 and 2.8 GPa, respectively. The monazite structure was stable at ambient pressure. This is illustrated in Fig. 1 by the pattern recorded after complete decompression.

Let us discuss now the crystal structure of the ambient pressure phase and the phase observed after the first phase transition. XRD patterns of both phases are shown in Fig. 2. The pattern collected at 2.5 GPa can be undoubtedly assigned to a monazite-type structure (space group $P2_1/n$). After a Rietveld refinement, the following structural parameters were obtained for PbCrO_4 : $a = 6.997(7) \text{ \AA}$, $b = 7.328(7) \text{ \AA}$, $c = 6.779(7) \text{ \AA}$, and $\beta = 101.1(2)^\circ$. At ambient pressure we obtained $a = 7.118(7) \text{ \AA}$, $b = 7.431(7) \text{ \AA}$, $c = 6.794(7) \text{ \AA}$, and $\beta = 102.4(2)^\circ$. The values determined at ambient pressure agree within 1% error in comparison with the unit-cell parameters reported in the literature [1, 5]. In order to perform the Rietveld refinements, the occupancy (SOF) and overall atomic displacement factors (B) were constrained to $\text{SOF} = 1$ and $B = 0.5 \text{ \AA}^2$. This was done, because SOF and B are correlated and more sensitive to background subtraction than positional parameters, and also to reduce the number of free parameters used in the refinement [17]. The atomic positions of oxygen atoms were further constrained to the positions refined in Ref. [5]. We used this approximation because the small x-ray

scattering cross section of oxygen causes uncertainties in the determination of the positions of the oxygen atoms. Consequently, it is not possible to accurately determine twelve atomic coordinates for different oxygen atoms from the present powder XRD experiments. Therefore, only the Pb and Cr positions were refined. The quality of the structural refinement is illustrated by the small residuals (see Fig. 2) and by the small R-factors and chi-squared achieved: $R_{WP} = 3.31 \%$, $R_P = 2.39 \%$, and $\chi^2 = 1.22$. The atomic positions, obtained for Pb and Cr at 2.5 GPa are (0.2241(9), 0.1511(7), 0.4039(9)) and (0.1973(4), 0.1638(6), 0.8839(8)), respectively. If we compare with ambient pressure positions [5], the atomic coordinates refined at 2.5 GPa differs by less than 1%.

On comparing the XRD patterns measured at 2.5 and 5 GPa, it is possible to see the subtle but detectable changes discussed above. In particular, they can be seen when comparing the angular regions shown in the inset. These changes are in agreement with the isomorphic transition proposed in Ref. [5]. Thus, we confirm the monazite-to-monazite-II transition previously proposed. Additionally, here we provide structural information on monazite-II. The structural refinement of this structure at 5 GPa is shown in Fig. 2. To perform the refinement we followed the same procedure carried out for low-pressure monazite. In this case, we obtained also small residuals, $R_{WP} 3.40 \%$, $R_P = 2.39\%$, and $\chi^2 = 1.36$. The structure of monazite-II also belongs to space-group symmetry $P2_1/n$. However, we detected abrupt changes at the transition in the pressure evolution of unit-cell parameters. In particular at 5 GPa, $a = 6.887(7) \text{ \AA}$, $b = 7.235(7) \text{ \AA}$, $c = 6.659(7) \text{ \AA}$, and $\beta = 101.6(5)^\circ$. In addition, we detected changes in the atomic positions of Pb (0.2333(6), 0.1489(5), 0.4076(6)) and Cr (0.2127(4), 0.1779(4), 0.8994(8)). These changes cause a coordination increase for Pb (coordination number changes from 9 to 10) if the change of oxygen positions is neglected. This coordination

change is in consonance with changes detected in the optical and electronic properties of the materials observed at the same pressure [11].

From the XRD patterns collected at different pressures for monazite and monazite-II, we extracted the pressure evolution of the unit-cell parameters of PbCrO_4 up to 7.2 GPa. Results are summarized in Fig. 3 and compared with earlier results [5]. There it can be seen that compression is non-isotropic. The a -axis is the most compressible axis and the c -axis is the least compressible axis. This behavior is fully consistent with that previously reported [5]. Reasons for this behavior have been already discussed in the literature [5]. In Ref. 5, it has been report that at the first phase transition there is a subtle change in the pressure evolution of different parameters at 3.25 GPa. In the present case, the higher resolution of the experimental set-up provides more evident for these changes. In particular, there is an abrupt change in the values of the unit-cell parameters when PbCrO_4 undergoes the phase transition around 3.8 GPa (see Fig. 3). However, as mentioned above, these changes involve a structural distortion of the monoclinic structure of PbCrO_4 , but not a change in the space-group symmetry of the crystal. Due to the small number of data points available for monazite and monazite-II phases, we fit their volume data shown in Fig. 3 with a second-order Birch-Murnaghan EOS ($B_0' = 4$) [18]. For monazite we obtained a volume at ambient pressure $V_0 = 351(1) \text{ \AA}^3$ and a bulk modulus $B_0 = 56(1) \text{ GPa}$. For monazite-II we obtained $V_0 = 352(2) \text{ \AA}^3$ and a bulk modulus $B_0 = 52(4) \text{ GPa}$. Both set of values agree within error bars and compare well with those parameters previously reported [5], confirming that PbCrO_4 is much more compressible than isomorphous vanadates [7, 8], phosphates [10, 19], selenates [9, 20], and sulfates [21].

As we mentioned above, a second phase transition is detected at 11.1 GPa. We made efforts to identify the structure of the HP phase, however, after excluding the

Bragg peaks assigned to Ne, we found impossible to index the rest of Bragg peaks with only one crystal structure. Phase coexistence is a common phenomenon in related oxides [22, 23]. Assuming this hypothesis, we have been able to index the XRD patterns measured at 11.1 GPa. In particular, the HP phase can be indexed with a mixture of two phases, one tetragonal (space group $I4_1/a$), that we will name as phase III, and the other monoclinic (space group $P2_1$), that we will name as phase IV. Owing to the presence of two phases the indexing of the tetragonal and monoclinic structures was not straightforward. In order to do it we follow a procedure similar to that used by Wang et al. for LiMoP_2O_7 [24]. We tested several combinations of structures and we found that a tetragonal scheelite-type structure [25] could explain part of the observed Bragg peaks. Finally, 20 peaks which were clearly not from the tetragonal phase were selected and successfully indexed with the monoclinic space group $P2_1$. Systematic absences of the type $0k0$, $k = 2n + 1$ were consistent with this space group. Assuming the structural model above described, small residuals are obtained when performing a Le Bail analysis [26] of the XRD pattern measured at 11.1 GPa (see Fig. 4). For the Le Bail refinement, the free parameters for each phase were the lattice parameters and a peak width independent of angle [27]. As initial values for the tetragonal structure we assumed the lattice parameters determined from the peaks we tentatively assigned to the (400) and (002) Bragg peaks of the scheelite-type structure. For the monoclinic structure we used as initial values the lattice parameters obtained from the indexing. At 11.1 GPa, the R-factors of the Le Bail refinement are $R_P = 8.97 \%$ and $R_{WP} = 12.66 \%$. These facts suggest that phase coexistence model is a plausible hypothesis to explain the changes observed in XRD patterns at 11.1 GPa. We would like to mention here that in the previous XRD experiment [5], only done up to 12 GPa, information on phases III and IV could not be obtained due to the used experimental set-up (in house diffractometer

with $\lambda = 0.7107 \text{ \AA}$ and smaller angular aperture in DAC than here). However, the existence of the transition at 11.1 GPa agrees with Raman experiments which detected it at 11.6 GPa [5] and with resistivity and optical experiments [11]. Regarding phase coexistence, we would like to comment that recently, it has been suggested that phase coexistence in HP powder XRD experiments is not of intrinsic origin but likely originates only from stress between grains [28]. To confirm or not this hypothesis single crystal experiments should be carried out in PbCrO_4 . Note that the transformation of one phase into two phases at similar pressure conditions have been observed before in related oxides [29].

We would like to comment now on the two structures found beyond 11.1 GPa. The presence of scheelite as a post-monazite structure is not surprising since the monazite-scheelite transition has been observed under compression in CaSeO_4 [9]. On the other hand, the monoclinic structure is associated to barite and to an orthorhombic structure (space group $P2_12_12_1$) found in related oxides [30, 31]. Its existence at HP in PbCrO_4 is consistent with the existence of barite as a post-monazite phase in LaPO_4 [3]. At 11.1 GPa, the unit-cell parameters of phase III and IV are: $a = 5.062(8) \text{ \AA}$ and $c = 11.57(1) \text{ \AA}$ and $a = 6.965(9) \text{ \AA}$, $b = 6.093(9) \text{ \AA}$, $c = 6.782(9) \text{ \AA}$, and $\beta = 92.2(2)^\circ$, respectively. The transition from monazite-II to phase III involves a 3 % volume contraction. The transition from monazite-II to phase IV implies a 7 % volume collapse. According with our experiments, the coexistence of phases III and IV is observed up to 18.5 GPa. At 21.1 GPa only the monoclinic phase is found. This phase is apparently stable up to 51.2 GPa (see Fig. 1), which agrees with conclusions extracted from resistivity experiments [11]. At 21.1 GPa, the unit-cell parameters of monoclinic phase IV are $a = 6.841(9) \text{ \AA}$, $b = 6.053(9) \text{ \AA}$, $c = 6.504(9) \text{ \AA}$, and $\beta = 93.1(3)^\circ$. The residuals are comparable to those obtained at 11.1 GPa, being the R-factors: $R_P = 10.09 \%$ and

$R_{WP} = 14.49 \%$. Therefore, we think that we have enough evidence to propose that the structural sequence of PbCrO_4 is monazite $\rightarrow$ monazite-II $\rightarrow$ HP tetragonal + HP monoclinic $\rightarrow$ HP monoclinic. The last two transitions are first order given the large volume changes associated with them.

Finally, we have examined the pressure evolution of the unit-cell parameters of phases III and IV. Results are summarized in Fig. 5. For phase III, there are only four data points, thus no statement can be made on the isotropy or anisotropy of the structural pressure behavior. In phase IV, the behavior is clearly non isotropic, In particular, the b -axis is the less compressible axis. On the other hand, the c -axis appears to follow a non-linear dependence, while the pressure evolution of the other two axes can be represented by a linear function. Regarding the monoclinic β angle of phase IV, we found that it gradually increases from 92.2° at 11.1 GPa to 93.7° at 51.2 GPa. In Fig. 6, we show the pressure dependence of the unit-cell volume. There it can be seen that phases III and IV are less compressible than monazite and monazite-II. For phase III, we do not have enough data points to determine the EOS. For phase IV, the fitted the pressure-volume data with a second-order EOS, following the same procedure used for the low-pressure phases. In this case we obtained: $V_0 = 303(1) \text{ \AA}^3$ and $B_0 = 80(2) \text{ GPa}$ ($B_0' = 4$). The last parameter is 45% larger than in the low-pressure phases. This fact confirms the smaller compressibility of phase IV, being consistent with the volume contraction detected at the transition.

IV Summary

Natural PbCrO_4 has been studied at RT using HP XRD up to 51.2 GPa using Ne as pressure-transmitting medium. We confirm the occurrence of a phase transition near 3.8 GPa. The crystal structure of the HP phase has been assigned to a structure isomorphic with the low-pressure monazite structure. Additional structural changes are

found at 11.1 and 21.1 GPa. Between these two pressures two phases coexist, one with a tetragonal structure and the other with a monoclinic structure. The last structure is the only one observed from 21.1 to 51.2 GPa. Structural details of these HP structures are given. All phase transitions are reversible upon decompression. Finally, the pressure dependence of the unit-cell parameters of the different phases is reported as well as the RT P-V EOS of the low- and high-pressure phases.

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Figure captions

Figure 1: Selection of XRD patterns measured at different pressures. Background has been subtracted. Pressures are indicated in the figure. The different phases observed are identified as well as the Ne peaks.

Figure 2: XRD patterns measured at 2.5 and 5 GPa (dots). The solid lines are the calculated patterns and the residuals. Ticks indicate the position of Bragg reflections. The insets show two angular regions selected to highlight differences between patterns. In both insets the trace in the top (bottom) corresponds to 5 GPa (2.5 GPa).

Figure 3: Pressure evolution of unit-cell parameters and volume for monazite and monazite-II. Empty symbols: this work. Solid symbols: Ref. [5]. In the top panel and the inset, lines are just a guide to the eye. In the bottom panel, the dashed line represents the fitted EOSs and the solid one the EOS reported in Ref. [5]. Error bars are comparable with symbols size.

Figure 4: XRD patterns measured at 11.1 and 21.1 GPa. Pressures are indicated. The background was subtracted and the residuals of the Le Bail refinement are shown as solid lines. The dots represent the measured patterns and the calculated profiles are shown as solid lines. Ticks indicate the position of Bragg reflections. The assignment to different structures is shown on the left hand side.

Figure 5: Pressure dependence of unit-cell parameters of phase III (squares) and phase IV (triangles). To facilitate comparison for phase III we plotted $c/2$ instead of c . Dotted lines are a guide to the eye. The inset shows the pressure evolution of the β angle (triangles). The line is a guide to the eye. Error bars are comparable with symbols size.

Figure 6: Unit-cell volume versus pressure. Circles and solid lines are the results shown in Fig. 3 for monazite and monazite-II. The squares (triangles) are results from phase III (IV). For phase IV the fitted EOS is shown as a dotted line. Error bars are comparable with symbols size.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6