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PRESSURE-INDUCED PHASE TRANSITION IN ThO_2 AND PuO_2

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Thorium and plutonium dioxides were studied under pressure by the energy dispersive X-ray diffraction method. A double conical slit assembly was used to collect simultaneously the diffracted radiation at five and seven degrees.

ThO_2 undergoes a phase transformation at 40 GPa. The high-pressure phase remains stable up to 55 GPa, the highest pressure reached in the experiment. For PuO_2, a structural transformation occurs near 39 GPa. The observed high-pressure phases of ThO_2 and PuO_2 exhibit similar diffraction spectra. Like for some other fluorite type compounds, the ThO_2 and PuO_2 high-pressure phase has been indexed in the $PbCl_2$-type structure. The bulk modulus has been calculated as $B_0 = 262$ GPa with a pressure derivative of $B'_0 = 6.7$ for ThO_2 and as $B_0 = 379$ GPa with $B'_0 = 2.4$ for PuO_2. The volume decrease at the transition is 12% for PuO_2 and 8% for ThO_2.

1 INTRODUCTION

The double aim of this work on actinide dioxides is to continue the general study of the behaviour of fluorite-type compounds under pressure and to investigate the influence of the 5f electrons on bonding in the crystal. Until now, some results have been obtained for fluorite behaviour under pressure. For the difluoride systems like BaF_2[1-3], SrF_2[4], CaF_2[2,3] and PbF_2[2] the high pressure phase has been interpreted as a $PbCl_2$-type structure. Several fluorite-type dioxides like ZrO_2[5], HfO_2[5], TbO_2[6], PrO_2[6] (quenching experiments) and CeO_2[7,8] also present a phase transformation and the orthorhombic high-pressure structure has been indexed as $PbCl_2$ or δ-Ni_2Si type, according to the compounds. In the case of the actinide dioxides (all have a fluorite structure at ambient pressure), the picture is less clear.

For UO_2[9,10] the high-pressure phase is not well established between the Pnma ($PbCl_2$) and Cmcm space groups, and for the high-pressure phase of NpO_2[11], an orthorhombic structure (Cmcm space group) has been obtained.

ThO_2 has been studied under pressure by X-ray diffraction[12] and by Raman spectroscopy[13]. The transition pressure observed is 40 GPa in the first case and 30 GPa in the second case. Raman spectra analysis has assigned a $PbCl_2$-type structure to the high-pressure phase of ThO_2. We have continued the systematic high-pressure study on actinide dioxides with ThO_2 and PuO_2.

2 EXPERIMENTAL PROCEDURE

The ThO_2 and PuO_2 samples consist of a polycrystalline powder. High-pressure studies have been performed on these compounds using a Syassen–Holzapfel type diamond anvil cell. The samples were loaded in a 0.20 mm diameter hole of an Inconel gasket and silicone oil was used as the pressure transmitting medium. A small ruby was placed with the sample and the pressure measurement carried out in situ according to the ruby fluorescence method. A tungsten X-ray source was used to obtain a continuous energy spectrum from 0 to 58 keV. Energy dispersive X-ray spectra were recorded with a multichannel analyser, at room temperature. The Bragg angle θ was fixed by a double conical slit. This equipment allows the simultaneous acquisition of data at Bragg angles of five and seven degrees and increases the number of available diffraction lines for determining the structure parameters. The precise angle values were determined using a UC reference sample of well known lattice parameters. More experimental details are given by Benedict and Dufour[14].

3 RESULTS

3.1 *ThO_2*

Thorium dioxide, as the other actinide dioxides, at room temperature and ambient pressure exhibits the f.c.c fluorite-type structure (Figure 1a). Its lattice parameter was determined on an X-ray powder diffractometer and was found to be $a = 559.5$ (1) pm in good agreement with literature values[15, 16].

Visual observation through the microscope showed a colour alteration near 30 GPa from the white original colour to golden tint. More detailed study of this effect is planned by optical absorption under pressure. Tests in optical reflectivity failed because of lack in reflecting power; ThO_2 revealed to be transparent from 0.5 to 5 eV in the pressure range up to 45 GPa. Some diffraction pattern modifications appear around 40 GPa and can be characterised by the growth of two new diffraction peaks between the 111 and 200 lines of the fluorite phase (Figure 1b). At 54.8 GPa, the characteristic f.c.c. diffraction peaks have disappeared and the high pressure phase seems to be pure (Figure 1c). Upon releasing pressure this phase remains stable down to 10 GPa, then the f.c.c. phase reappears. Combining the five and seven degrees data and using the Birch and Murnaghan equation[17, 18], we have calculated an average bulk modulus of 262 GPa and a pressure derivative of 6.7, using 21 experimental values.

As in previous publications on other fluorite-type compounds[1–12], we have obtained two possible structures, $\delta-Ni_2Si$ and $PbCl_2$ for the high pressure phase. Both have the same space group, Pnma, with a difference in the positional parameters that affects only the diffraction peak intensities. We cannot use the intensity values to select one of these structures due to a possible orientational effect. But there is a dependence of both these structure types with the axial ratios (*a/c* and *b/c*), which were used for CeO_2[8] to attribute the $PbCl_2$ structure to the high pressure phase. This method is based on the comparison between the axial ratios of different compounds having the Pnma space group at ambient conditions and those of the ThO_2 high pressure phase. Figure 3 shows that the $PbCl_2$ solution fits better than δ-Ni_2Si for the thorium dioxide high pressure phase. The lattice parameters calculated are at 41.2 GPa (transition pressure) $a = 590$ pm, $b = 358$ pm, $c = 681$ pm and at 54.8 GPa (highest pressure) $a = 579$ pm, $b = 358$ pm and $c = 674$ pm (Figure 4). Table 1 gives the observed and calculated *d* spacings for the highest pressure reached.

Further, we are now able to complete the V/V_0 versus pressure plot for the $PbCl_2$ type phase (Figure 2) and to calculate a volume collapse of 8% (the index 0 refers to the ambient pressure volume).

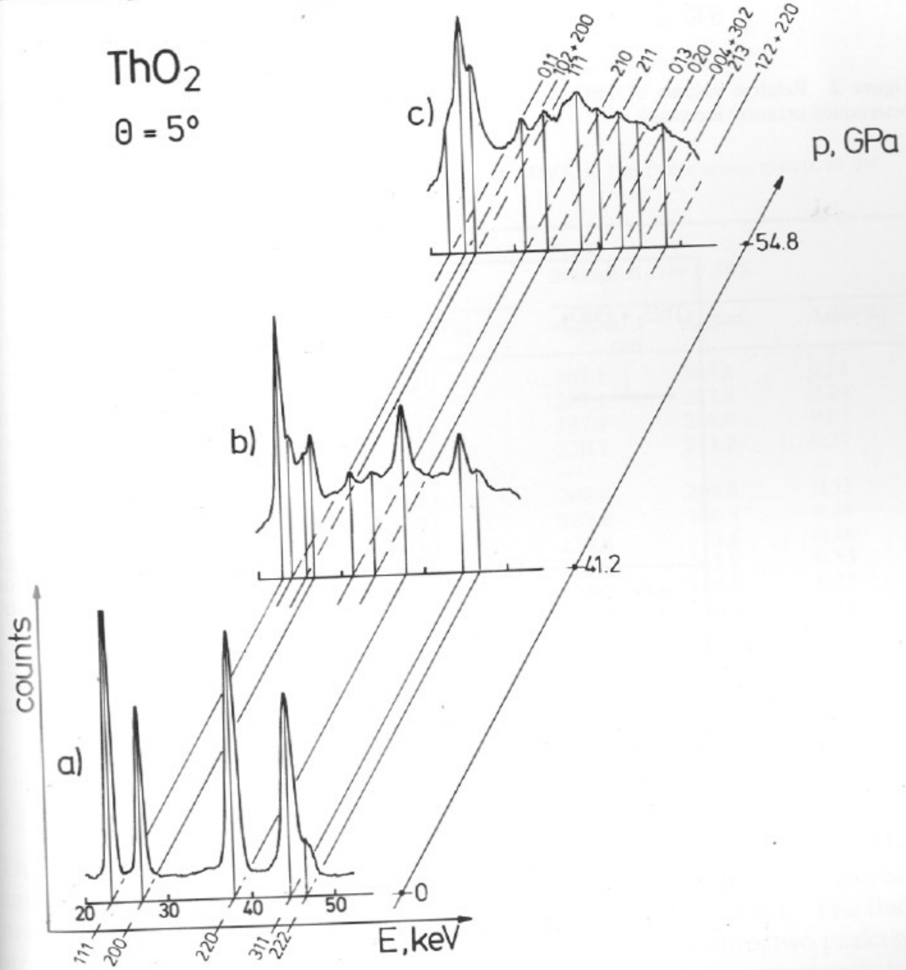

Figure 1 Evolution with pressure of ThO_2 X-ray diffraction spectra. (a) Fluorite phase, (b) mixture of fluorite phase and high-pressure phase, (c) high pressure phase.

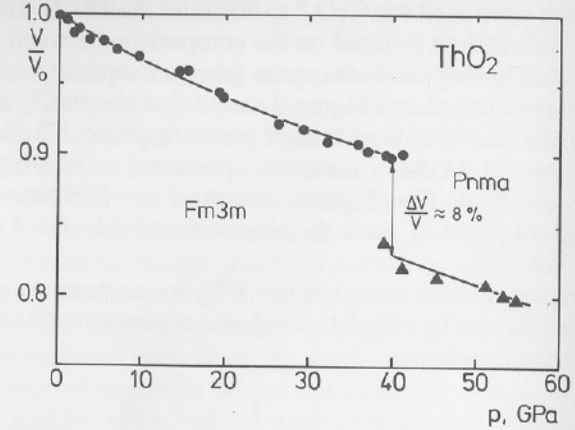

Figure 2 Relative volume of ThO$_2$ versus pressure. ● Fluorite type, ▲ high-pressure phase (both determined pressure increase).

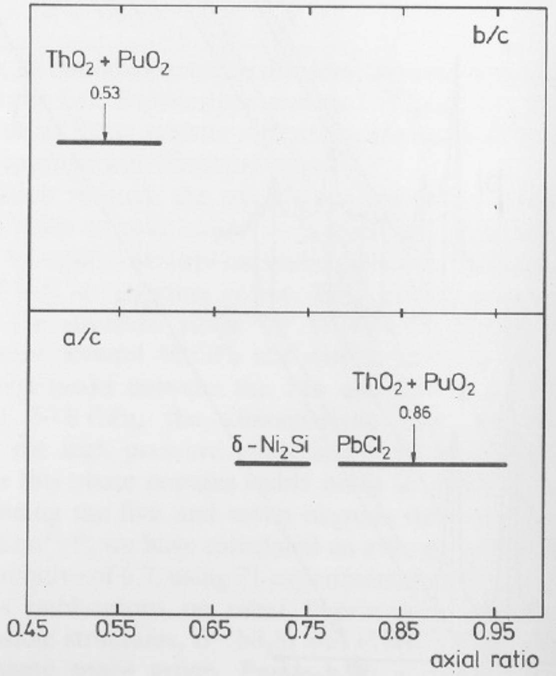

Figure 3 Comparison of the axial ratios of ThO$_2$ and PuO$_2$ high pressure phase with some other compounds of Pnma space group. Both fall in the PbCl$_2$-like group.

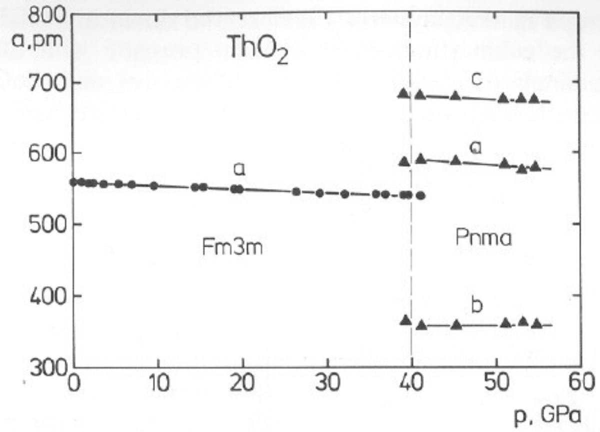

Figure 4 Variation of ThO$_2$ lattice parameters with pressure.

Table 1 Observed and calculated *d* spacing for ThO$_2$ and PuO$_2$ in the Pnma space group, at the highest pressure reached for each compound.

	ThO$_2$ *average* $\Delta d/d = 0.39\,\%$			*PuO$_2$* average $\Delta d/d = 0.38\,\%$		
hkl	d_{obs}(pm)	d_{cal}(pm)	$\Delta d/d$(%)	d_{obs}(pm)	d_{cal}(pm)	$\Delta d/d$(%)
011	315.7	315.4	0.10	307.1	307.8	0.23
102	291.4	292.1	0.24	287.1	287.8	0.24
200	291.4	291.7	0.10	287.1	286.9	0.07
111	277.4	277.5	0.04	270.2	271.2	0.37
210	228.0	225.8	0.96	—	—	—
211	211.6	214.2	1.23	208.8	209.9	0.52
013	189.9	190.3	0.21	187.8	186.9	0.48
020	179.9	178.4	0.83	174.8	173.6	0.46
302	169.0	168.5	0.30	166.7	165.8	0.53
004	169.0	168.7	0.18	166.7	166.3	0.23
213	159.6	159.4	0.13	158.4	156.6	1.14
122	151.7	152.3	0.40	148.8	148.6	0.13
220	151.7	152.2	0.33	148.8	148.5	0.20

3.2 *PuO$_2$*

The PuO$_2$ lattice parameter has been determined as 539.5 (3) pm for the fluorite ambient pressure structure, using X-ray powder diffractometry. Upon increasing pressure, the spectra show a similar evolution as observed for ThO$_2$. The fluorite structure (Figure 5a) remains stable up to 39 GPa. At this pressure, two peaks grow between the 111 and 200 fluorite peaks (Figure 5b). Figure 5c corresponds to the spectrum of the new structure obtained at 49 GPa, highest pressure attained. On releasing pressure, a marked hysteresis is observed down to 11 GPa. The sample retransforms to the cubic structure at ambient pressure with the initial lattice parameter. The similarity between ThO_2 (Figure 1c) and PuO_2 (Figure 5c) postfluorite spectra has led us to select the $PbCl_2$ structure type using the same arguments (Figure 3) as explained before for the thorium dioxide. The lattice parameters calculated at 39 GPa (transition pressure) are $a=564$ pm, $b=338$ pm, $c=657$ pm and $a=562$ pm, $b=344$ pm, $c=649$ pm at 49 GPa (highest pressure).

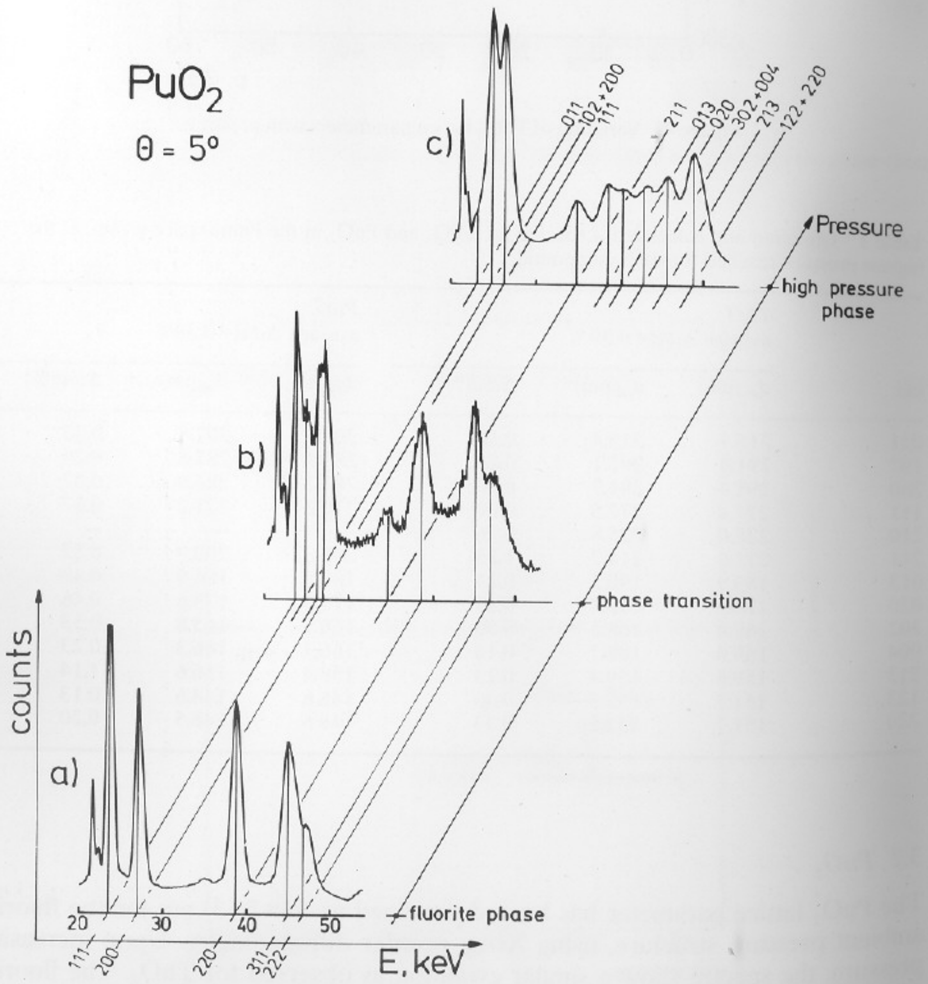

Figure 5 Evolution of PuO_2 diffraction spectra with pressure. (a) fluorite phase, (b) mixture of fluorite and high-pressure phase, (c) high pressure phase.

The observed and calculated d spacings, at the highest pressure obtained, are tabulated in Table 1. Figure 6 shows the lattice parameters of PuO_2 versus pressure. From the relative volume variation versus pressure (Figure 7), we have calculated a bulk modulus of 379 GPa and a pressure derivative of 2.4, using 21 experimental values. The volume collapse at the transition is 12%.

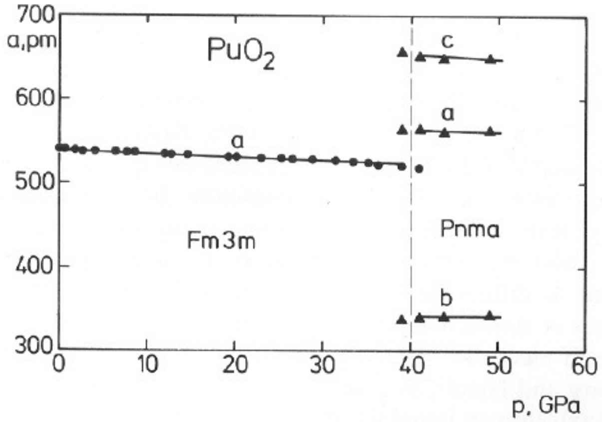

Figure 6 Variation of PuO_2 lattice parameters versus pressure.

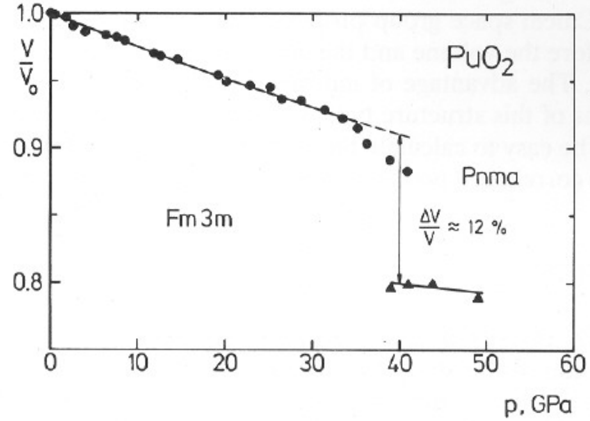

Figure 7 Relative volume of PuO_2 versus pressure. ● Fluorite type, ▲ high-pressure phase (both determined on pressure increase).

4 DISCUSSION

In the case of ThO_2, our results can be compared with previous results obtained by Raman spectroscopy[13]. In both cases, a hysteresis is observed down to about

10 GPa and the $PbCl_2$-type structure is assigned to the high pressure phase. Different values are reported for the phase transition pressure, 40 GPa by X-ray diffraction[12] (this work) and 30 GPa by Raman spectroscopy[13]. This last value has been established on the appearance of a single new vibrational mode and the next measurement has been made at about 38 GPa and shows five new vibrational modes. From these considerations, we conclude that the transition starts between 38 and 40 GPa.

The experimental bulk modulus of 262 GPa, found in this work, for ThO_2 is intermediate to previous experimental values, 193 GPa[19] and 278 GPa[12]. The theoretical value of 290 GPa[20] is higher than the experimental values.

The high bulk modulus of PuO_2 (379 GPa), compared with the other actinide dioxide values (ThO_2, 262 GPa; UO_2[9], 207 GPa; NpO_2[11], 200 GPa) and with the theoretical value of 190 GPa[20] remains at present unexplained. It seems interesting to continue the pressure investigation on actinide dioxides (AmO_2) to check for further evolution of the compressibility with increasing Z of the actinide.

On the one hand the similar behaviour of these compounds with the other fluorite materials as difluorides and non-actinide dioxides, on the other hand the low 5f occupancy of thorium, leads us to assume that the observed transition is not induced by the 5f electrons. The structural change can be described, as done by Kessler, Monberg and Nicol[2], as a shift of half of the cations from the [111] plane along the [111] axis into an immediately adjacent upper plane, and of the other half of the cations into the lower adjacent plane.

To obtain more information about the origin of the phase transition, it seems useful to have a homogeneous indexation of the high pressure phase for all actinide dioxides. The Cmcm space group proposed for UO_2[9] and NpO_2[11] is a supergroup of Pnma; therefore the volume and the atomic position calculated in both groups is relatively close. The advantage of indexing in the $PbCl_2$ type is that we know the atomic positions of this structure type in several compounds at ambient pressure[16] and it will thus be easy to calculate the average interatomic distances in the actinide dioxides and to correlate, if possible, these results with the phase transition.

5 CONCLUSION

ThO_2 and PuO_2 transform to a high-pressure phase of the $PbCl_2$ type around 40 GPa. Extension of the study to heavier actinide dioxides should provide some more information with a view to explain the high bulk modulus of PuO_2 with respect to those observed for other actinide dioxides. A unified description of the high-pressure phases of the actinide dioxides in space group Pnma should be tried.

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