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Pressure-induced zircon-type to scheelite-type phase transitions in $YbPO_4$ and $LuPO_4$

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ABSTRACT

The tetragonal orthophosphates, $YbPO_4$ and $LuPO_4$, were studied by in situ X-ray diffraction (XRD) at pressures up to 52 and 43 GPa, respectively. A reversible phase transition from the zircon structure-type to the scheelite structure-type was found at ~22 GPa for $YbPO_4$ and 19 GPa for $LuPO_4$. Coinciding with the transition from the zircon structure-type to the scheelite structure-type, there is a ~10% reduction in volume and a significant increase in the bulk modulus for both compounds.

1. Introduction

Rare-earth element orthophosphates, $REEPO_4$ can form either in the tetragonal xenotime structure ($REE = \text{Tb–Lu}$) or the monoclinic monazite structure ($REE = \text{La–Gd}$) [1]. Both structures are closely related to that of zircon. Orthophosphates are important ceramic materials that have attracted an increasing level of interest in recent years. Their main potential applications include host matrices for the immobilization of certain types of radioactive wastes [2,3], solid ion conductors [4], and multi-layered weak-bonded ceramic composites [5]. The tetragonal ($I4_1/amd$) orthorphosphates, $YbPO_4$ and $LuPO_4$, are composed of isolated PO_4 tetrahedra that are joined in edge-sharing chains parallel to the *c*-axis. The PO_4 tetrahedra alternate eight-fold coordination polyhedra that contains the lanthanide ion (Fig. 1a) and these orthophosphates are isostructural with zircon ($ZrSiO_4$) at ambient conditions [1,6].

A pressure-induced phase transition to the scheelite structure-type was observed in zircon many years ago [7,9]. For the zircon case, the scheelite structure-type is reidite, and the zircon-to-reidite phase transition is irreversible [10]. The structural properties and compressibility of zircon and reidite have been intensively studied during the past few decades with both hydrostatic and dynamic compression methods [5–15]. Reidite was regarded as the hardest materials that are composed of SiO_4 tetrahedra [8,15]. A similar pressure-induced phase transition has been observed in other ABO_4 compounds that are isostructural with zircon, such as YVO_4 [16]. The structural stability of the scheelite-type ABO_4 oxides at high pressures has also been under investigation since the 1970s [17–19], especially in the case of the alkaline metal tungstates, and several complicated high-pressure structures were identified recently [19]. For the rare-earth orthophosphates, the synthesis, optical, transport and thermo-chemical properties [20–22], as well as the structural response to ion irradiation [23], have recently been studied, however, no investigations for the structural response of these materials to high pressures are reported. In this paper, we studied the structural response of two rare-earth orthophosphates, $YbPO_4$ and $LuPO_4$, to high pressurization using in situ synchrotron X-ray diffraction (XRD), and reported a reversible phase transformation from the zircon structure-type to the scheelite structure-type.

2. Experimental details

Single crystals of $YbPO_4$ and $LuPO_4$ were grown by a high-temperature flux method. Details of this synthesis process are described elsewhere [22]. In carrying out the XRD measurements, the single crystals were crushed into fine powders in a mortar

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until no obvious separated spots can be found in diffraction image and the average grain size was estimated to be less than 2 μm. High-pressure experiments were performed with a diamond anvil cell (DAC) using hardened stainless-steel gaskets for the XRD measurements. Standard methanol/ethanol (4:1) liquid was used as the pressure medium, which can keep good hydrostatic conditions below 10–12 GPa. The in situ high-pressure XRD measurements for $YbPO_4$ were performed using a synchrotron radiation X-ray source (0.4066 Å) at the X17C station of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. The beam was focused to a spot size less than $25\times25\,\mu m^2$, and the Debye rings were recorded with image-plate techniques in the transmission mode. The XRD patterns for $LuPO_4$ were collected at the Cornell High Energy Synchrotron Source (CHESS) with a monochromated X-ray beam (0.4960 Å and beam size ~50 μm), and the diffraction rings are recorded with a Mar345 CCD detector. All of the XRD patterns were integrated from the images using the FIT2d software package [24]. The pressure in all of the experiments was measured by the ruby fluorescence method, and the XRD patterns were refined by the Rietveld method (Fullprof in the software package Winplotr [25]) based on the known structural models.

3. Results and discussion

Fine powders of the orthophosphates $YbPO_4$ and $LuPO_4$ were studied by XRD up to pressures of 52 and 43 GPa, respectively, and selected XRD patterns are shown in Fig. 2. The XRD patterns of both phosphates at lower pressures confirmed the zircon

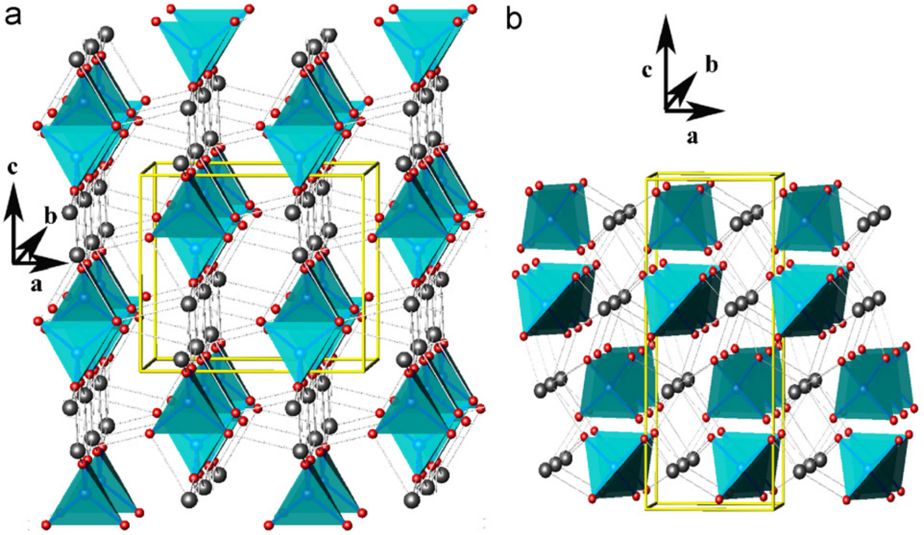

Fig. 1. Structures of (a) zircon structure-type orthophosphates and (b) high-pressure scheelite structure-type orthophosphates. The tetrahedra are PO_4 units and the spheres are lanthanides.

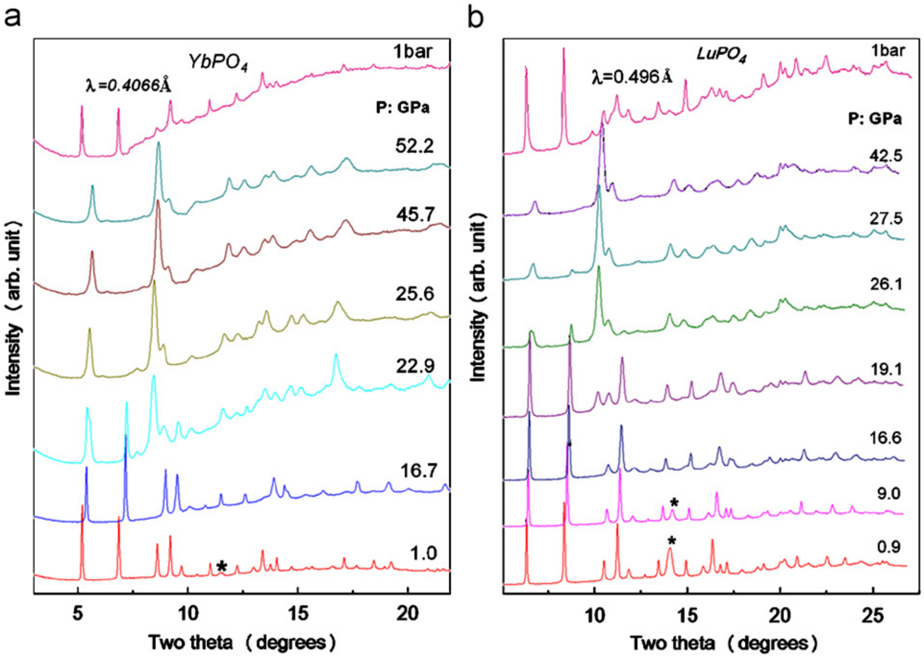

Fig. 2. Selected XRD patterns at various pressures for (a) $YbPO_4$ and (b) $LuPO_4$. The diffraction peaks marked with a star are from the steel gasket. The top patterns measured at 1 bar are from the quenched sample.

structure type. A pressure-induced phase transition was clearly observed in the XRD patterns, and the initiation of the phase transition occurred at ~22 GPa for $YbPO_4$ and 19 GPa for $LuPO_4$. For both $YbPO_4$ and $LuPO_4$ the high-pressure phase has the same structure. Based on the zircon-to-reidite structural transition, the high-pressure phase is isostructural with reidite (Fig. 1b). The tetragonal scheelite structure of both phosphates is stable up to the maximum pressure reached in our experiments. The XRD patterns of the samples after release of the pressure are also included in Fig. 2 (top patterns). The quenched samples show mainly the zircon structure-type, though some weak diffraction peaks from the scheelite-type high-pressure phase are still evident for $LuPO_4$. These results clearly show that the pressure-induced zircon-type to scheelite-type structural transitions in $YbPO_4$ and $LuPO_4$ are reversible, and the scheelite high-pressure phase cannot be quenched at ambient conditions. This behavior is different from that of both zircon ($ZrSiO_4$) and YVO_4, where the high-pressure phases in these two systems can be quenched to room conditions.

The structure of ABO_4 compounds is composed of two basic sublattices—BO_4 tetrahedra and AO_8 polyhedra. Errandonea et al. [26] have pointed out that the transition pressure depends on the ratio of BO_4 tetrahedron and A-cations. The observed transition pressure for ABO_4 compounds with scheelite structure fit the empirical formula in general. To the studied phosphates, the ratio of size of PO_4 polyhedron and A^{3+} is 1.76–1.78 and the predicted transition pressure is around 10 GPa, much lower than the observed pressures. The higher transition pressures in our experiments are not due to the non-hydrostatic effect, because non-hydrostatic conditions usually make phase transition earlier [27], but due to the different crystal structures. The empirical formula used in Ref. [26] may need some modifications in order to describe the transition pressure of phosphates with zircon-type structure.

The observed XRD patterns of the zircon-type and scheelite-type polymorphs of both phosphates were refined, as noted above, by the Rietveld method, using software Fullprof based on the known structural models of zircon and reidite. In fact, the ratio of the intensity of the first two strong diffraction peaks—(011) and (020)—of the zircon-type structure in Fig. 2 are not well consistent in our patterns. This is due to the orientation effect (contributed by some large particles) in the sample. Though it has no effect on the refinement of lattice parameters, but it does hurt the accuracy of the refined atomic positions. Fig. 3 shows the fitting results for $LuPO_4$ at 19.1 and 42.5 GPa. The XRD pattern at 19.1 GPa was refined considering the presence of multiple phases, and convergence was achieved at residuals of $R_{B1} = 9.6\%$, $R_{B2} = 10.2\%$ and $\chi^2 = 1.1$. Table 1 lists the refined lattice parameters for both the zircon and scheelite structure types of $YbPO_4$ and $LuPO_4$ at the indicated pressures.

Although the high-pressure structure of these orthophosphates is also tetragonal, the space group ($I4_1/a$) is different from that of the low-pressure structure ($I4_1/amd$). Both the zircon- and scheelite-type phases of phosphates are characterized by isolated PO_4 tetrahedra. The A-cations in both phases are coordinated by eight oxygen ions forming a trianglular dodecahedron, but the central A-cations experience a change in crystal field due to the different bond length and bond angles [28]. The variation of lattice parameters for $YbPO_4$ and $LuPO_4$ with increasing of pressure, is similar (Fig. 4), but the behaviors of the zircon and scheelite structure types, with increasing pressure, are different. The unit cell of the zircon structure-type orthophosphate along the a-axis is "soft" because the ratio of c/a increases with increasing pressure; however, the high-pressure scheelite structure shows the opposite trend (Figs. 4a and b). The pressure dependence of the unit cell volumes of $YbPO_4$ and $LuPO_4$ is shown in Figs. 4c and d. There is a ~10% volume reduction during the phase transition for both phosphates, which is similar to that of other related zircon structure types [16]. In order to determine the bulk modulus B_0, the pressure–volume data for both systems were

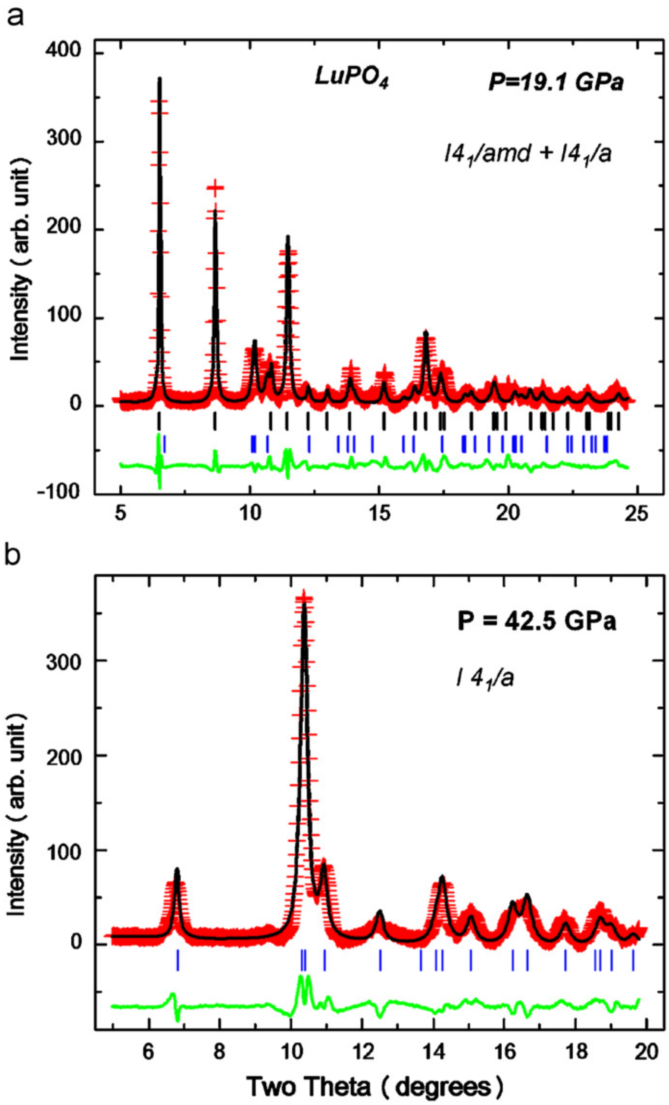

Fig. 3. Reitveld refinement results for $LuPO_4$ at: (a) 19.1 GPa, mixture of zircon-type structure ($I4_1/amd$) and scheelite-type structure ($I4_1/a$); (b) 42.5 GPa, scheelite-type high-pressure phase.

Table 1
Structural parameters of zircon- and scheelite-type orthophosphates at selected pressures

	P (GPa)	S.G.	a (Å)	c (Å)	O-site	x	y	z
$YbPO_4$	1.0	$I4_1/amd$	6.801(2)	5.965(2)	16f	0	0.9392(6)	0.7836(6)
	45.7	$I4_1/a$	4.491(5)	10.352(13)	16f	0.2486(8)	0.5754(9)	0.5800(4)
$LuPO_4$	0.9	$I4_1/amd$	6.789(3)	5.960(3)	16f	0	0.9377(5)	0.7926(6)
	42.5	$I4_1/a$	4.552(1)	10.393(4)	16f	0.2665(7)	0.5892(4)	0.5808(2)

In the zircon-type phase, the special positions for the cations are: Yb(or Lu) at 4a $(0,\frac{3}{4},\frac{1}{8})$ and P at 4b $(0,\frac{1}{4},\frac{3}{8})$. Those for the scheelite phase are Yb (or Lu) at 4b $(0,\frac{1}{4},\frac{5}{8})$ and P in 4a $(0,\frac{1}{4},\frac{1}{8})$. $Z = 4$.

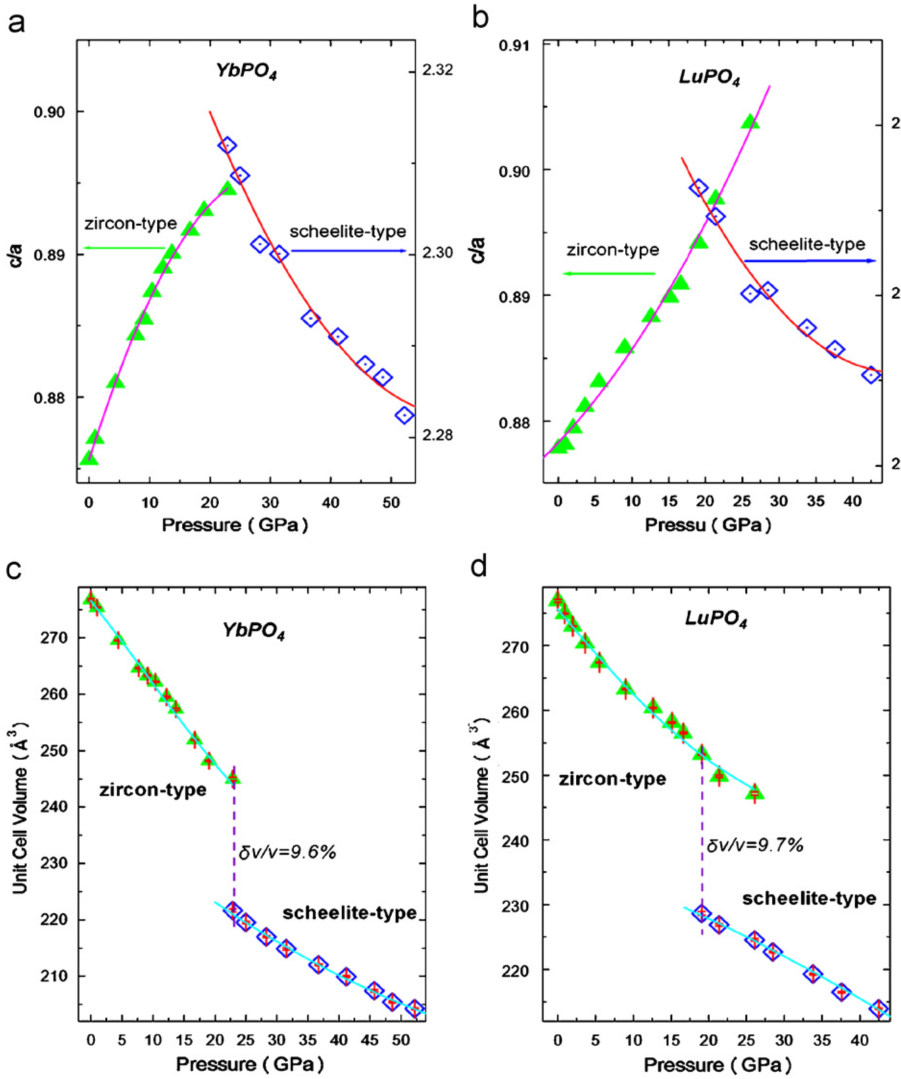

Fig. 4. The pressure dependence of the c/a ratio (a and b) and unit cell volume (c and d) for the orthophosphates $YbPO_4$, $LuPO_4$ and their high-pressure structures. There is a ~10% volume reduction at the transition pressure for both compositions.

fitted with the Birch–Murnaghan equation of state [29]:

$$p = \frac{3}{2}B_0(x^{-7/3} - x^{-5/3})\left[1 - \frac{3}{4}(4 - B_0')(x^{-2/3} - 1)\right] \tag{1}$$

where $x = V/V_0$, V is the volume per formula unit at pressure p, and V_0 is the corresponding volume at zero pressure, B_0 and B'_0 are the bulk modulus and its pressure derivative evaluated at zero pressure.

The fit of the p–V data yields a bulk modulus of $B_0 = 150(5)$ and 218(2) GPa for the zircon-type and scheelite-type $YbPO_4$, when the pressure derivative B'_0 is fixed at 4, and the corresponding values for $LuPO_4$ are $B_0 = 184(4)$ GPa (zircon-type) and 226(3) GPa (scheelite-type). The scheelite-type high-pressure phases have larger bulk moduli than the zircon-type phases. The larger bulk modulus of the scheelite-type structures indicates that the high-pressure phases are less compressible. The bulk modulus of the zircon-type orthophosphates and their high-pressure forms are less than the values of zircon and reidite [10,11,30]. However, the observed bulk modulus of the high-pressure form of the orthorphosphates is compatible to the theoretical values for reidite, which were calculated with the density functional method [14].

We note that there are other phosphates of similar stoichiometry, but a different structure, such as $AlPO_4$ and $FePO_4$. In these structures, the phosphorous is in six-fold coordination. These structures were widely investigated and numerous pressure-related phenomena have been observed [31–33], such as pressure-induced transformations and amorphization. For $YbPO_4$ and $LuPO_4$, the phosphorus remained in four-fold coordination, and there was no evidence of amorphization. However, compared to structures with phosphorus in six-fold coordination [33], the orthophosphates are less compressible and have larger bulk modulus.

Hazen and Prewitt [34] found that the bulk modulus of certain binary oxides or silicates can be directly correlated to the compressibility of the A-cation coordination polyhedra. To most scheelite-related ABO_4 structures, the bulk modulus obeys a linear relationship to the compressibility of AO_8 polyhedron in the following empirical formula [35]:

$$B_0 = 610(110)\frac{z_A}{d^3_{A-O}}, \tag{2}$$

where B_0 is the bulk modulus in GPa, z_A is the formal charge of A-cations ($1 \leqslant z_A \leqslant 4$), and d_{A-O} is the average A–O distance (Å) in the AO_8 polyhedron. The calculated bulk modulus for the

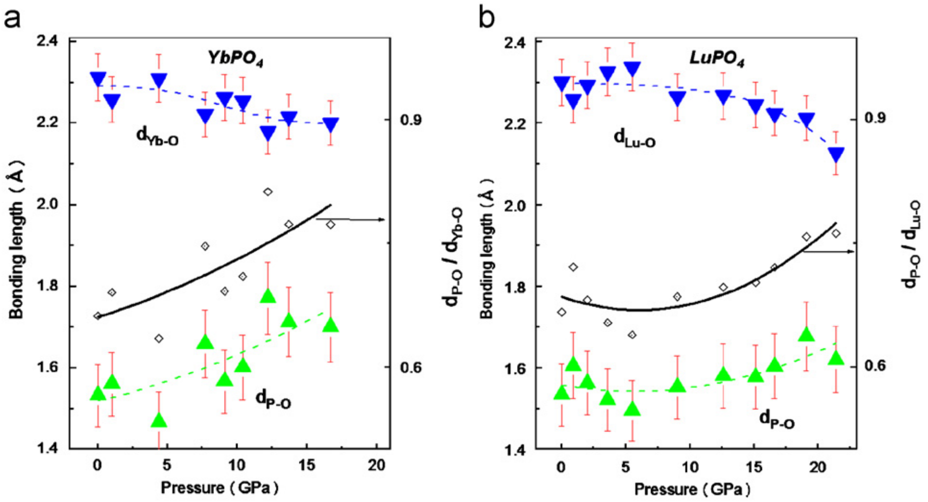

Fig. 5. Pressure dependence of the bonding length P–O in PO_4 tetrahedra and A–O in AO_8 polyhedra. The symbols in the middle of both figures represent the ratio of the bond lengths. All the dashed and solid lines are guide for eyes.

low-pressure phase zircon-type phosphates is around 150 GPa for both $YbPO_4$ and $LuPO_4$, which fits the observed values quite well. However, the bulk modulus of the scheelite structure calculated with above formula is less than 160 GPa, which is obviously lower than the measured values. If we change the formal charge for Lu and Yb to 4, the calculated bulk modulus will be 214 and 203 GPa for $YbPO_4$ and $LuPO_4$, respectively, which fits the observed values quite well.

The pressure dependence of the average bonding length in the PO_4 tetrahedra and AO_8 polyhedra in the zircon-type $YbPO_4$ and $LuPO_4$ was plotted in Fig. 5. The average bond length of Yb–O and Lu–O decreases with the increase of pressure, however, the bond length of P–O in both compounds shows a tendency to increase with pressure. This slight increase may be realized through the tune of bonding angles in PO_4 tetrahedron. The ratio of the average bonding length $\langle r_{\text{P–O}}\rangle/\langle r_{\text{A–O}}\rangle$ increases with pressure. The results clearly indicate that the AO_8 polyhedra are easier to be compressed in the zircon-type orthophosphates. To the scheelite-type high-pressure phase, our data of bond length are too dispersive. The dispersion of the bonding length at high pressure may be caused by the non-hydrostatic conditions. However, the refinement of the lattice parameters for the high-pressure phase is reliable.

The diffraction peaks at high pressure are quite broad and some additional weak diffraction peaks seem to appear in the patterns (Fig. 2), such as the XRD patterns after 42.5 GPa for $LuPO_4$ and 45.7 GPa for $YbPO_4$. A second-phase transition was reported recently in zircon-type $LuVO_4$ [36], and a similar phase transition sequence of zircon–scheelite–fergusonite is expected to occur in rare-earth phosphates. Due to the very close structural relations and very similar XRD patterns of scheelite- and fergusonite-type structures, we cannot judge the existence of the second-phase transition in our samples and this should be another related topic for orthophosphates.

4. Conclusions

In summary, $YbPO_4$ and $LuPO_4$ with the zircon structure-type were studied by in situ XRD at high pressures. A pressure-induced phase transition to the scheelite structure was observed in both systems at ~22 and 19 GPa, respectively. The compressibility of the zircon structure-type and the high-pressure phase were determined based on the pressure–volume data. The pressure dependence of bond length revealed that the compress of AO_8 polyhedra is dominant in the zircon-type phosphates. The high-pressure scheelite structure types are less compressible than the low-pressure zircon structure type, and the high-pressure phase of the orthophosphates was not quenchable at ambient conditions.

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