Raman study of zircon-structured RPO\(_4\) (R = Y, Tb, Er, Tm) phosphates at high pressures

E. Stavrou, A. Tatsi, E. Salpea, Y.C. Boulmetis, A.G. Kontos, Y.S. Raptis and C. Raptis
Physics Department, National Technical University of Athens, GR-15780, Athens, Greece

craptis@central.ntua.gr

Abstract. The Raman spectra of tetragonal RPO\(_4\) (R = Y, Tb, Er, Tm) phosphates belonging to the zircon-structure class (space group \(D_{4h}^{19}\)) have been measured at high pressures up to 7.9 GPa (YPO\(_4\), ErPO\(_4\)) and 15.5 GPa (TbPO\(_4\), TmPO\(_4\)). Most of the 12 Raman active modes of this crystal class have been observed at high pressures using a Diamond Anvil Cell. A characteristic feature in the spectra of all crystals studied is the anomalous pressure dependence of the \(B_{2g}\) symmetry internal bending mode which softens substantially with increasing pressure to the extent that a level crossing occurs between this mode and one normal \(E_g\) rotational mode. These observations imply that an incipient structural phase transition of the crystals may occur at a higher pressure. Such a phase transition has been observed for TbPO\(_4\) at a pressure of \(-9.5\) GPa. The abrupt spectral variations observed at this pressure, indicate that TbPO\(_4\) undergoes a first-order phase transition from tetragonal zircon to a lower symmetry structure which is quenchable upon pressure release.

1. Introduction
Rare-earth phosphates RPO\(_4\) have attracted considerable interest in the past for their magnetic properties at low temperatures [1-7], and as possible host materials for laser-active media and for long-term storage of radio-active wastes [8,9]. These compounds crystallize in two closely related structures at ambient conditions: those with the heavier rare-earth ions (R = Tb to Lu) [8,9] have the zircon structure [10] (ZrSiO\(_4\), \(D_{4h}^{19}\) space group, two formula units in the primitive cell), while the lighter ones (R = La to Gd) crystallize in the monoclinic monazite structure [8,9] (CePO\(_4\), \(C_{2h}^{5}\) space group, four molecules in the primitive cell). Apart from the heavy rare-earth phosphates, other phosphates, such as YPO\(_4\) and ScPO\(_4\), also crystallize in the zircon structure [8,9].

In the zircon-structured phosphates, the phosphorus atoms are four-fold coordinated by oxygen forming strongly bound (PO\(_4\))\(^{3-}\) tetrahedral units, while the R\(^{3+}\) cations are eight-fold coordinated to oxygen in RO\(_8\) dodecahedral arrangements; the two types of polyhedra link in an alternating edge-sharing fashion forming linear chains parallel to the \(c\) axis [9]. Either of the R\(^{3+}\) and (PO\(_4\))\(^{3-}\) ions occupy \(D_{4d}\) symmetry sites, with the oxygen atoms being in \(C_{i}\) sites. On the other hand, the monazite structure is, in fact, a distorted zircon structure, but with higher compactness since the coordination of R\(^{3+}\) cation increases to nine resulting in the formation of RO\(_9\) polyhedra [9] in place of RO\(_8\) dodecahedra. Considering the rare-earth phosphates as polymorphs, it has been suggested [9] that the monazite structure is the low-temperature form of these compounds, while the zircon structure corresponds to the high-temperature form; this idea has been supported by reports [1,2] that TbPO\(_4\) undergoes a phase transition from zircon- to monoclinic (probably monazite) structure at 2.15 K.

Generally, crystals with the zircon-type structure are known, from X-ray [11,12] and Raman studies [12-15], to sustain an irreversible pressure-induced phase transition to tetragonal scheelite-type structure (\(C_{4h}^{6}\) space group, two molecular units in the primitive cell), thus lowering slightly their symmetry to a more compact structure. Those studies [11-15] have dealt with rare-earth vanadates RVO\(_4\) [11-13] and certain chromat MCrO\(_4\) (M = Ca, Y) [14,15]. As for the zircon-structured rare-earth phosphates, there is only one relevant report [16] recently on DyPO\(_4\) whose Raman spectrum has been measured up to a pressure of 7.5 GPa, but without any evidence for a completed structural modification over this pressure range.

In this article, we present high-pressure Raman studies of zircon-structured phosphates, namely, the rare-earth phosphates TbPO\(_4\), ErPO\(_4\) and TmPO\(_4\), and YPO\(_4\). Primary objective of the work is to investigate whether these crystals sustain any pressure-induced structural modifications. The investigations are motivated by the close relation between the zircon and monazite structures and
the fact that application of pressure lowers, in most cases, the crystal symmetry. Hence, Raman spectra of these crystals have been measured up to 7.9 GPa (YPO4, ErPO4) and 15.5 GPa (TbPO4, TmPO4) with the use of a Diamond Anvil Cell (DAC). Such an anticipated lowering of the crystal symmetry has been observed in TbPO4 which displays a first-order phase transition at a pressure of about 9.5 GPa.

From group theory considerations, it is known that there are 12 Raman active modes for the zircon \( D_{4h} \) structure having the following symmetries: \( 2A_{1g} + 4B_{1g} + B_{2g} + 5E_g \); of these, seven \( (2A_{1g} + 2B_{1g} + B_{2g} + 2E_g) \) are internal modes \([8,10]\) corresponding, in the case of the RPO4 compounds, to vibrations of oxygen atoms in the \((PO_4)^3^-\) units, four \( (2B_{1g} + 2E_g) \) are external translational due to translations of the \((PO_4)^3^-\) and \( R^{3+} \) ions, and one \( (E_g) \) is rotational of whole \((PO_4)^3^-\) units. The atomic displacements of all normal modes of the zircon structure have been known \([10]\) for a long time.

The Raman spectra of zircon-structured phosphates at ambient conditions were reported by different researchers \([8,17,18]\) who also made mode symmetry assignments based on polarized Raman measurements and oriented single crystals. As those mode assignments \([8,17,18]\) are not in full agreement among each other, we have also performed (at ambient conditions, outside the DAC) polarized Raman measurements on oriented single crystals and produced our own mode assignments for the heavy rare-earth phosphates.

2. Experimental

Polarized Raman measurements at ambient conditions have been carried out using flux-grown oriented single crystals and a 90\(^\circ\) scattering geometry. Details on the polarized Raman experiments and mode assignments of crystals will be published elsewhere \([19]\).

Small chips of RPO4 \((R = Y, Tb, Er, Tm)\) crystals, with nominal dimensions 50-80 \( \mu m \), cut from larger single crystals were loaded into a Syassen-Holzapfel-type DAC, along with ruby chips for determining the pressure (through the photoluminescence of ruby). Typical diameter values of \(~200 \mu m\) were used for the gasket hole which was filled with 4:1 methanol-ethanol pressure transmitting medium. Raman spectra were obtained up to 15.5 GPa for TbPO4 and TmPO4, and up to 7.9 GPa for YPO4 and ErPO4 in sequences of both increasing and decreasing pressure.

The Raman spectra were excited basically by the 514.5 nm line of an Ar\(^+\) laser, but in certain experimental sessions (for example, in the case of ErPO4) the 476.2 nm line of a Kr\(^+\) laser was used to avoid intense levels of photoluminescence. Scattered light from the DAC was analyzed and detected by a system of a SPEX 1403 double spectrometer, a cooled photomultiplier and a photon counting unit. Most of the high-pressure Raman measurements were not polarized, thus making possible detection of all mode symmetries in one spectral run. However, in some occasions, in order to resolve some increasingly overlapping (with pressure) Raman peaks, such as that involving the crossing of the \( B_{2g} \) internal and the nearby \( E_g \) rotational modes, detailed slow-scans were obtained using parallel- and cross-polarization configurations.

3. Results and Discussion

As a representative example of the polarized measurements at ambient conditions, Figure 1 shows the \( xx, yy, \) and \( yz \) polarized components of the Raman spectrum of TbPO4 corresponding to \( A_{1g}, (A_{1g} + B_{1g}), B_{2g} \) and \( E_g \) mode symmetries, respectively. Application of selection rules on these polarized spectra enabled us to make symmetry assignment for the eleven (out of twelve expected) Raman modes of TbPO4, and the results of this assignment are given in Table I, along with other interesting quantities discussed below. Similar mode assignments were conducted for the other three crystals of the study, with the results being, more or less, the same. Also, the mode frequencies of the other crystals are very close to those of TbPO4 as the masses of the rare-earth \( R^{3+} \) ions are almost the same. Our mode assignment for the heavy rare-earth phosphates is in full agreement with that of Ref. 17, but differs from those of Refs 8 and 18 for three only modes.

In Table I, apart from the symmetry and character (internal, external) assignments, ambient conditions frequencies \( \omega_0 \) and normalized \((1/\omega_0)(\partial^2\omega/\partial P)T\) slopes for the 11 observed Raman modes of TbPO4 are also shown. The normalized slopes are given in place of Grüneisen parameters whose determination is not feasible because of the lack of elastic constants data in the literature for TbPO4 or any other crystal of this study.
Table I. Ambient conditions frequencies $\omega_0$, assignments, and normalized $(1/\omega_0)(\partial\omega/\partial P)_T$ slopes of the Raman active modes of TbPO$_4$.

| $\omega_0$ (cm$^{-1}$) | Assignment | Character     | $(1/\omega_0)(\partial\omega/\partial P)_T$ (10$^{-3}$ GPa$^{-1}$) |
|------------------------|------------|---------------|---------------------------------------------------------------|
| 130                    | $E_g$      | Extern. Transl. | -0.5                                                          |
| 141                    | $B_{1g}$   | Extern. Transl. | 7.3                                                           |
| 185                    | $E_g$      | Extern. Transl. | 0.5                                                           |
| 293                    | $E_g$      | Rotational     | 13.4                                                          |
| 331                    | $B_{2g}$   | Internal       | -1.7                                                          |
| 484                    | $A_{1g}$   | Internal       | 1.5                                                           |
| 576                    | $E_g$      | Internal       | 1.7                                                           |
| 649                    | $B_{1g}$   | Internal       | 3.0                                                           |
| 995                    | $A_{1g}$   | Internal       | 5.3                                                           |
| 1014                   | $E_g$      | Internal       | 4.9                                                           |
| 1049                   | $B_{1g}$   | Internal       | 5.0                                                           |

The evolution of the Raman spectrum of YPO$_4$ with pressure is given in Figure 2. Ten Raman modes were observed at ambient pressures when the crystal was inside the DAC. As the pressure is increased, an additional band appears at ~210 cm$^{-1}$ (at 4.7 GPa); such a band was not observed in the other crystals of this work, but had been reported previously [8] in YPO$_4$ without symmetry assignment. The pressure-independent peak at 418 cm$^{-1}$ (Fig. 2) is due to Raman scattering from the sapphire (Al$_2$O$_3$) window [20] of the DAC and has proved useful for calibration of spectra. Similarly, as the pressure is increased and the $E_g$ internal mode at 576 cm$^{-1}$ shifts, an additional
peak emerges at this frequency which remains pressure-independent throughout the pressure range; this peak is also attributed to scattering from the sapphire window [20]. In the spectra of Fig.2, it is interesting to note the softening with pressure of the \( B_{2g} \) internal bending [10] mode to such an extent that it crosses the \( E_g \) rotational mode. Such level crossings have been also observed in the other three rare-earth crystals of this study, as well as in DyPO\(_4\) in a previous study [16]. The softening with pressure of the \( B_{2g} \) mode is, in fact, an indication for an incipient phase transition at a higher pressure, which has not been detected for YPO\(_4\) up to 7.9 GPa. Recording of spectra was not possible above 7.9 GPa for YPO\(_4\) and ErPO\(_4\) as a combined result of low Raman signal and gasket hole deformation. Similar spectral evolution with pressure was observed in ErPO\(_4\) and TmPO\(_4\), again without evidence for a completed phase transition over their respective pressure ranges. Mode frequency-pressure plots for the YPO\(_4\), ErPO\(_4\) and TmPO\(_4\) crystals are given in Figure 3. In these plots the level crossing of the \( B_{2g} \) and \( E_g \) modes is seen at about 5.7, 6.0 and 4.8 GPa for YPO\(_4\), ErPO\(_4\) and TbPO\(_4\), respectively.

The pressure dependence of the Raman spectrum of TbPO\(_4\) is, however, significantly different compared to the other three crystals of the study. After the level crossing at about 7.0 GPa, it is clearly evident that at a pressure \( P_c \approx 9.5 \) GPa, substantial qualitative and quantitative changes take place (Figure 4), with the most notable being the abrupt nature of these changes and the increase of the Raman bands from 11 to, at least, 20. These results imply a definite first-order phase transition of TbPO\(_4\) from tetragonal zircon to a lower symmetry structure. All spectral changes are reversible up to 9.5 GPa, but above this pressure the observed drastic changes are irreversible, thus showing that the phase transition is quenchable. These changes are also illustrated in the frequency-pressure plots of Figure 5 for TbPO\(_4\) in which mode discontinuities and decrease of \( \left( \frac{\partial \omega}{\partial P} \right)_T \) slopes are evident. Only few Raman bands of the low-pressure zircon phase appear to evolve continuously to a corresponding band of the high-pressure phase. Other crystals with the zircon structure are known [11-15] to irreversibly transform to the scheelite structure which displays 13 Raman active modes. From the large number (20) of Raman modes observed above \( P_c \), it is clear that the scheelite structure should be excluded as a probable high-pressure phase for TbPO\(_4\). In this situation, a transition to an even lower symmetry structure, such as a monoclinic one, looks likely. This proposition is supported by the resemblance of the high-pressure spectrum of TbPO\(_4\) to those of the light rare-earth phosphates which crystallize in the monoclinic monazite structure [8,9]. The latter structure has four molecules in the primitive cell and 36 Raman active optic modes (18\( A_g \) + 18\( B_g \)), so it can be considered as a likely candidate for the high-pressure phase of TbPO\(_4\). The absence of a similar pressure-induced transition in YPO\(_4\), ErPO\(_4\) and TmPO\(_4\) may be due to a higher \( P_c \) required for these compounds. It is reminded that, among the heavy rare-earth phosphates, TbPO\(_4\) is closest
to the family of the light RPO$_4$ ones (R = La to Gd). Therefore, it should be expected that the pressure threshold ($P_c$) required for a phase modification will be the lowest for TbPO$_4$ in comparison to the other members of the heavy rare-earth phosphates family. Further discussion on the high-pressure phase transition of TbPO$_4$ will be given in a forthcoming article [19].

4. Conclusions
The pressure dependence of the Raman spectra of four zircon-structured phosphates, namely YPO$_4$, ErPO$_4$, TmPO$_4$ and TbPO$_4$, has revealed (in all crystals) an anomalous softening of the $B_{2g}$ internal bending mode, as well as a level crossing of this mode with the $E_g$ rotational mode. The anomalous softening of the $B_{2g}$ mode is an indication for an incipient phase transition in the crystals at a higher pressure.

The abrupt spectral variations observed in TbPO$_4$ at ~9.5 GPa imply clearly that the anticipated transition occurs in this crystal lowering its symmetry from tetragonal zircon to a most likely monoclinic structure, unlike other zircon-structure crystals [11-15] whose high-pressure phase is that of scheelite. The phase transition is of first order and irreversible upon pressure release. One of the likely structures for the high-pressure phase of TbPO$_4$ is the monoclinic monazite one in which the lighter rare-earth ion (La to Gd) phosphates crystallize. Such a possibility appears feasible as TbPO$_4$ is closest to this group of phosphates. The fact that a similar transition has not been observed in ErPO$_4$ or TmPO$_4$ may be understood in terms of a higher critical pressure $P_c$ required by them considering that these heavy rare-earth phosphates are distant (relatively to TbPO$_4$) from the light phosphates group. As for YPO$_4$, the range of pressures applied (up to 7.9 GPa) may be narrow to observe structural changes.

References
[1] H. Suzuki and T. Nakajima, J. Phys. Soc. Japan 47, 1441 (1979).
[2] W. Nägele, D. Hohlwein and G. Domann, Z. Physik B 39, 305 (1980).
[3] S. Bluck and H.G. Kahle, J. Phys. C 21, 5193 (1998).
[4] G.K. Liu, C.-K. Loong, F. Trouw, M.M. Abraham and L.A. Boatner, J. Appl. Phys. 75, 7073 (1994).
[5] P. Morin, J. Rougy and Z. Kazei, Phys. Rev. B 50, 12625 (1994).
[6] P. Morin, J. Rougy and Z. Kazei, J. Phys.: Condens. Matter 8, 7967 (1996).
[7] Y. Hirano, S. Skanthakumar, C.-K. Loong, N. Wakabayashi and L. Boatner, Phys. Rev. B 66, 024424 (2002).
[8] G.M. Begum, G.W. Beall, L.A. Boatner and W.J. Gregor, J. Raman Spectrosc. 11, 273 (1981).
[9] A. Meldrum, L.A. Boatner and R.C. Ewing, Phys. Rev. B 56, 13805 (1997).
[10] P. Dawson, M.M. Hargreave and G.R. Wilkinson, J. Phys. C 4, 240 (1971).
[11] X. Wang, I. Loa, K. Syassen, M. Hanfland and B. Ferrand, Phys. Rev. B 70, 064109 (2004).
[12] A. Jayaraman, G.A. Kourouklis, G.A. Espinoza, A.S. Cooper and L.G. VanUitert, J. Phys. Chem. Solids 48, 755 (1987).
[13] S.L. Duclos, A. Jayaraman, G.P. Espinoza, A.S. Cooper and R.G. Maines Sr, J. Phys. Chem. Solids 50, 769 (1989).
[14] Y.W. Long, W.W. Zhang, L.X. Yang, Y. Yu, R.C. Yu, S. Ding, Y.L. Liu and C.Q. Jin, Appl. Phys. Lett. 87, 181901 (2005).
[15] Y.W. Long, L.X. Yang, Y. Yu, F.Y. Li, R.C. Yu, S. Ding, Y.L. Liu and C.Q. Jin, Phys. Rev. B 74, 054110 (2006).
[16] A.G. Kontos, E. Stavrou, V. Malamos, Y.S. Raptis and C. Raptis, Phys. Status Solidi b 244, 386 (2007).
[17] R.J. Elliott, R.T. Harley, W. Hayes and S.P.R. Smith, Proc. Roy. Soc. Lond. A 328, 217 (1972).
[18] P.C. Becker, N. Edelstein, G.M. Williams, J.J. Bucher, R.E. Russo, J.A. Koningstein, L.A. Boatner and M.M. Abraham, Phys. Rev. B 31, 8102 (1985).
[19] A. Tatsi, E. Stavrou, Y.C. Boulmetis, A.G. Kontos, Y.S. Raptis and C. Raptis, to be published.
[20] G.A. Watson Jr, W.B. Daniels and C.S. Wang, J. Appl. Phys. 52, 956 (1981).