Raman study of pressure-induced phase transitions in $RbIO_4$

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The pressure dependence of the Raman spectra of $RbIO_4$ has been investigated up to 27.3 GPa at room temperature using the diamond-anvil cell. The changes in the Raman spectra show clearly two pressure-induced phase transitions at 5.3 GPa from scheelite to pseudoscheelite and at 7.2 GPa from pseudoscheelite to wolframite. There is an indication of a possible phase transition at 18.3 GPa from wolframite to a denser complex structure. These transitions follow the same sequence as in other compounds such as alkali perrehenates, which crystallize in the scheelite structure. The systematics in pressure-induced phase transitions in alkali periodates is discussed.

I. INTRODUCTION

Systems of the type ABO_4 (A cation = alkali metal, alkaline earth metals, Tl, and Hg; B cation = W, Re, Mo, and I) crystallize in the scheelite (tetragonal) or the pseudoscheelite (orthorhombic) structure.[1] High-pressure Raman studies on tungstates,[2-4] perrehenates,[5,6] and molybdates[3,7] have revealed several pressure-induced structural phase transitions, many of which are believed to be due to polyhedral tilting. High-pressure Raman studies of potassium periodate[8] (KIO_4) reveal a phase transition at 6.5 GPa which is completed at 9.8 GPa. In our earlier work on cesium periodate[9] ($CsIO_4$) carried out up to 12 GPa, three phase transitions were observed at 1.5, 4.5, and 6.2 GPa in an increasing pressure cycle. In the decreasing pressure cycle the high-pressure phase is nearly quenched to ambient pressure.

Rubidium periodate, $RbIO_4$, crystallizes in the scheelite structure in the space group $I4_1/a$ (C_{4h}^6) similar to KIO_4 whereas $CsIO_4$ crystallizes in the pseudoscheelite structure in the space group $Pnma$ (D_{2h}^{16}). The purpose of this work is to study pressure-induced structural phase transitions in $RbIO_4$ with a view to understand the systematics of pressure effects in alkali periodates, in particular to explore if there is any correlation between the size and mass of the cation and the volume dependence of the crystal structure of the compound. Our studies, carried out up to 27.3 GPa, reveal two phase transitions in $RbIO_4$ at ~ 5.3 and 7.2 GPa. There are some indications of a possible phase transition at 18.3 GPa. At a pressure of ~ 7.2 GPa a transparent crystal of $RbIO_4$ turns brownish black as revealed by direct optical microscopy observations, suggesting a large volume change associated with this transition. Another interesting observation is the appearance of two new Raman modes at 734 and 756 cm^{-1} from the sample inside the diamond-anvil cell (DAC) at as low a pressure as 0.2 GPa and subsequent softening of these phonons. These modes are present with considerable intensities in the pressure-quenched samples. These results will be presented and discussed in this paper.

II. EXPERIMENTAL DETAILS

High-pressure Raman experiments were carried out up to 27.3 GPa on gel-grown single crystals of $RbIO_4$ using a gasketed Mao-Bell-type DAC.[10] A 4:1 methanol-ethanol mixture was used as a pressure transmitting medium. The pressure was calibrated *in situ* by the ruby fluorescence technique.[11] The Raman spectra were recorded at room temperature using the 5145 Å line from an argon ion laser (Coherent Innova 300) incident at 45° to the face of the diamond anvil. The laser power in front of the DAC was measured to be ~ 20 mW. The scattered light was analyzed using a DILOR XY spectrometer equipped with a liquid-nitrogen-cooled charge-coupled-device (CCD) detector. The Raman spectra were recorded in both increasing and decreasing pressure cycles.

III. RESULTS AND DISCUSSION

As mentioned earlier, $RbIO_4$ crystallizes in the scheelite structure with space group $I4_1/a$ (C_{4h}^6) and contains two formula units per primitive cell (four formula units per body-centered unit cell). Group theory predicts that the total number of optical modes belong to the irreducible representations $3A_g(R) + 5B_g(R) + 5E_g(R) + 4A_u(\mathrm{IR}) + 4E_u(\mathrm{IR}) + 3B_u$, where R (IR) represents Raman- (infrared-) active mode.[8,12] Out of these, the external modes belong to $A_g(R) + 2B_g(R) + 3E_g(R) + A_u(\mathrm{IR}) + 2E_u(\mathrm{IR}) + B_u$ and the internal modes belong to $2A_g(R) + 3B_g(R) + 2E_g(R) + 3A_u(\mathrm{IR}) + 2E_u(\mathrm{IR}) + 2B_u$. The resultant seven Raman-active internal modes of the $IO_4{}^-$ ion are the stretching ν_1 (A_g), ν_3 (B_g), and ν_3 (E_g), and bending ν_2 (A_g), ν_2 (B_g), ν_4 (B_g), and ν_4 (E_g).[6,8,12]

In this work, the mode frequencies, linewidths, and intensities were extracted from the measured spectra by least squares fit of the data using a sum of an appropriate number of Lorentzian functions.

A. Increasing pressure

In Fig. 1, curve (a) shows the Raman spectrum of $RbIO_4$ at ambient pressure outside the DAC which is similar to earlier reported spectra.[8] The external modes, comprised of the translational and librational modes, appear at 54, 68, and 84 cm^{-1}. The internal modes of the IO_4^- tetrahedron are in the spectral region of 270–340 cm^{-1} and 790–860 cm^{-1}. Polarization studies[8] have assigned these as follows: 798 cm^{-1}, associated with symmetric stretching vibration ν_1; 847 and 858 cm^{-1}, related to asymmetric stretching vibration ν_3; 274 and 287 cm^{-1}, symmetric bending ν_2; 328 and 336 cm^{-1}, asymmetric bending ν_4. In total, there are seven internal modes, in agreement with the group theoretical prediction for the scheelite structure. In this paper the Raman modes will be referred to by their peak positions at the ambient pressure.

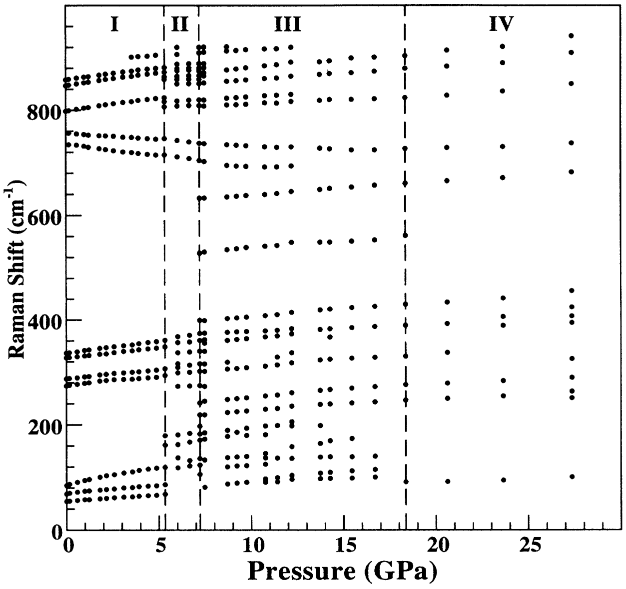

FIG. 2. Pressure dependence of the Raman modes in the increasing pressure run. The vertical dashed lines represent the phase transitions I → II → III → IV.

In Fig. 1 curves (b)–(f) are Raman spectra recorded at (b) 0.6, (c) 6.0, (d) 8.7, (d) 16.7, and (f) 27.3 GPa. These are the representative spectra for the four phases, viz., I, II, III, and IV. The phases are identified from discontinuities in the Raman peak positions ω and changes in the pressure derivative of ω, as well as changes in the number of observed Raman lines, as shown in a plot of ω vs pressure in Fig. 2. The dashed vertical lines in Fig. 2 mark the phase transitions. Figure 3 shows plots of the intensities (solid circles for increasing pressure and open circles for decreasing pressure cycles) of some modes which show considerable pressure dependence. Table I lists the mode frequencies and corresponding pressure derivative $d\omega/dP$ for the four phases obtained by the linear least squares fit of the data. The following salient features are noteworthy from Figs. 1–3.

(i) In the spectra taken above 5.3 GPa (phase II) we see splitting of the internal modes and a significant shift

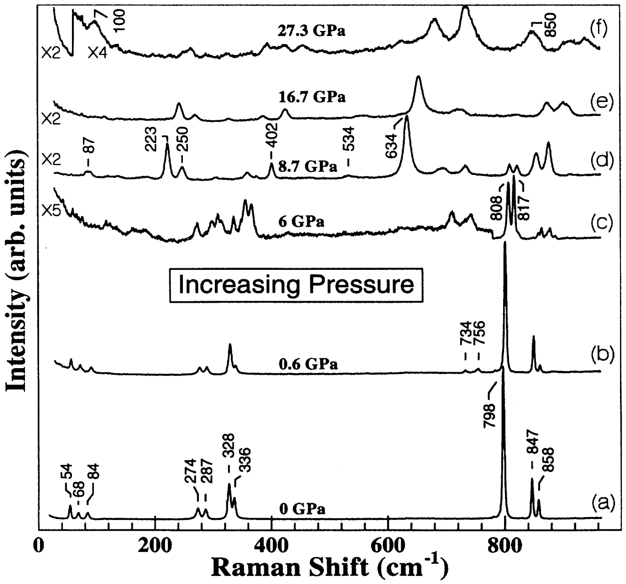

FIG. 1. Raman spectra of $RbIO_4$ at (a) ambient pressure (outside the DAC), (b) 0.6 GPa, (c) 6.0 GPa, (d) 8.7 GPa, (e) 16.7 GPa, and (f) 27.3 GPa in the increasing pressure run. The magnification factor is given along with each curve.

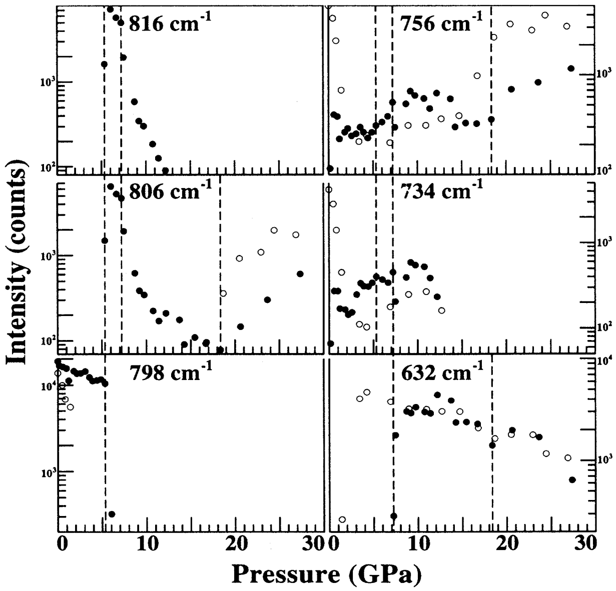

FIG. 3. Pressure dependence of the intensities of the Raman modes at 798, 806, 816, 756, 734, and 632 cm^{-1}. The solid and open circles represent the data in the increasing and decreasing pressure runs, respectively.

in the peak position of the external modes (see Fig. 2). The four Raman modes in the region of 250–400 cm^{-1} corresponding to the ν_2–ν_4 vibrational modes split into six modes. Similarly two ν_3 modes split into six modes and the ν_1 mode splits into two Raman lines, making a total of 14 internal modes. There is a decrease in the frequency of the ν_1 mode by ~ 1 %. This drop in the frequency of ν_1 in phase II corresponds to a decrease in the force constant $\Delta f/f \sim -2\%$ ($\omega^2 \propto f$). The decrease in the force constant can be due to the increase in the I-O bond length[13] which can occur due to the rearrangement of the tetrahedra to accomodate the change in volume. The latter is reflected in the shift of the external modes to higher frequencies, signifying a decrease of the unit cell volume. We suggest that phase II has the pseudoscheelite structure (space group D_{2h}^{16}) which has 14 Raman-active modes,[14] the same as seen by us in phase II.

(ii) A number of new peaks appear at a pressure of 7.2 GPa. The most significant of these is the appearance of a strong peak at $\sim$ 632 cm^{-1} and a doublet at 219 and 241 cm^{-1}. The transparency of the crystal is also altered at this pressure when observed under a microscope (magnification of 40×). The crystal appears brownish black in color, similar to the observations on $CsIO_4$ at $P \sim$ 6.2 GPa.[9] We suggest that this transition II $\rightarrow$ III at 7.2 GPa is strongly first order which involves a large volume change, producing large internal strains and cracking of the sample. The large change in volume will lead to a change in the coordination of iodine. We suggest phase III to be wolframite which has octahedral coordination for both the iodine and rubidium ions. At $\sim$ 13 GPa, most of the Raman modes of phase II disappear and only the modes related to phase III remain. From Fig. 3, we observe that the intensities of the ν_1-split counterparts (806 and 816 cm^{-1}) decrease drastically around 8 GPa and subsequently the 816 cm^{-1} mode disappears at around 13 GPa. The disappearance of the most intense mode of phase II could be considered as marking the end of the coexistence phase and the phase transition II $\rightarrow$ III to be complete. This also suggests that this phase transition, II $\rightarrow$ III, is sluggish, a known characteristic of a strongly first-order phase transition.[7]

(iii) In Fig. 1 the Raman spectrum (b) at $P = 0.6$ GPa shows the appearance of two new Raman peaks at 734 and 756 cm^{-1}. In our earlier work on $CsIO_4$,[9] we observed similar modes at 745 and 760 cm^{-1} which were very weak at ambient pressure and became strong at a moderate pressure of $\sim$ 1 GPa. Interestingly, these

TABLE I. Observed Raman frequencies of $RbIO_4$ in the four different phases in the increasing pressure run and their corresponding pressure derivatives.

Phase I 0 GPa		Phase II 6.0 GPa		Phases II and III 8.7 GPa		Phase III 13.7 GPa		Phase IV 23.6 GPa	
ω (cm^{-1})	$\frac{d\omega}{dP}$ (cm^{-1}/GPa)	ω (cm^{-1})	$\frac{d\omega}{dP}$ (cm^{-1}/GPa)	ω (cm^{-1})	$\frac{d\omega}{dP}$ (cm^{-1}/GPa)	ω (cm^{-1})	$\frac{d\omega}{dP}$ (cm^{-1}/GPa)	ω (cm^{-1})	$\frac{d\omega}{dP}$ (cm^{-1}/GPa)
54	2.4			87	1.8	97	1.8	94	1.3
68	3.1	118	0.8	120	0.8	108	3.0		
84	6.4	137	0.4	138	0.4	139	0.4		
		162	4.0	178	4.0	164	6.1		
		181	2.7	189	2.7	198	2.7		
				223	2.2	238	2.2	254	2.2
				248	2.4	264	2.4	283	2.4
		273	0.2						
274	3.3	299	2.3	306	3.1	323	3.1		
287	3.4	309	3.8	319	3.8				
		337	2.0					389	-
328	3.9	356	3.7	361	3.5				
336	4.5	368	4.8	376	1.8	381	1.6	406	4.7
				402	2.8	419	2.8	442	2.8
				534	2.7	549	2.7		
				634	2.5	649	2.5	671	2.5
		711	-4.3	694	-4.3				
		742	-2.2	734	-2.2	727	-2.2	730	1.1
		808	1.5	810	1.5	818	1.5	836	2.3
798	4.7	817	2.1	823	2.1				
		850	1.1	855	2.6	868	2.6	890	2.6
		859	0.4						
		865	1.0						
847	4.5	875	-0.2	877	3.3	892	3.3	921	3.3
858	4.4	879	1.4						
		888	0.9						
		905	2.3	913	2.3				
		920	4.6	921	4.6				

modes soften with increasing pressure until ~ 17 GPa, after which the slope $d\omega/dP$ becomes positive. We propose that these modes could be the difference modes involving, most probably, the ν_1 (A_g symmetry) mode and two of the external modes of the same A_g symmetry. The negative pressure coefficient of the difference mode can arise if the pressure coefficient of the external mode is larger than that of the internal mode. After 12 GPa we are unable to resolve the low-frequency component of the new modes (734 and 756 cm^{-1}) which probably merges with the 632 cm^{-1} mode. The change in the sign of the $d\omega/dP$ of the 756 cm^{-1} mode could be a signature for a densely packed phase (IV) in which all the modes only harden. At around 18.3 GPa, we observe the appearance of a Raman mode at ~ 90 cm^{-1} and see that the intensities of the 806 and 756 cm^{-1} modes start increasing (Fig. 3). These observations suggest that this may be the beginning of phase IV. As most of the Raman modes of phase III still exists in the new phase, the phase transition is perhaps not complete until 27.3 GPa. A definitive conclusion regarding this phase transition is difficult due to some unavoidable nonhydrostatic characteristics of the pressure beyond 15 GPa where the pressure transmitting alcohol mixture freezes.

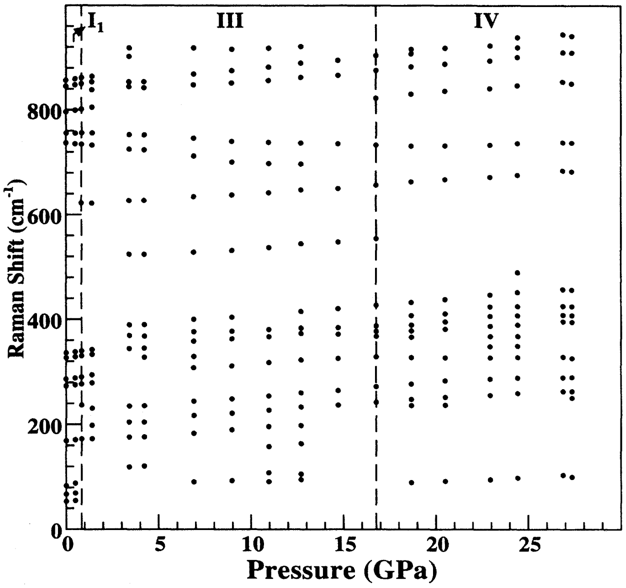

FIG. 5. Pressure dependence of the Raman modes in the decreasing pressure run. The vertical dashed lines represent the phase transitions IV → III → I_1.

B. Decreasing pressure

Figure 4, curves (a)–(e), shows the Raman spectra obtained in the decreasing pressure cycle at (a) 22.9, (b) 14.7, (c) 3.4, (d) 1.4, and (e) 0 GPa. Figure 5 shows the pressure dependence of the Raman peak frequencies for the decreasing pressure cycle. We can see from Fig. 5 that the signatures of phase IV are present until 17 GPa and phase III is stable until 1.4 GPa. At around 1.4 GPa, the modes of the scheelite structure appear. The most intense 632 cm^{-1} mode of phase III persists until the return pressure of 0.8 GPa, implying that the phase transition occurs at around 0.8 GPa. It is interesting to observe that the 734 and 756 cm^{-1} modes of the increasing pressure run are present in the spectrum at ambient pressure inside the DAC and start increasing in intensity from about 1.4 GPa (see the intensities shown by open circles in Fig. 3). This is similar to the case of $\mathrm{CsIO_4}$ where the corresponding modes are also intense at the ambient pressure inside the DAC.[9] Thus we suggest that the ambient pressure phase in the pressure-cycled $\mathrm{RbIO_4}$ has a "memory" of the earlier phase and label it as phase I_1. We find that all the external modes of the scheelite structure are present in phase I_1 along with 734 cm^{-1}, 756 cm^{-1} modes, and a mode at 169 cm^{-1} which has a large width of ~ 20 cm^{-1}. This broad peak could be a second-order Raman peak of the external mode at 84 cm^{-1}.

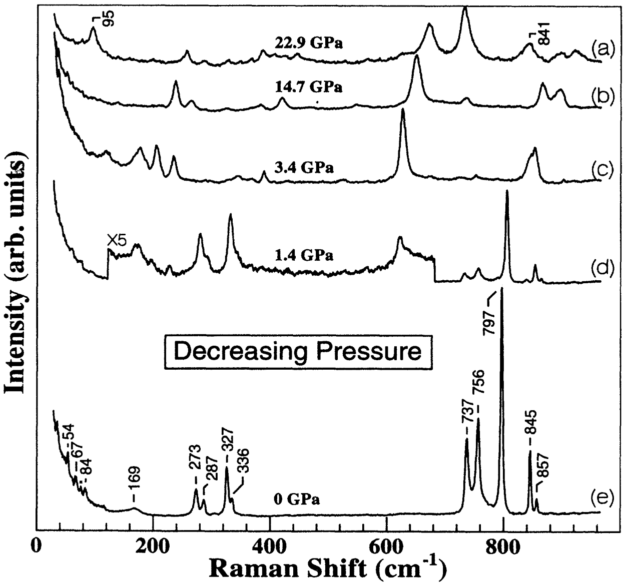

FIG. 4. Raman spectra of $\mathrm{RbIO_4}$ at (a) 22.9 GPa, (b) 14.7 GPa, (c) 3.4 GPa, (d) 1.4 GPa, and (e) 0 GPa (inside the DAC) in the decreasing pressure run. The magnification factor is given along with each curve.

From Fig. 4, we see that the Raman modes at ~ 90 and 830 cm^{-1} (values at 18.3 GPa in the increasing pressure cycle) of phase IV disappear around 16.5 GPa whereas all the other modes persist until the phase transition III → I_1 at 0.8 GPa. Another noteworthy observation is the behavior of the 734 and 756 cm^{-1} modes in decreasing pressure. These modes show a change of $d\omega/dP$ from positive to negative at 16.5 GPa. This strengthens our suggestion of a possible phase transition III → IV at around 18.3 GPa in the increasing pressure cycle which is reversible and occurs at ~ 16.5 GPa in the decreasing pressure run. A small hysteresis suggests this phase transition to be of first order in nature.

C. Nature of pressure-induced transitions in $RbIO_4$

In the absence of x-ray studies, we can apply general principles of crystal chemistry to predict the nature of structural phase transitions observed in the high-pressure studies of $RbIO_4$. From the work of Sleight[15] on $AB\text{O}_4$-type molybdates and tungstates, we see that these compounds crystallize in scheelite or wolframite structures. There is a "critical" cell volume below which compounds crystallize in the wolframite structure and above this critical cell volume these crystallize into the scheelite structure. From this we can expect that the structural phase transitions in the scheelite structures should be towards lower symmetries with an increase in pressure. From high-pressure studies of alkaline earth tungstates,[2–4] molybdates,[3,7] alkali perrehenates,[6] and $TlReO_4$,[5] the following pressure-induced sequence of phase transitions has been proposed:[6] scheelite ⟶ pseudoscheelite ⟶ wolframite ⟶ denser complex structure.

Applying this here, we suggest that phase I, which is scheelite with (8,4) coordination of rubidium and iodine ions, goes to the pseudoscheelite structure (phase II) at 5.3 GPa. This is significant from the fact there is a doubling of the internal modes as expected by group theoretical analysis.[14]

The phase transition II → III begins at around 7.2 GPa and is completed at around 13 GPa. We suggest that phase III has the wolframite structure. This structure has (6,6) coordination for the rubidium and iodine ions as compared to the (8,4) coordination for the pseudoscheelite structure. In this phase, new Raman peaks appear in external and internal mode regions. Using nuclear site group analysis[12] and a knowledge of the nuclear sites[1] we can easily determine the internal and external modes for a typical wolframite structure (e.g., $NiWO_4$, $CdWO_4$), with space group C_{2h}^4 ($P112/b$). Group theory predicts that the optical modes belong to the irreducible representations $8A_g(R,\text{IR}) + 7A_u(\text{IR}) + 10B_g(R,\text{IR}) + 8B_u(\text{IR})$. Out of these $5A_g(R,\text{IR})+5A_u(\text{IR})+4B_g(R,\text{IR})+4B_u(\text{IR})$ correspond to the internal modes and $3A_g(R,\text{IR}) + 2A_u(\text{IR}) + 6B_g(R,\text{IR}) + 4B_u(\text{IR})$ correspond to the external modes. Thus we have 9 Raman-active internal modes for the wolframite structure as compared to the 14 Raman-active internal modes in the pseudoscheelite structure.[14] From Fig. 2 and Table I we see that after 13 GPa we have 9 internal modes 238, 265, 381, 419, 549, 649, 818, 868, and 892 cm^{-1} (values at a pressure of 13.7 GPa). From the above discussion it becomes clear that the phase transition II → III is pseudoscheelite → wolframite and the transition is complete only after 13 GPa. The appearance of a strong mode at around 632 cm^{-1} in $RbIO_4$ is similar to the 640 cm^{-1} mode in $CsIO_4$ at 6.2 GPa (Ref. 9) and $\sim$ 635 cm^{-1} in KIO_4 at 6.5 GPa.[8] Hence this phase transition at 7.2 GPa is analogous to the phase transition in $CsIO_4$ at 6.2 GPa, in KIO_4 at 6.5 GPa, and in perrehenates at $\sim$ 14 GPa.[7] There is a large volume change associated with this phase transition accompanied by a change from tetrahedral to octahedral coordination for the iodine ion.

The appearance of a new mode at $\sim$ 90 cm^{-1}, an increase in the intensity of the 806 and 756 cm^{-1} modes, and a change in the sign of the pressure coefficient of the 756 cm^{-1} mode suggest a phase transition III → IV at around 18.3 GPa to a denser phase. As most of the Raman modes of phase III are present in phase IV, the phase transition is not complete up to a maximum pressure of 28 GPa.

Finally, we attempted to correlate the size of the alkali cation and the phase transition pressures in these $AB\text{O}_4$ compounds. From the available data on pressure studies of KIO_4 (Ref. 8) and $CsIO_4$,[9] we are limited to compare only one of the phase transitions, viz., the phase transition at 6.5 GPa in KIO_4, at 6.2 GPa in $CsIO_4$, and at 7.2 GPa in $RbIO_4$. These transitions are from the pseudoscheelite to wolframite structure. In our view, the transition from the scheelite to pseudoscheelite has been missed in earlier work[8] on KIO_4 where the pressure increments are rather large. Comparing KIO_4 and $RbIO_4$ which crystallize in the scheelite structure, the transition pressure P_c of the pseudoscheelite → wolframite phase transition increases with an increase in the ionic radius (compare $\text{K}^+ = 1.33$ Å and $\text{Rb}^+ = 1.48$ Å). As mentioned before, there is a critical volume V_c below which these crystallize in the wolframite structure.[15] In the present case of alkali periodates, the larger cation radius results in a higher unit cell volume V_0 at ambient pressure (V_0 for $KIO_4 = 417.6$ Å^3 and for $RbIO_4 = 457.6$ Å^3).[1] It is easy to see that

$$P_c = \frac{1}{\kappa}\left(1 - \frac{V_c}{V_0}\right), \tag{1}$$

where κ is the compressibility. Then

$$\frac{(P_c)_\text{K}}{(P_c)_\text{Rb}} = \frac{\left[1 - \left(\frac{V_c}{V_0}\right)_\text{K}\right]}{\left[1 - \left(\frac{V_c}{V_0}\right)_\text{Rb}\right]} \times \frac{(\kappa)_\text{Rb}}{(\kappa)_\text{K}}, \tag{2}$$

where the subscripts K and Rb refer to the values for KIO_4 and $RbIO_4$. From the work of Sleight[15] on $CdMoO_4$ (scheelite structure) and $CdWO_4$ (wolframite structure), the critical volume V_c is 297.3 Å^3. There are no data available as yet on the compressibilities of KIO_4 and $RbIO_4$. Assuming $(\kappa)_\text{K} = (\kappa)_\text{Rb}$, from Eq. (2), we get $(P_c)_\text{K}/(P_c)_\text{Rb} = 0.82$, which is close to the observed $(P_c)_\text{K}/(P_c)_\text{Rb} = 6.5/7.2 = 0.9$. The fact that the transition pressure is lower in $CsIO_4$ can be qualitatively understood as it is already in the pseudoscheelite structure unlike the other two which crystallize in the scheelite structure. Similar observations can be made in the alkali perrehenates.[7]

IV. CONCLUSION

High-pressure Raman studies of $RbIO_4$ reveal three phase transitions in the pressure range of 0–28 GPa. The two modes at 734 and 756 cm^{-1} at 0.2 GPa could be the difference modes. The splitting of the internal modes and shift in the peak position of the external modes suggest the phase transition at 5.3 GPa to be a pseudoscheelite structure (phase II). The transition at 7.2 GPa involves a large volume change and an abrupt change in crystal transparency. We suggest phase III to be of a wolframite structure which is completed at around 13 GPa. There is a possible phase transition from phase III to phase IV at ~ 18.3 GPa from a wolframite structure to a denser complex phase which is not completed up to the maximum pressure achieved in this study. This is reversible in nature with a small hysteresis. In the decreasing pressure cycle, the transition from a wolframite structure to a phase which has characteristics of a scheelite structure with some "memory" of the earlier phase occurs at 0.8 GPa. The phase transitions in $RbIO_4$ are similar to the observed sequence of phase transitions in other ABO_4 compounds. The transition pressures corresponding to the pseudoscheelite → wolframite phase transition in $RbIO_4$ and KIO_4 follow the critical volume criterion.[15] High-pressure x-ray studies on $RbIO_4$ would help in a definitive understanding of the high-pressure phases.

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