Phase Transitions in I_2O_5 at High Pressures: Raman and X-ray Diffraction Studies

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Abstract

We have studied the pressure-induced phase transitions of I_2O_5 in diamond anvil cells using optical spectroscopy and x-ray diffraction. X-ray and Raman data indicate that the linear structure of phase I isostructurally transforms into a stacking layer structure of phase II at 5 GPa and, then, into an amorphous network of phase III at 15 GPa. Phase III further transforms into amorphous solid at 23 GPa, which can be recovered at ambient condition. Anisotropic van der Waals interaction between lone pairs of iodines and neighboring molecules drives to the observed phase change with increasing of iodine coordination number.

I. INTRODUCTION

It is known that Group VII elements (fluorine down to astatine) have high electron negativities, high electron affinities, and high ionization energies. As a result, their compounds become excellent oxidizing agents [1,2]. Among those halides, iodine compounds have been considered as powerful neutralizers against chemical and biological agents. Especially, iodine forms thermally stable oxides in ambient conditions, thus iodine oxides have been used for various environmental, industrial, and defense applications. Diiodine pentoxide (I_2O_5), for example, is a well known ozone depletion agent [3]. The free radical I-O bond in iodine oxides reacts with ozone to produce iodine oxide radicals ($\text{IO}\cdot$) and oxygen, which in turn, react with other ozone. In addition, I_2O_5 can readily oxidize carbon monoxide to carbon dioxide at room temperature. Mixed with small metal particles I_2O_5 becomes a non-conventional energetic material, more powerful yet more stable than thermite mixtures and often used for propellants.[4] Thermally less stable I_2O_4 and I_2O_9 have also been studied both experimentally [7-13] and theoretically [12,13] at ambient pressures. Strong chemical reactivity and instability of these materials have been challenges in further studies at high pressures.

Diiodine pentaoxide (I_2O_5 in Fig. 1) is a thermally stable, but hygroscopic, white crystalline solid at room temperature. The crystal structure and vibrational properties of I_2O_5 at ambient temperature are well studied [5,6,8]. I_2O_5 crystallizes into a monoclinic structure ($P2_1/c$, $a=11.036 \text{ \AA}$, $b=5.063 \text{ \AA}$, $c=8.135 \text{ \AA}$ and $\beta=107.18^\circ$) with four molecules per unit cell, each made of two pyramidal IO_3 units connected by a common oxygen. The crystal structure, therefore, exhibits an intermediate nature between molecular and polymeric solids. For appreciable intermolecular van der Waals interaction, molecular units composed cross-linked two dimensional chains stacked in parallel along the normal direction of layers, which gives pseudo five-fold coordinated iodine. For understanding the peculiar geometrical arrangement of crystalline I_2O_5 , Wu et al.[14] proposed that

anisotropic van der Waals interaction has important role to highly anisotropic reflection on the crystal structure and its polymeric nature. By improving equilibrium volume calculation with anisotropic van der Waals correction, Wu et. al.[14] proposed anisotropic van der Waals interaction between monomeric I_2O_5 in-layer or inter-layer significantly related to the crystal structure.

The ambient structure of I_2O_5 is interesting to be considered as a pseudo-polymeric I_2O_5 cluster bound by weak van der Waals interactions, which can be subjected to large distortion under pressure. However, there have been no pressure studies on I_2O_5 and structural stability and associated chemical bonding at high pressures are not known yet. In this study, we have investigated the pressure-induced vibrational and structural changes of I_2O_5 to 32 GPa using micro-Raman spectroscopy and synchrotron x-ray diffraction and have found the evidences for phase transitions of quasi-1D phase I to 2D-layer phase II at 5 GPa, to 3D-network phase III at 15 GPa, and to amorphous solid above 23 GPa.

II. EXPERIMENTAL PROCEDURES

Colorless transparent powder samples of I_2O_5 were synthesized and provided in vacuum-sealed ampules by the energetic materials group at University of Southern California. Because of highly hygroscopic nature of I_2O_5 , the samples were loaded into diamond anvil cells (DACs) in an Ar-filled dry box maintained with small positive pressure. A small amount of I_2O_5 powder samples were filled about 30% of the sample chamber (~ 0.13 mm hole drilled on a Re-gasket), together with a few Ruby particles for pressure measurements, and then sealed with two diamond anvils (~ 0.3 mm flat, Type Ia) for loading quasi-hydrostatic helium pressure medium in our high-pressure gas loader.

Raman spectra of the sample were collected in a back-scattering geometry, using a home-built confocal micro-Raman system with a $514.5 \mu\text{m}$ Ar^+ ion laser. In these experiments, we have used the minimum level of laser power in order to avoid any

photochemical damage of the sample. Angle resolved x-ray diffraction experiments were performed at the micro-diffraction beamline, 16 IDB of the HPCAT, at the Advanced Photon Source (APS), using a monochromatic x-ray at $\lambda = 0.4024 \text{ \AA}$ and high resolution image plate (MAR345). The x-ray diffraction image was integrated using the Fit2D program [15] for crystal structure analysis using GSAS (General Structure Analysis System) [16] and ESPOIR [17].

III. RESULTS

Fig. 2 presents the Raman spectra of I_2O_5 phases up to 32 GPa at room temperature. Based on the monoclinic structure of I_2O_5 of space group $P2_1/c$ (C_{2h}^5) (Fig. 1), there are a total of 81 fundamental vibration modes; 60 internal modes ($\Gamma_{\text{internal}} = 15 A_g(\text{R}) + 15 B_g(\text{R}) + 15 A_u(\text{IR}) + 15 B_u(\text{IR})$) and 21 lattice modes ($\Gamma_{\text{lattice}} = 6 A_g(\text{R}) + 6 B_g(\text{R}) + 5 A_u(\text{IR}) + 4 B_u(\text{IR})$). 21 modes among 39 Raman active modes are spatially resolved at room temperature (Fig. 2) and the Raman spectrum agrees well with the previous data.[8-10] The observed Raman modes are grouped for convenience into three regions: the librational and translational region below 110 cm^{-1} (including the modes ν_1 to ν_6); the bending and rocking modes of IO_3 terminal units between 110 and $\sim 410 \text{ cm}^{-1}$ (ν_7 to ν_{21}); and the symmetric and asymmetric stretching modes of terminal I-O bonds and I-O bonds in IO_3 unit (ν_{22} to ν_{34}) above 410 cm^{-1} . Of these modes, most dominate features are (i) the (B_g) at 810 cm^{-1} representing the symmetric stretching mode of bridging I-O-I bond of I_2O_5 units, (ii) the ν_{26} (A_g) at 690 cm^{-1} , in-phase symmetric stretching mode of terminating IO_3 , (iii) the ν_{27} (B_g) at 720 cm^{-1} , the antisymmetric I-O stretching mode of I_2O_5 . These peaks remain to be sharp and strong to 22 GPa; then, they broaden rapidly as I_2O_5 polymerizes above 23 GPa. Note that unlike all other modes, these stretching modes shift toward lower frequencies as pressure increases. It is likely that these spectral changes, the red shift and broadening of the stretching modes, reflect large variations in oxygen positions and IO distances, which will be discussed later in the x-ray results.

Figure 3 summarizes the pressure-induced Raman shifts, indicating that I_2O_5 undergoes three phase transitions from Phase I to II at ~5 GPa, to Phase III at ~15 GPa, and to an amorphous solid above 23 GPa. The amorphization of I_2O_5 is evident from the broad spectral characteristics in both Raman and X-ray diffraction as shown in Fig. 4. The I-to-II and II-to-III phase transitions, on the other hand, are apparent from characteristic Raman spectral changes. For example, the phase I to II transition is signified by (i) the appearance of new peaks including ν_1 , ν_7 , ν_{10} , ν_{13} , ν_{33} , (ii) the disappearance of the peaks, ν_5 , ν_{14} , ν_{18} , ν_{30} , ν_{32} , (iii) the splitting of the peaks, ν_7 , ν_9 , ν_{13} , ν_{16} , ν_{20} , ν_{29} , ν_{33} , and (iv) the merging of the peaks, ν_{24} and ν_{25} . On the other hand, the phase II-to-III transition is evident by the disappearance of ν_1 to ν_3 , ν_7 , ν_9 to ν_{11} , ν_{15} , ν_{19} to ν_{23} , ν_{27} at 15 GPa, and the splitting of the peak ν_{28} .

Such distinctive pressure induced phase transition accompanies by correlated complex spectral changes of the stretching, bending and lattice modes. When I_2O_5 changes from Phase I to II, translational modes, ν_3 and ν_5 , disappear and new bending (or rocking) modes, ν_7 , ν_9 , ν_{10} , ν_{13} , ν_{16} , ν_{20} , emerge at 5 GPa, and then disappear at 15 GPa. Simultaneously, stretching modes of the terminal I-O and IO_3 units, ν_{22} to ν_{25} , ν_{27} , ν_{30} and ν_{32} , disappear at 15 GPa. Such unique Raman features in phase II strongly suggests that monomeric I_2O_5 transforms to a polymeric form by the formation of intermolecular I-O bonds and a reduction of interlayer distance. New I-O bonds suppress translational modes of monomeric I_2O_5 and produce more I-O-I and O-I-O bending modes in the polymeric I_2O_5 chains. On the other hand, when I_2O_5 changes into Phase III, the stretching modes of terminal I-O, ν_{32} , OIO stretching mode, ν_{31} , and an asymmetric IO_3 with IO(OIO) stretching mode, $\nu_{26}(\nu_{25})$, show strong red shifts, which signifies again either a formation of another I-O bonds or enhanced inter- or intra-molecular interactions under pressure. Complex Raman features in phase transitions may ascribe to the reconfiguration of a local arrangement of molecular I_2O_5 and the formation of polymeric links between them. Strong repulsion between lone pairs of iodines disturbs

molecular arrangements and further induces electron disproportionations of lone pairs of iodines and oxygen to produce I-O bonds. Peak shift of lattice modes toward higher frequencies due to the reduction of inter- or intra-molecular bond distances under pressure.

Above 20 GPa, all Raman features get weak and broad with a strong background and eventually loses all but one broad peak at $\sim 700\text{ cm}^{-1}$ (see Fig. 2). This spectral change above 20 GPa occurs irreversibly upon pressure cycling, likely indicating more likely amorphization above 20-23 GPa. The recovered sample is opaque under transmitting light but appears gray upon reflecting light with a non-uniform texture. In addition to the amorphous phase, the Raman spectrum of the recovered product contains a small amount of unconverted I_2O_5 as well as other iodine oxides species. We conjecture these by-products are produced by the secondary chemical transformation or laser-induced decomposition of phase III. Laser-induced decomposition was observed over the entire pressure range, but significantly lesser degree for the polymerized sample. Up to 60 GPa, the polymeric product shows no apparent decomposition or reaction with Re-gasket were observed.

Fig. 4 shows angle-dispersed x-ray diffraction patterns of I_2O_5 phases and Rietveld refinement result of phase I at 4 GPa. The simulated diffraction pattern at ambient pressure [8] is also presented in Fig. 4(a). The selective diffraction patterns at 6.5 GPa of phase II and at 15 GPa of phase III resemble the diffraction pattern at ambient pressure, at least in their qualitative aspects including the number of peaks, the relative intensities, and the Bragg reflections. This indicates that the crystal structure of high-pressure phases (both II and III) remains same as the monoclinic structure of phase I. Above 18 GPa, a broad diffraction band centered at $\sim 7.4^\circ$ emerges and become dominant as pressure increases above 23 GPa, indicating an amorphization which is consistent with the Raman data. Two major peaks in amorphous phase, at $\sim 7.5^\circ$ and $\sim 8.6^\circ$ at 24 GPa, calculated d -values of 3.08 and 2.68 Å respectively, which may present strong scattering by heavy

iodines. Nevertheless the lack of number of diffraction peak of polymerized sample at 25 GPa, the best fit is an orthorhombic structure with the lattice parameters of $a=9.23\text{\AA}$, $b=4.35\text{\AA}$, $c=3.66\text{\AA}$ with two molecular per unit cell. Such structure shows $\sim 7\%$ volume reduction comparing to the estimated volume of monoclinic structure at 24 GPa from an equation of state in Fig. 6(c). Note that solid iodine at this pressure transform to a body centered-orthorhombic structure[18] with $\sim 5\%$ volume compression comparing to the estimated volume of polymerized I_2O_5 . The spurious peak in low angle region at 5° to 5.7° is likely from impurities of other iodine oxide species presumably produced by an x-ray photolysis.

Fig. 4(b) presents the Rietveld refined x-ray pattern at 4 GPa using the reported $P2_1/c$ structure of I_2O_5 at ambient pressure. The best fit at 4 GPa yields the lattice parameters of $a=10.738(9)\text{\AA}$, $b=4.866(7)\text{\AA}$, $c=7.649(7)\text{\AA}$ and $\beta=107.43^\circ(2)$. All iodine and oxygen atoms assigned at $4e(x,y,z)$ site. Iodine coordinates refined primarily for its strong scattering reflection. In order to optimize the oxygen positions, whose contribution to the diffraction intensities was much weaker than that of iodines, we applied Monte Carlo simulation with a pseudo-simulated annealing method in ESPOIR. Subsequently, the scale factor, zero-shift, lattice parameters and angle, peak profile, u , v , w , and atomic positions with anisotropic temperature factors. No preferred orientation was included in the refinement procedure. Repeating these procedure few times with constraint of IO distance within $1.7\text{\AA}$ to $2.2\text{\AA}$, which represent a double bonded or reduced single bonded IO distance and an extended single bonded IO distance respectively, and we achieved a reasonably good R -factors of $wR_p = 3.88\%$, $R_p = 2.39\%$ with a reduced- $\chi^2=1.42$. We applied the same method to analyze the x-ray diffraction patterns at 7 GPa and 15 GPa. Note that, for 15 GPa x-ray data, oxygen atoms assigned to two special positions at $2a(0,0,0)$ and $2b(1/2,0,0)$, which provided better intensity fitting overall and assigning to the peaks in the higher angle region better. Due to the strong scattering from iodines, it is practically difficult to refine an accurate position of oxygen. However, the

estimated oxygen position was well understood regarding intra- and intermolecular bond distances and bond angles in presented crystal models in Fig. 5.

Fig. 5 presents the suggested crystal models of solid phases of I_2O_5 based on the structure analysis. Crystal structure of I_2O_5 in phase I can be yet considered as a molecular solid, composed by two IO_3 units shared by single oxygen and the intermolecular distances in the inlayer and in the interlayer, $\sim 3 \text{ \AA}$ and $\sim 4 \text{ \AA}$ respectively, are too large to form a real chemical bonds. Distinctive feature of I_2O_5 structure in phase II is a complex distortion on the planes and rotation of I_2O_5 driven by anisotropic response of the directional arrangement between iodine lone pairs and neighboring molecules. For example, there is less change of angle β to $\sim 6 \text{ GPa}$, then increases to $\sim 13 \text{ GPa}$ while other lattice parameters reduce monotonically with pressure. Such distortion results in an I-O-I angle ($\angle \text{I}_1\text{-O}_3\text{-I}_2$ in Fig. 1) of $\sim 130^\circ$, slightly reduced from the ambient value of $\sim 139^\circ$ yet the same nature of inter/intra-molecular bonding. The average bond distance from an iodine to a terminal oxygen, $d(\text{I}_1\text{-O}_1)$ (or $d(\text{I}_2\text{-O}_5)$) = $1.91 \text{ \AA}$ (or $1.82 \text{ \AA}$) is slightly shorter than $2.03 \text{ \AA}$ (or $1.91 \text{ \AA}$) at ambient and the bond distance between iodine and a bridging oxygen, $d(\text{I}_1\text{-O}_3)$ (or $d(\text{I}_2\text{-O}_3)$) = $1.91 \text{ \AA}$ ($1.96 \text{ \AA}$) is almost same to $1.92 \text{ \AA}$ ($1.98 \text{ \AA}$) at ambient between iodine and the terminal oxygen atoms. Contrary to the reduction of bond distances in phase II with respect to those of phase I, the average I-O distance in phase III elongates to about $1.8 \text{ \AA}$ to $2.0 \text{ \AA}$ and the average I...O distance reduces to about $2.6 \text{ \AA}$ to $2.8 \text{ \AA}$. Although the I...O distance is still longer than extended I-O distance (~ 1.9 to $2.0 \text{ \AA}$), the reduction of intermolecular or interlayer distance must be apparent considering the collapse of a typical intermolecular distance of I...O from $\sim 4 \text{ \AA}$ to $\sim 2.8 \text{ \AA}$. The evolution of I-O and I...O distances suggest a series of structure transformation to a 2D strip-like layer structure for phase II and a 3D network structure for phase III. These structural models reveal that the pressure-induced phase transitions accompany a progressive increase of the average coordination number of iodine from three in phase I to four in phase II, and a mixed coordination of four and six in phase III.

Considering relatively large uncertainty in the refined atomic positions (± 0.3 Å), the disparity of 0.7 Å between the intra I-O (2.0 Å) and inter I...O (2.7 Å) is relatively small and the iodine coordination number of phase III should be considered the average of five.

Fig. 6 presents the pressure-dependent changes of (a) lattice parameters, (b) angle, and (c) unit cell volume of I_2O_5 . Lattice parameters a , b and c decreases linearly with increasing pressure, while lattice angle, initially stays at $\sim 107^\circ$ to 4 GPa, then increases to $\sim 111^\circ$ at 11 GPa and higher pressures. Comparing to the initial structural distortion between ac -plane and along the c -direction, pressure dependence of lattice parameters and angles showed strong anisotropic compressibility on ac -plane. In phase I, the relative reduction of lattice constant along the a - and b -axis are 3.3% and 3.4% respectively, while that along c -axis is substantially large 7.5%. For example, $a = 11.04$ Å $b = 5.06$ Å at ambient becomes 10.68 Å and 4.89 Å at 5 GPa; whereas, $c = 8.14$ Å becomes 7.53 Å at 5 GPa which leads to a large distortion of lattice angle at initial compression. In phase II, the compression to b -axis is larger than those of other directions and the relative reductions of lattice parameters to those at 5 GPa were 2.8%, 7.9% and 0.8% along the a -, b -, and c -axis respectively. The unit cell volume as a function of pressure, Fig. 6(c), were fitted with third order Birch-Murnaghan equation of state and obtained a bulk modulus of $B_0 = 18.5(2.3)$ GPa with $B'_0 = 8.9(1.3)$. This value is good agreement with theoretically prediction of 21.3 GPa [14], at its density of $\rho = 6.343$ g/cm³.

The suggested crystal model clearly represents how a monomeric I_2O_5 undergoes to a pseudo-polymeric solid, then to a polymeric I_2O_5 with pressure. In low pressure region, a local structural distortion is mainly governed by an anisotropic van der Waals interaction.[19] With increasing pressure above 5 GPa, monomeric I_2O_5 begins to polymerize by the formation of new covalent I-O bonds between intermolecular I_2O_5 . Density of I_2O_5 increases from 5.08 g/cm³ to 6.66 g/cm³ with a volume reduction of 23.8% at 15 GPa, which shows that the densification of I_2O_5 is accompanied by an

increase in the average coordination number of iodine with oxygen atoms from three in phase I to four in phase II, and mixed four and six in phase III.

The crystal model of phase III presents the mixed coordination number of iodine of four and six alternatively and wide variation of I-O and I...O distances. I-O bond between ~ 1.8 Å to ~ 2.2 Å speculates a compromised intra-molecular I-O single bond between two physical facts, a reduction of single bonded distance by compression and an extension of I-O distance by a charge disproportionation of iodine and oxygen by the formation of new I-O bond. On the other hand, the bond between ~ 2.5 Å to ~ 2.8 Å may suggest that a pseudo chemical I...O bonds between inter-molecular I_2O_5 . Such model suggests the polymerized I_2O_5 may be not a perfectly ordered 3D-network structure, which leads to the amorphization above 15 GPa.

IV. CONCLUSION

In this paper, we have presented the spectral and structural evidences for pressure-induced phase transitions of I_2O_5 from an one-dimensional (*1D*) linear-chain structure of phase I (monoclinic, $P2_1/c$) to a 2D stacking layer structure of phase II at 5 GPa and a 3D network of phase III at 15 GPa, as well as for irreversible transformation of phase III at 23 GPa to a gray amorphous solid that can be recovered at ambient condition. The crystal structures of phase II and III are modeled based on isostructural monoclinic structures to 15 GPa, which yields $B_0 = 19.7$ GPa with $B'_0 = 9$ Fig. 6.8 for solid I_2O_5 . The phase transitions are driven by the densification resulting from the progressive increase in the iodine coordination number from 3 in phase I to mixed 4 and 6 in phase III. We attribute the observed spectral complexity in Raman spectra of I_2O_5 at high pressures to this extended nature of I_2O_5 structures in phase II and III and their structural distortions. Considering the pressure-induced increase of the number of oxygen atoms surrounding each iodine atom, we suggest that the recovered amorphous solid would be a good candidate for high energy density materials.

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Figure Captions:

Figure 1. (color online) Crystal structure of I_2O_5 at room temperature[8] which is composed by two IO_2 groups via an oxygen bridge. The I-O bond distance in IO_2 units and the bond length of I-O bridge are $\sim 1.8 \text{ \AA}$ and $\sim 1.9 \text{ \AA}$ respectively.

Figure 2. Raman spectra of I_2O_5 with helium pressure medium up to 32 GPa at room temperature. Each plot represents corresponding phases.

Figure 3. (color online) Pressure dependence of Raman frequencies up to 20 GPa. Suggested phase transitions are indicated by dotted lines. Solid red line guides a peak shift under pressure.

Figure 4. (color online) (a) Evolution of angle resolved powder x-ray diffraction patterns of I_2O_5 under pressure. For comparison, the x-ray pattern at ambient is simulated using structure parameters in Ref.[8], (b) Rietveld refinement of x-ray pattern of I_2O_5 at 4 GPa. The observed (dotted 'x'), calculated (black line), and difference (red line) are presented. The blue tick mark indicates reflections of space group. Diffraction peaks from small amount of impurities of iodine oxide species marked with '*'.

Figure 5. (color online) crystal models of I_2O_5 , $2 \times 1 \times 2$ unit cells, projected along [010] and along [001] directions. Each unit cell has four I_2O_5 . (a) a monomeric 3-fold coordinated iodine at phase 1, red(blue) curve presents a shift of oxygen(iodine) with pressure, (b) 4-fold coordinated iodine constructs layered stripe structure along the b-direction at 7 GPa. The normal distance between two strip is $\sim 3.2 \text{ \AA}$ weakly bound with van der Waals interaction, (c) 3-dimensional network structure of solid I_2O_5 at 15 GPa. 4 and 6-fold coordinated iodines show alternatively and interspatial gap between bar disappeared. The I...O bonds, presented as a dotted line, between 4-fold coordinated

iodines to the nearest neighboring oxygen of 4-fold (6-fold) coordinated iodine is about 2.6 Å (2.8 Å).

Figure 6: (color online) (a) The evolution of lattice parameters as a function of pressure. (b) The evolution of lattice angles as a function of pressure. The solid curves serve as a guide. (c) The pressure-dependence of the specific volume of the I_2O_5 . Data were fitted to a 3rd-order Birch-Murnaghan equation of state (red line) with $B_0=18.5(2.3)$ GPa and $B'_0=8.9(1.3)$. Vertical dotted line presents phase transition. Closed square box represents lattice parameters and cell volume at ambient pressure.

Figure-1

Figure-2

Figure-3

Figure-4

Figure-5

Figure-6

(a) Phase I (ambient)

(b) Phase II (7 GPa)

(c) Phase III
(15 GPa)