First-order isostructural phase transition induced by High-pressure in $Fe(IO_3)_3$

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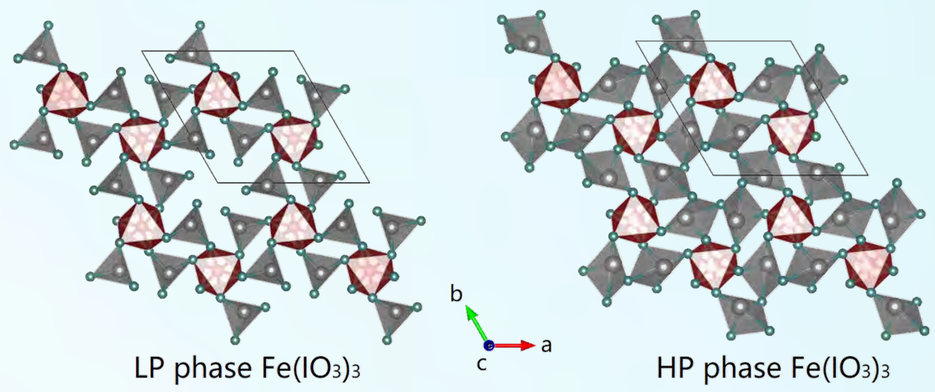
GENERALITAT VALENCIANA | Proyecto EFIMAT PROMETEO 2018 / 123

Introduction

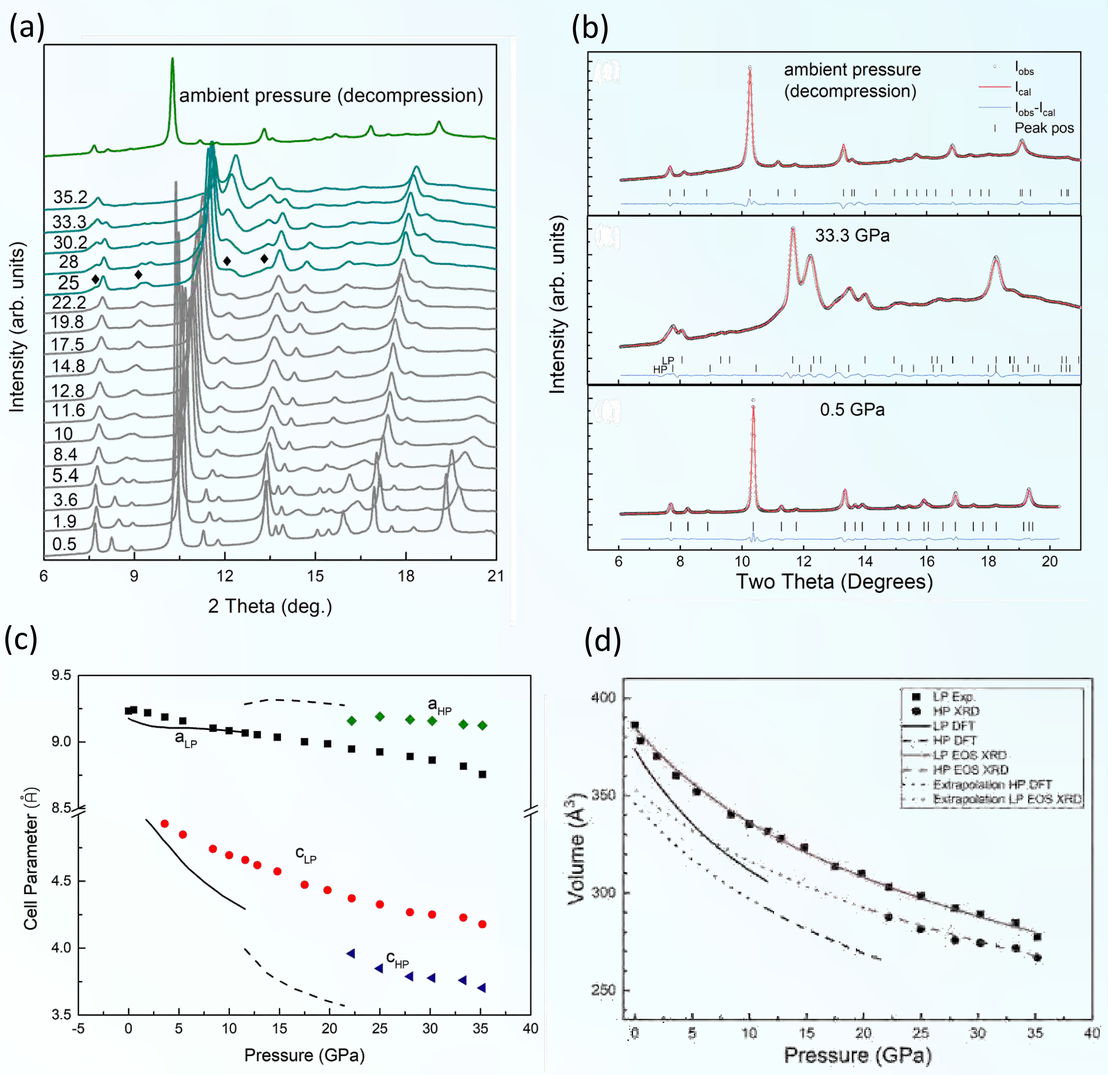
The family of metal iodates has been extensively studied at ambient pressure because of their dielectric, magnetic, or nonlinear optical properties. Many of them have been also studied for the reason that they are superionic conductors. Such properties make them excellent barocaloric materials, very promising for the development of ecofriendly solid-state cooling technologies. On the other hand, numerous iodates are fascinating because they have IO_3 units with lone-pair orbitals, which give materials particular characteristics. High-pressure (HP) research is known to be an efficient tool to determine the characteristics of materials. Among iodates, only $LiIO_3$, KIO_3, and $AgIO_3$ have been studied under HP. No phase transitions have been found in $LiIO_3$ up to 73 GPa. In contrast, KIO_3 shows phase transitions around 7 and 14 GPa. On the other hand, in $AgIO_3$ a new phase was found at 2.7 GPa and 240 °C. These facts suggest that the HP behavior of metal iodates can be extremely complex and should be further studied for the better understanding of the HP behavior of this family of compounds.

LP and HP crystal structure



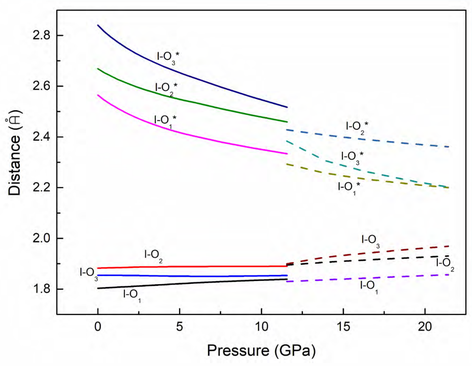
Crystal structure of LP and HP phase of Fe(IO3)3, both of them can be described by space group P63

HP XRD



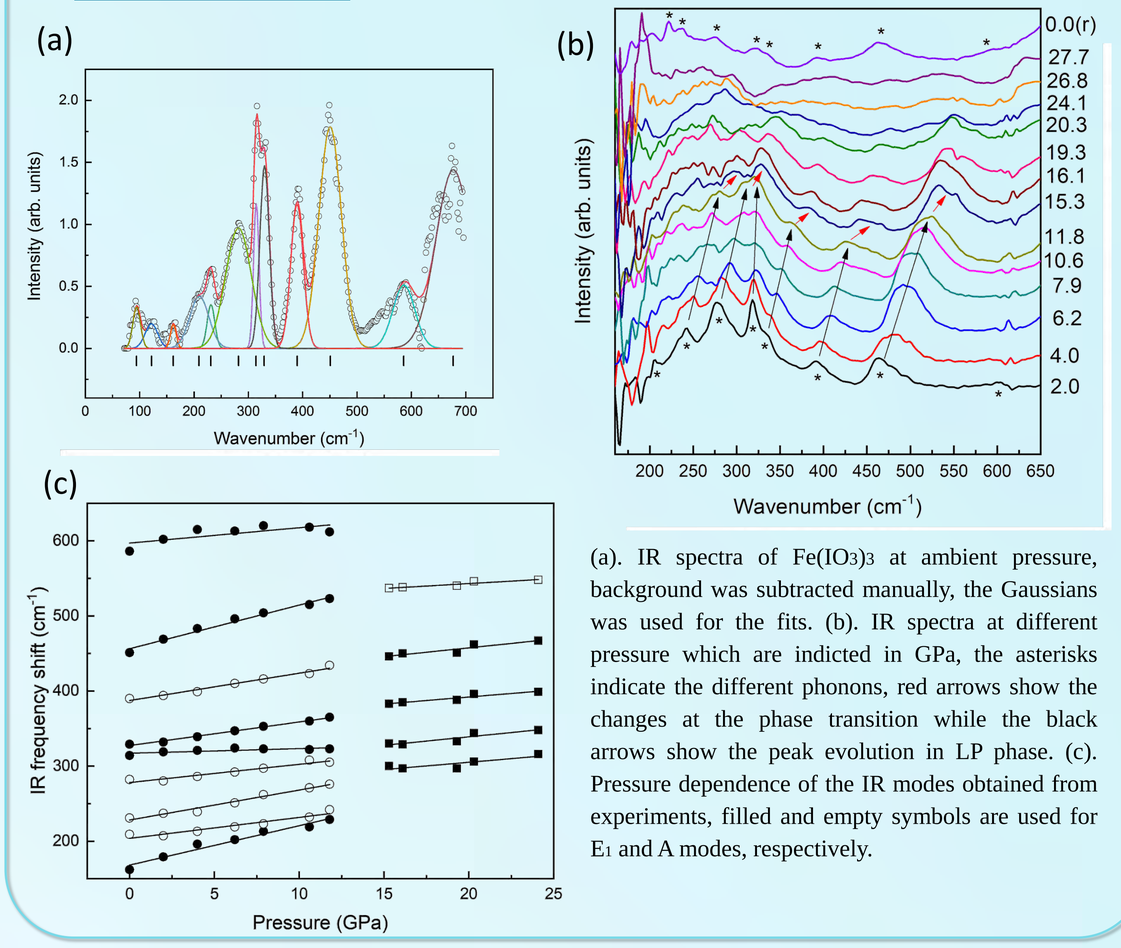
(a). Selected XRD pattern of $Fe(IO_3)_3$ at different pressure and the unit is GPa, black diamond indicate the appearance of peaks of the HP phase. (b). Typical refinement of the XRD patterns at lowest pressure, highest pressure which contain both the LP and HP phase, and at the ambient pressure released from the HP XRD experiment. (c). Pressure dependence of the unit-cell parameter in experiment (symbols) and calculation (line). (d) pressure dependence of the unit-cell volume in experiment (symbols) and calculation (lines).

Calculated I -O bond distance under pressure



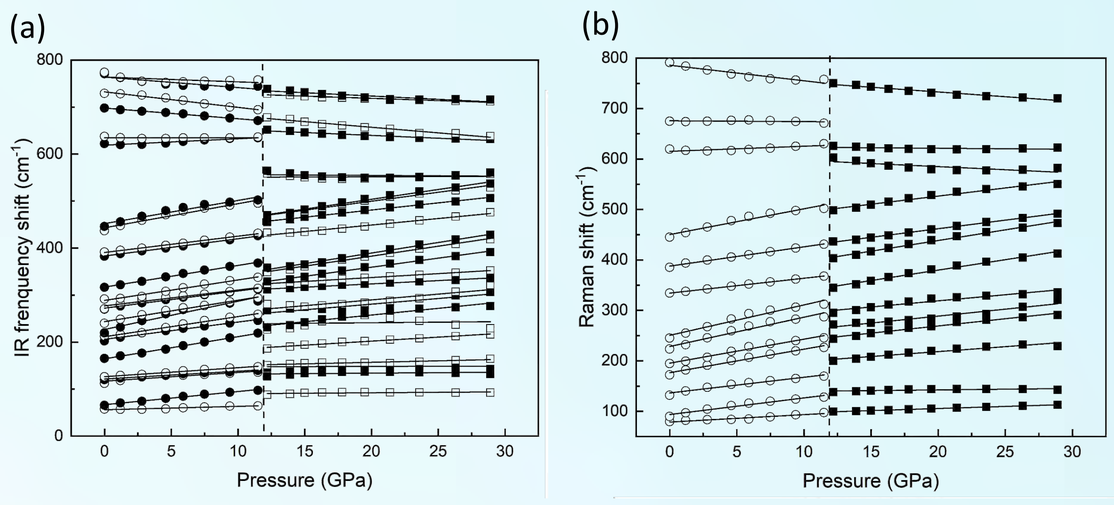
Calculated pressure dependence of I-O bond distance, solid line is for LP and dash line is for HP phase

HP Infrared



(a). IR spectra of $Fe(IO_3)_3$ at ambient pressure, background was subtracted manually, the Gaussians was used for the fits. (b). IR spectra at different pressure which are indicted in GPa, the asterisks indicate the different phonons, red arrows show the changes at the phase transition while the black arrows show the peak evolution in LP phase. (c). Pressure dependence of the IR modes obtained from experiments, filled and empty symbols are used for E_1 and A modes, respectively.

Calculated pressure dependence of vibration modes



(a). Calculated pressure dependence of the Raman and IR-active modes (A and E_1 modes, filled and empty symbol are used for E_1 and A modes, respectively). (b) calculated pressure dependence of Raman-active modes only (E2 mode).

Conclusion

1. Pressure induced phase transition on $Fe(IO_3)_3$ happened at 22 GPa in HP XRD and 15 GPa in HP IR, different phase transition pressure is because of different PTM.
2. According to the refinement of the HP XRD spectra, the HP phase can be described in the same space group as the LP phase, $P6_3$.
3. The phase transition accompanied by a gradually increase of the coordination of I atoms, which is due to the lone-pair electrons existed in I atoms.
4. The phase transition companied by a substantial c/a ratio and a volume collapse large than 5%. The nature of the phase transition is first-order.
5. The bulk modules of the LP and HP phase were B_0=55(2) GPa and B_0=73 GPa in experiment and B_0=36(1) GPa and B_0= 48(3) GPa in calculation.

Acknowledgements

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