

Comparative study of the high-pressure behavior of ZnV_2O_6 , $\text{Zn}_2\text{V}_2\text{O}_7$, and $\text{Zn}_3\text{V}_2\text{O}_6$

D. Díaz-Anichtchenko ^a, D. Santamaria-Perez ^a, T. Marqueño ^a, J. Pellicer-Porres ^a, J. Ruiz-Fuertes ^b, R. Ribes ^a, J. Ibañez ^c, S.N. Achary ^d, C. Popescu ^e, D. Errandonea ^a

^a Departamento de Física Aplicada-ICMUV, Universidad de Valencia, Dr. Moliner 50, Burjassot, 46100, Valencia, Spain

^b DCITIMAC, MALTA Consolider Team, Universidad de Cantabria, 39005, Santander, Spain

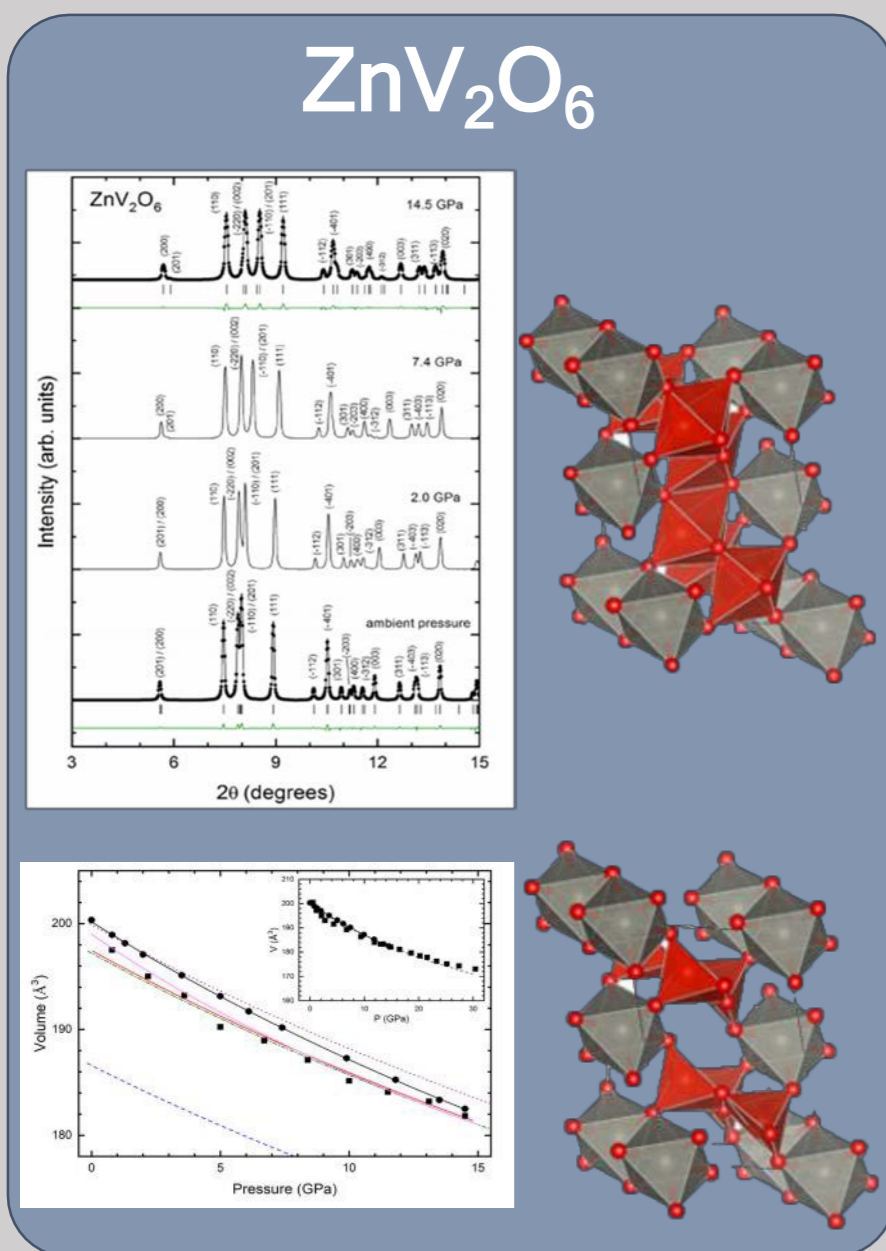
^c Institute of Earth Sciences Jaume Almera, MALTA Consolider Team, CSIC, 08028, Barcelona, Spain

^d Chemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai, 400085, India

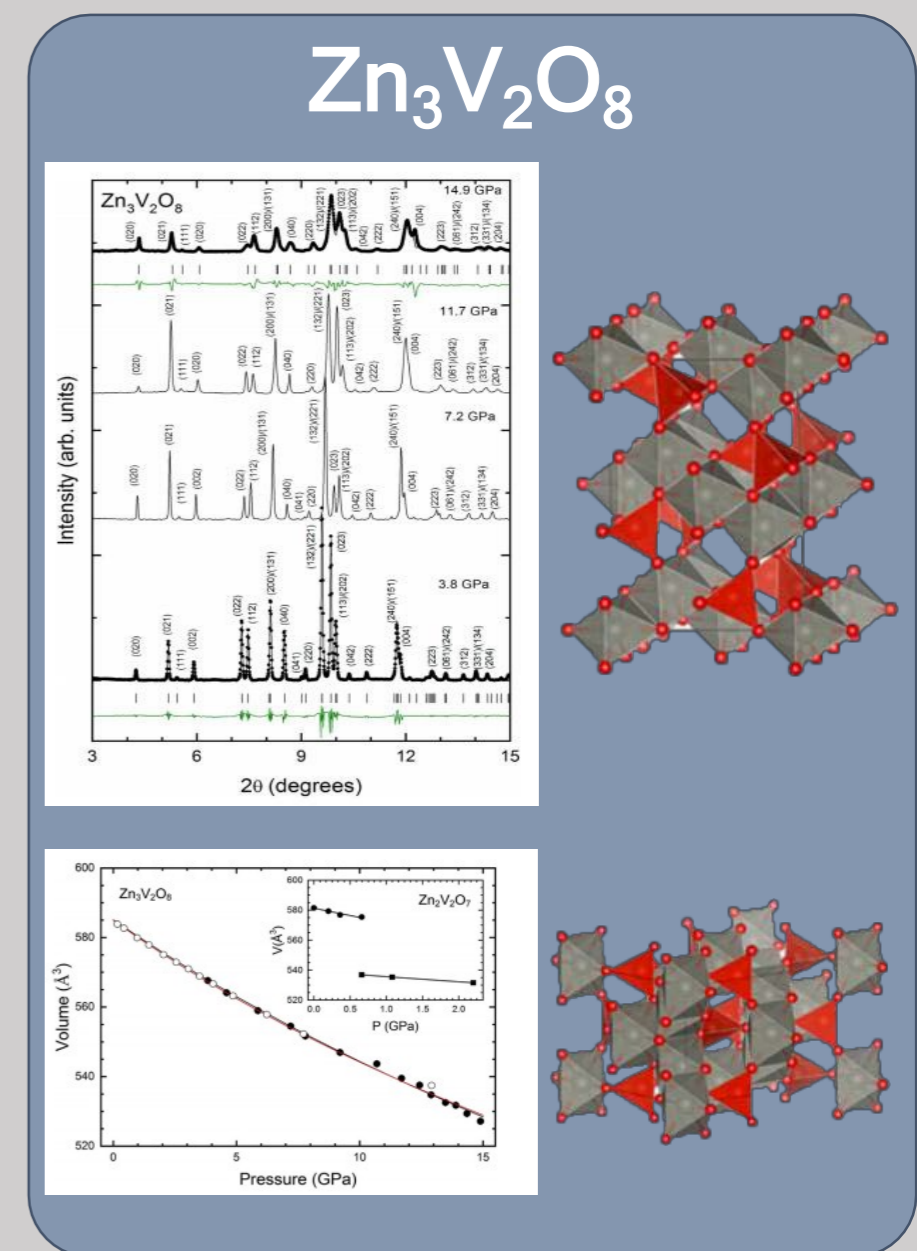
^e CELLS-ALBA Synchrotron Light Facility, Cerdanyola, 08290, Barcelona, Spain

We report a study of the high-pressure structural behavior of ZnV_2O_6 , $\text{Zn}_2\text{V}_2\text{O}_7$, and $\text{Zn}_3\text{V}_2\text{O}_8$, which has been explored by means of synchrotron powder x-ray diffraction. We found that ZnV_2O_6 and $\text{Zn}_3\text{V}_2\text{O}_8$ remain in the ambient-pressure structure up to 15 GPa. In contrast, in the same pressure range, $\text{Zn}_2\text{V}_2\text{O}_7$ undergoes three phase transitions at 0.7, 3.0, and 10.8 GPa, respectively. Possible crystal structures for the first and second high-pressure phases are proposed. Reasons for the distinctive behavior of $\text{Zn}_2\text{V}_2\text{O}_7$ are discussed. The compressibility of the different polymorphs has been determined. The response to pressure is found to be anisotropic in all the considered compounds and the room-temperature equations of

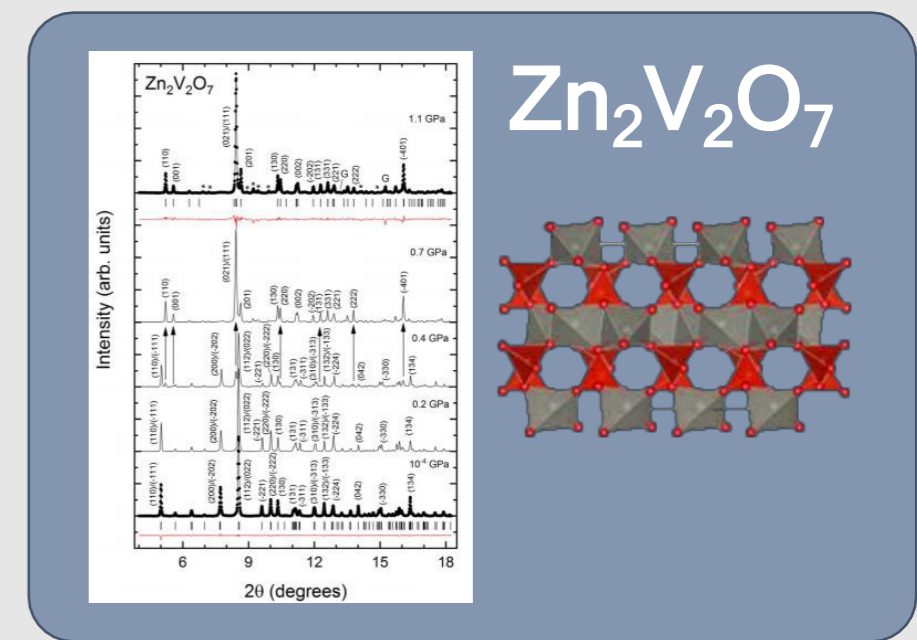
state have been determined. The bulk moduli of ZnV_2O_6 (129(2) GPa) and $\text{Zn}_3\text{V}_2\text{O}_8$ (120(2) GPa) are consistent with having a structural framework composed of compressible ZnO_6 octahedra and uncompressible VO_4 tetrahedra. In contrast, $\text{Zn}_2\text{V}_2\text{O}_7$ is highly compressible with a bulk modulus of 58(9) GPa, which is almost half of the bulk modulus of the other two vanadates. The large compressibility of $\text{Zn}_2\text{V}_2\text{O}_7$ and its sequence of structural transitions are related to the fact that this material is less dense than the other zinc vanadates and to the penta-coordination of Zn atoms by oxygen atoms in $\text{Zn}_2\text{V}_2\text{O}_7$. A comparison to the high-pressure behavior of related compounds is presented.



- Third-order Birch-Murnaghan equation of state from ZnV_2O_6 and $\text{Zn}_3\text{V}_2\text{O}_8$, respectively $V_0 = 200.16(6) \text{ \AA}^3$, $K_0 = 129(2) \text{ GPa}$, $K_0' = 4.1(3)$ and $V_0 = 585.0(4) \text{ \AA}^3$, $K_0 = 115(2) \text{ GPa}$, $K_0' = 5.1(6)$.
- The pressure dependence for unit-cell parameters is anisotropic for both. Respectively $\lambda_1 = 4.59(5) \cdot 10^{-3} \text{ GPa}^{-1}$, $\lambda_2 = 1.29(4) \cdot 10^{-3} \text{ GPa}^{-1}$, $\lambda_3 = 0.39(1) \cdot 10^{-3} \text{ GPa}^{-1}$ and $\lambda_1 = 2.5(1) \cdot 10^{-3} \text{ GPa}^{-1}$, $\lambda_2 = 2.4(1) \cdot 10^{-3} \text{ GPa}^{-1}$, $\lambda_3 = 1.4(1) \cdot 10^{-3} \text{ GPa}^{-1}$.
- ZnV_2O_6 : Octahedral chains Zn-O distances: $1.981 \text{ \AA} \times 2$ (apical) and $2.244 \text{ \AA} \times 4$ (equatorial) and tetrahedral chains V-O distances: 1.659 \AA , 1.681 \AA , and $1.856 \text{ \AA} \times 2$.
- $\text{Zn}_3\text{V}_2\text{O}_8$: Close packing arrangement of O atoms. Zn atoms occupy octahedral sites and the V atoms occupy tetrahedral positions.



- Second-order Birch-Murnaghan equation of state from $\text{Zn}_3\text{V}_2\text{O}_8$, $V_0 = 581.4(6) \text{ \AA}^3$, $K_0 = 58(2) \text{ GPa}$. The high-pressure phase have $V_0 = 269.6(6) \text{ \AA}^3$, $K_0 = 151(4) \text{ GPa}$.
- Zn and five O form chains of distorted trigonal bipyramids that share edges along the [110] direction. V atoms are four coordinated and each pair of $[\text{VO}_4]$ slightly distorted tetrahedra is linked by a common O atom.
- We observe three different phase transition at 1.1 GPa, 3.0 GPa and 10.8 GPa.



Acknowledgements:

Financial support given by the Spanish Ministry of Science, Innovation and Universities under Grant Nos. PID2019-106383GB-C41 and RED2018-102612-T (MALTA Consolider-Team) and by Generalitat Valenciana under Grant Prometeo/2018/123 (EFIMAT).