High pressure infrared study of $SmVO_4$

J. Pellicer-Porres[1*], T. Marqueño[1], E. Bandiello[1], A. Liang[1], A. Segura[1], A. Muñoz[2], P. Rodríguez-Hernández[2], D. Errandonea[1] and I. Yousef[3]

[1]ICMUV, MALTA Consolider Team, Depto. Física Aplicada, Ed. Investigación, c/Dr. Moliner 50, 46100 Burjassot (Valencia), Spain
[2]Departamento de Física, Instituto de Materiales y Nanotecnología, Universidad de La Laguna, La Laguna 38200, Tenerife, Spain
[3]CELLS-ALBA Synchrotron Light Facility, Cerdanyola del Valles, E-08290 Barcelona, Spain

*e-mail: Julio.Pellicer@uv.es

Introduction

Rare earth orthovanadates have been extensively characterized under high pressure [1]. In $SmVO_4$, as in nearly the whole family of compounds, lattice vibrations have been characterized by Raman spectroscopy[2]. The knowledge of modes with only infrared activivity is, however, scarce. We describe in this communication the results of high-pressure FTIR experiments performed on $SmVO_4$. The experimental results are complemented with ab-initio simulations.

Experimental

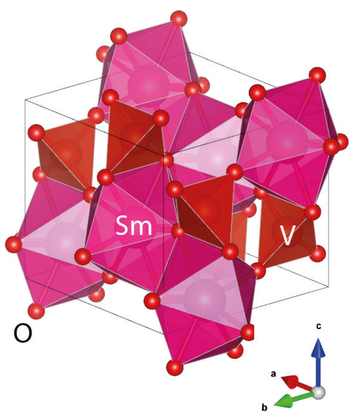
One of the two experiments were performed at the MIRAS beamline of the ALBA synchrotron light source facility. High pressure was generated with a membrane diamond anvil (MDAC). The size of the diamond culets and gasket hole was 500 and 250 μm, respectively. The pressure transmitting medium was CsI. The sample was in powder form, pre-compacted to form some 5 μm thick pellets. The measurements were perfomed in the transmission mode of operation (100-660 cm^{-1}).

The second experiment was performed in a laboratory set-up, which includes a Michelson FTIR spectrometer and a globar thermal source. In this case the reflectance of an oriented single crystal was acquired in the spectral domain from 700-1200 cm^{-1}. Polarization was selected parallel and perpendicular to the c-axis. High pressure generation was done with similar conditions as those of the first experiment, except that the pressure transmitting medium was KBr.

Calculations

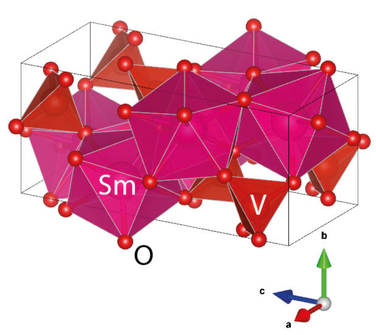
Computer simulations were performed with the Vienna ab initio Simulation Package within the framework of the density functional theory. The pseudopotentials were generated with the projector augmented wave scheme, including the 4f core electrons. The generalized-gradient approximation with the AM05 prescription was used for describing the exchange-correlation energy. We used a basis of plane waves up to a kinetic energy cutoff of 520 eV and a dense Monkhorts-Pack k-special points grid to perform the integrations on the Brillouin zone (BZ), which guarantees highly converged results. Starting with a set of selected volumes, we optimized the structural configurations by minimizing the forces on the atoms and the stress tensor. Our optimization criteria were to achieve forces smaller than 0.006 eV/Å and differences among the diagonal components of the stress tensor lower than 0.1 GPa. Simulations were performed assuming T = 0K.

Zircon



$\Gamma(IR)=3A_{2u}+4E_u$

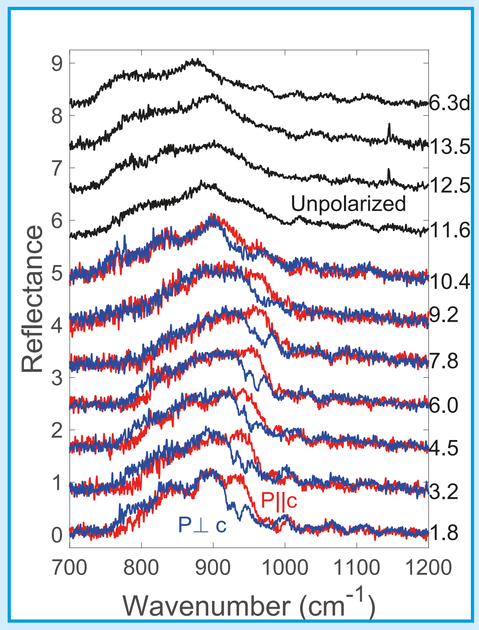
Scheelite



$\Gamma(IR)=4A_u+4E_u$

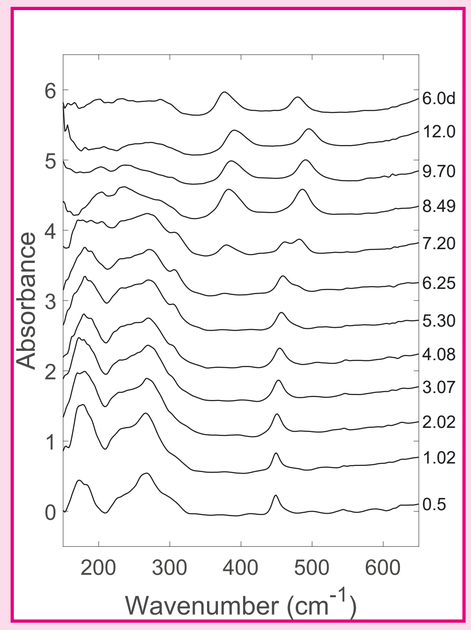
Laboratory set-up

Single crystal sample



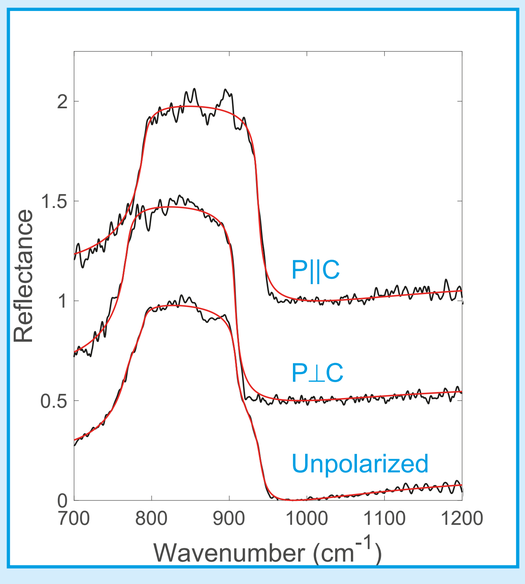
MIRAS beamline

Sample in powder form



Laboratory set-up

Single crystal sample

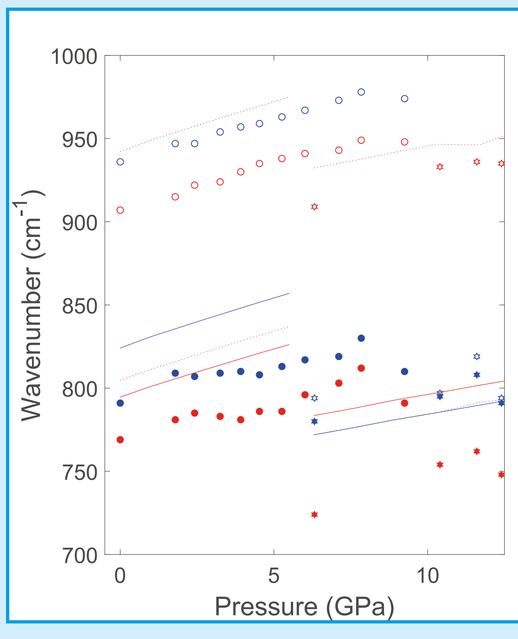


Laboratory set-up

Zircon
- A2u(TO)
- A2u(LO)
- Eu(TO)
- Eu(LO)

Scheelite:
- Au(TO)
- Au(LO)
- Eu(TO)
- Eu(LO)

Ab-initio
- A2u, Au(TO)
- A2u, Au(LO)
- Eu(TO)
- Eu(LO)

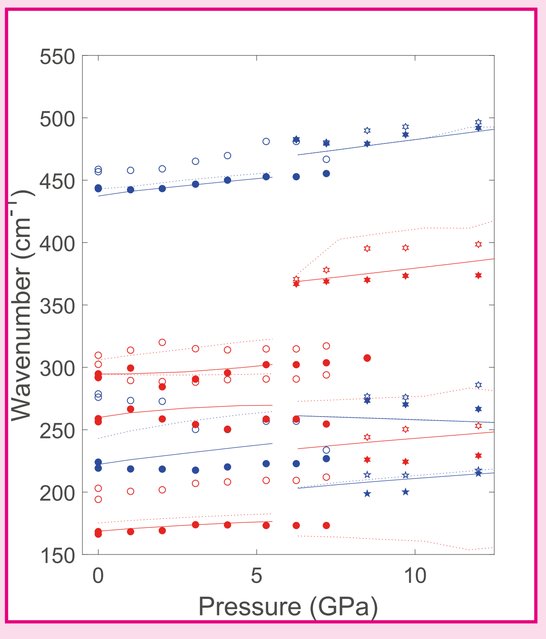


Synchotron

Zircon
- A2u(TO)
- A2u(LO)
- Eu(TO)
- Eu(LO)

Scheelite:
- Au(TO)
- Au(LO)
- Eu(TO)
- Eu(LO)

Ab-initio
- A2u, Au(TO)
- A2u, Au(LO)
- Eu(TO)
- Eu(LO)



Zircon	Calculated		Experimental	
	σ (cm^{-1})	dσ/dP (cm^{-1}/GPa)	σ (cm^{-1})	dσ/dP (cm^{-1}/GPa)
Eu(LO)	800(20)	5.9(1)	907(2)	6.1(3)
Eu(TO)	790(20)	5.8(1)	769(2)	3.1(3)
A2u(LO)	940(30)	6.0(1)	936(4)	5.1(3)
A2u(TO)	820(30)	6.0(1)	791(2)	3.3(3)
A2u(LO)	443(10)	2.5(1)	456(5)	2.8(3)
A2u(TO)	440(10)	2.8(1)	439(5)	2.6(3)
Eu (LO)	306(9)	3.1(1)	308(5)	3.7(5)
Eu (TO)	294(9)	0.6(1)	294(5)	-0.4(5)
Eu (LO)	294(9)	-0.2(1)	291(5)	-0.7(5)
Eu (TO)	261(8)	1.7(1)	259(5)	-0.6(5)
A2u(LO)	244(7)	3.8(1)	277(5)	-5.0(5)
A2u(TO)	223(6)	3.0(1)	220(5)	0.6(5)
Eu (LO)	175(5)	1.6(1)	198(3)	2.5(5)
Eu (TO)	169(5)	1.7(1)	167(3)	1.9(1)

Scheelite	Calculated at 9 GPa		Experimental at 9 GPa	
	σ (cm^{-1})	dσ/dP (cm^{-1}/GPa)	σ (cm^{-1})	dσ/dP (cm^{-1}/GPa)
Eu (LO)	940(30)	3.2(1)	922(5)	3.4(0.3)
Eu (TO)	790(20)	3.3(1)	740(5)	4.8(3)
Au(LO)	780(20)	3.4(1)	799(5)	2.3(3)
Au(TO)	780(20)	3.3(1)	790(5)	3.6(3)
Au(LO)	480(10)	4.8(1)	491(5)	1.8(2)
Au(TO)	480(10)	3.3(1)	482(5)	3.4(.2)
Eu (LO)	410(10)	1.5(1)	395(5)	1.0(2)
Eu (TO)	380 (10)	2.9(1)	371(5)	0.9(2)
Au(LO)	259(8)	-0.9(1)	276(5)	2.8(5)
Au(TO)	259(8)	-0.9(1)	289(5)	-1.9(5)
Eu (LO)	275(8)	2.8(1)	247(5)	2.4(5)
Eu (TO)	241(7)	2.0(1)	225(5)	1.1(5)
Au(LO)	211(6)	2.1(1)	214(5)	1.1(5)
Au(TO)	209(6)	1.9(1)	199(7)	5(1)
Eu (LO)	172(4)	-1.1(1)	-	-
Eu (TO)	149(4)	-1.6(1)	-	-

Conclusions

- We have characterized the high pressure behaviour of all IR active modes of the zircon phase and most of the scheelite phase.
- In the powder experiment we observe a structural phase transition beggining at 6.2 GPa, in perfect agreement with Raman results 6.5 GPa[2]. In the single crystal experiment the high pressure phase is not clearly observed until 10.4 GPa. This is not only due to different pressure conditions but also to smaller differences in the high frequency *internal* modes corresponding to both phases.
- The structural modifications inherent to the pase transition changes the symmetry of the modes: A2u(Z)→Au(S), Eu-(Z)→Eu(S). As a rule of thumb, the frequency of the modes decrease across the phase transition. In the scheelite phase the TO-LO splitting of Au modes is considerably reduced.

Acknowledgments

This work was supported by the Spanish Ministry of Science, Innovation and Universities under Grant Nos. MAT2016-75586-C4-1/3-P, PID2019-106383GB-C41/43 and RED2018-102612-T (MALTA Consolider-Team network) and by Generalitat Valenciana under Grant No. Prometeo/2018/123 (EFIMAT).

References

[1] D. Errandonea, D. A. B. Garg, Progress in Materials Science 2018, 97, 123-169
[2] D. Errandonea, S. N. Achary, J. Pellicer-Porres and A. K.Tyagi, Inorganic Chemistry 52 (9), 5464-5469 (2013)