Phase Behaviour of Ag$_2$CrO$_4$ under Compression: Structural, Vibrational, and Optical Properties

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Phase behaviour of Ag$_2$CrO$_4$ under compression: Structural, vibrational, and optical properties.

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Abstract.- We have performed an experimental study of the crystal structure, lattice dynamics, and optical properties of silver chromate (Ag_2CrO_4) at ambient temperature and high pressures. In particular, the crystal structure, Raman-active phonons, and electronic band gap have been accurately determined. When the initial orthorhombic *Pnma* Ag_2CrO_4 structure (Phase I) is squeezed up to ∼4 GPa, a previously undetected phase (Phase II) has been observed with a 0.95% volume collapse. The structure of Phase II can be indexed into a similar orthorhombic cell as Phase I, and the transition can be considered as an isostructural transition. This collapse is mainly due to the drastic contraction of the *a* axis (~1.3%). A second phase transition to Phase III occurs at ∼13 GPa, to a structure not yet determined. First-principles calculations have been unable to reproduce the isostructural phase transition likely due to electronic considerations in chromium atoms. Calculations propose the stabilization of a spinel-type structure at 11 GPa. This phase is not detected in experiments probably due to the presence of kinetic barriers.

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1.- Introduction

Silver chromate has been extensively studied at ambient conditions due to its unusual red color, which makes this compound unique as pigment and for colouring applications. Although it remains as a controversial subject, some authors concluded that the intense absorption centred at 450 nm could be explained by a $^1T_2 \leftarrow {}^1A_1$ transition of the $[CrO_4]^{2-}$ anion, red-shifted in the silver salt[1,2]. Regarding its crystal structure, Ag_2CrO_4 crystallizes in the orthorhombic space group *Pnma* (Nr. 62), with lattice constants: $a = 10.063(11)$ Å, $b = 7.029(4)$ Å, and $c = 5.540(2)$ Å and four formula units per cell (Z = 4) at ambient conditions[3]. The topology of this olivine-like structure is typically described as consisting of isolated chromate $[CrO_4]$ groups, whose oxygen atoms are coordinated to the silver atoms to generate the tridimensional network (see Fig. 1). Two different types of silver-centred oxygen polyhedra exist: elongated octahedra and distorted off-centered tetrahedra. This crystal structure is also adopted by other ternary oxides such as forsterite Mg_2SiO_4[4], Al_2BeO_4[5] or Ag_2MnO_4[6]. The structures of some alkaline-metal chromates like those of potassium[7], rubidium[8] and cesium[9], differ significantly from that of silver chromate even if described in the same space group. Compared to these compounds, the shorter metal-oxygen distances of silver chromate point to a greater degree of covalent bonding between cations and anions[10].

Few experimental studies on Ag_2CrO_4 at high temperature (HT) or high pressure (HP) have been reported[11-14]. A reversible first-order structural transformation was observed at 490ºC by differential thermal analysis, electrical conductivity measurements, and temperature-variable x-ray diffraction[11,12,14]. The HT phase appears to be hexagonal with Z=16 and lattice parameters $a = 9.92(4)$ Å and $c = 19.76(8)$ Å at 506ºC[11]. The phase diagram of silver chromate was studied by Pistorious up to 4 GPa and 900ºC and,

besides the aforementioned HT phase, no additional polymorphs were found[13,14]. With regard to polymorphism at extreme conditions, a complementary description of the silver chromate structure based on the topology of it cation Ag_2Cr subarray could be relevant[15]. This cationic framework adopts the Ni_2In structural type, formed by trigonal prisms of Ag atoms connected by common edges forming straight chains which run parallel to the *ab* plane (see Fig. 1). Adjacent chains of prisms are shifted $1/2a$ along this axis. The Cr atoms ([CrO_4] groups) are located in the center of such prisms. Alkaline-metal chromates of K, Rb, and Cs adopt, however, a Co_2Si-type structure which also consists of trigonal prisms of metal atoms but in a zig-zag configuration. This alternative view of crystal structures of oxides, together with the well-established fact that cations in oxides tend to reproduce the structure of the corresponding or intimately-related alloy, could provide a tool to qualitatively predict new pressure-induced phases[15]. Thus, high-pressure studies on several oxides have shown that high-pressure transformations involve an increase of the number of neighbour atoms in their second coordination sphere[16-18]. Moreover, the behaviour of M_2X compounds (where M = group IA or IB elements) under compression[19-25] could give some hints of the potential transition mechanisms in Ag_2CrO_4.

Taking this background into account, this work aims at giving a detailed picture of the structure and physical properties of silver chromate up to 20 GPa. Angle-dispersive x-ray diffraction (ADXRD), Raman spectroscopy, and optical absorption measurements suggest that the initial orthorhombic phase undertakes an isostructural transition with a drastic volume collapse above 4 GPa and a subsequent transition above 13 GPa. Preliminary first-principles calculations are unable to reproduce the isostructural phase transition likely due to electronic considerations in chromium atoms.

2.- Experimental details

Commercial silver chromate powder with 99.9% purity (Alfa Aesar, Prod. Nr. 7784-01-2) was crushed in a mortar to obtain micron-sized samples. These samples were used to carry out HP-ADXRD, HP-Raman, and HP-optical absorption measurements at room temperature.

2.1.- ADXRD experiments. Three independent HP-ADXRD experiments were conducted in diamond-anvil cells up to 20 GPa. Experiment 1 was carried out using an in-house Xcalibur diffractometer with K_α molybdenum radiation (0.7107 Å). The same set-up was previously used to successfully characterize the high-pressure phases of other compounds in the same pressure range[22-24]. Experiments 2 and 3 were performed at the I15 beamline of Diamond and the MSPD beamline[26] of ALBA synchrotron light sources, respectively, with a 40×40 μm-focused incident monochromatic beam of 0.4246 Å. The Ag_2CrO_4 metallic-lustered powder samples were loaded in a 150 μm-diameter hole of a stainless-steel gasket preindented to a thickness of about 40 μm. A 16:3:1 methanol:ethanol:water mixture was used as pressure-transmitting medium. Preliminary data reduction was done using the Fit2D software[27]. Pressure was measured by three different methods: (i) the ruby fluorescence scale[28]; (ii) the equation of state (EOS) of silver[29], which was added as external pressure calibrant in experiments 1 and 2; and (iii) the EOS of copper[30] in experiment 3. These methods give a maximum pressure uncertainty of 0.2 GPa at the highest pressure of this study. The observed intensities were integrated as a function of 2θ in order to give one-dimensional diffraction profiles. The indexing and refinement of the powder diffraction patterns were performed using the FULLPROF[31] and POWDERCELL[32] program packages.

2.2.- Raman experiments. Unpolarized HP-Raman scattering measurements at room temperature were performed on powder samples in backscattering geometry with a LabRAM HR UV microspectrometer coupled to a Peltier-cooled CCD camera. A 632.81 nm (1.96 eV) HeNe laser excitation line with a power around 1 mW and a spectral resolution better than 2 cm^{-1} were used. During Raman experiments, samples were checked by monitoring the time dependence of the Raman signal at different accumulations and by visual inspection before and after each measurement in order to be sure that no heating effects occur during the measurements by the incoming laser excitation since the laser energy was above the band gap energy (1.80 eV). In order to analyze the Raman spectra, Raman peaks have been fitted to a Voigt profile (Lorentzian profile convoluted by a Gaussian profile) where the spectrometer resolution is taken as a fixed Gaussian width (1.5 cm^{-1}). For HP studies the samples were loaded in a membrane-type DAC. A 16:3:1 methanol:ethanol:water mixture was used as pressure-transmitting medium and pressure was measured by the ruby fluorescence scale.[28]

2.3.- Optical absorption measurements. For optical absorption studies, we used 20-μm-thin platelets cleaved from small single crystals. The single crystals were obtained compressing the Ag_2CrO_4 powder to 1 GPa using a large volume press equipped with Brigmann anvils and using hexagonal boron nitride disc as pressure medium and to isolate the sample from the tungsten carbide anvils[33]. Measurements in the visible-near-infrared range were done in an optical setup, which consisted of a deuterium lamp, fused silica lenses, reflecting optics objectives, and a visible-near-infrared spectrometer[34]. For HP-optical absorption studies the samples were loaded in a membrane-type DAC with similar configuration as in HP-ADXRD and HP-Raman experiments. The optical-absorption spectra were obtained from the transmittance

spectra of the sample, which were measured using the sample-in, sample-out method[35,36].

2.4.- First-principles calculations. Total-energy *ab initio* simulations have been performed within the density-functional theory (DFT) framework as implemented in the Vienna *ab initio* simulation package (VASP) (see Refs. [37] and [38] and references therein). The program performs *ab initio* structural calculations with the plane-wave pseudo-potential method. The set of plane waves employed extended up to a kinetic energy cutoff of 520 eV. Such a large cutoff was required to achieve highly converged results within the projector-augmented-wave (PAW) scheme [38,39]. The PAW method takes into account the full nodal character of the all-electron charge density distribution in the core region. The exchange-correlation energy was taken in the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) prescription[40]. It is well known that the GGA approach typically underestimates the cohesion energy [41] (in turn producing an overestimation of the equilibrium volume). We used dense special point grids appropriate to each structure considered to sample the Brillouin zone (BZ), thus ensuring a high convergence of 1–2 meV per formula unit in the total energy of each structure as well as an accurate calculation of the forces over the atoms. At each selected volume, the structures were fully relaxed to their equilibrium configurations through the calculation of the forces on atoms and the stress tensor[41]. In the relaxed equilibrium configuration, the forces were smaller than 0.006 eV/Å, and the deviation of the stress tensor from a diagonal hydrostatic form was less than 0.1 GPa.

Lattice-dynamic calculations of phonon modes were performed at the zone center ($\Box$ point) of the BZ. We used a direct force-constant approach (or supercell method)[42] that it is conceptually simple. These calculations provide information about the

symmetry of the modes and their polarization vectors, and allowed us to identify the irreducible representations and the character of the phonon modes at the □ point.

3.- Crystal structure under compression

Figures 2 and 3 show the ADXRD data for Ag_2CrO_4 at several selected pressures in experiment 3. The other data sets present similar features. At ambient conditions, the X-ray diffraction pattern corresponds to the orthorhombic olivine-like structure previously reported (S.G. *Pnma*, No. 62) with similar lattice parameters: $a = 10.065(4)$ Å, $b = 7.013(3)$ Å and $c = 5.538(2)$ Å. ADXRD patterns can be indexed in the initial low-pressure (LP) orthorhombic phase up to 3.5 GPa. Atomic coordinates do not change significantly in this pressure range. For instance, the ADXRD pattern at 2.7 GPa was refined by the Rietveld method (see Fig. 2) with an olivine-like model, obtaining the final atomic positions collected in Table I. The evolution of the unit-cell volume and lattice parameters of this phase are shown in Fig. 4a and 4b, respectively. It can be seen that the contraction of the lattice parameters is rather anisotropic. For instance, according to our experiments, the relative contractions for *a*, *b,* and *c* between room pressure and 3.5 GPa are 1.51, 1.17, and 3.15%, respectively. A third-order Birch-Murnaghan EOS gives the following characteristic parameters: (i) a zero-pressure volume $V_0 = 391.3(3)$ Å^3, (ii) a bulk modulus $B_0 = 52(2)$ GPa, and (iii) its first pressure derivative $B'_0 = 5.4(9)$. It is worth to mention that, even considered as an olivine-like structure, the different chemical content of Ag_2CrO_4 generates different b/a and c/a axes ratios which cause two distinct coordination spheres for the silver atoms (C.N. 6 and 4), instead of the quite regular $[MgO_6]$ octahedra in olivine. This distribution of polyhedra and the fact that the Ag – O bonds are significantly more compressible that the Cr – O bonds, make compression parallel to the *b* axis much more restricted than parallel to *c*.

Axial compressibility of different olivine-like polymorphs differ considerably due to different cation sizes and valences[5,43]. Resultant bulk moduli also have a huge variability, from 242(5) GPa in Al_2BeO_4 chrysoberyl ($B'_0 = 4$, fixed)[5] to the value obtained in this work for Ag_2CrO_4. Note also that the compressibility of K_2CrO_4, with a Co_2Si-type cation subarray, is significantly larger ($B_0 = 26(2)$ GPa and $B'_0 = 6.0(5)$) than that of Ag_2CrO_4, with a Ni_2In-type cation network[44].

The LP phase starts to transform into a new HP phase (named HP1) at 3.5 GPa. The ADXRD patterns between this pressure and 5 GPa present five new low intense peaks below $2\theta = 8.4°$ (synchrotron radiation) and some of the existing Bragg peaks seem to slightly broaden. Diffractograms in this pressure range could not be unequivocally indexed but the stability of the positions and intensities of most of the peaks suggests that only a small distortion of the lattice occurs. Between 5 and 12.5 GPa, the ADXRD patterns could be indexed in an orthorhombic cell, whose reflection conditions are consistent with a *Pnma* symmetry, similarly to the ambient structure. The formation of this new phase entails a volume decrease of 0.95%, mainly caused by the 1.3% collapse of the *a* axis (see Fig. 4b). The olivine-like structural model was used as a starting point for a Rietveld refinement. The HP1 phase (depicted in Fig. 5) turned out to have the same structure that the LP phase. As shown in Table I, the refinement suggests that the Ag_2Cr cation subarray seems not to change significantly and only a strong distortion of the $[CrO_4]$ tetrahedra is observed, with Cr – O distances at 6.4 GPa ranging from 1.565 to 1.84 Å (compare to 1.58 – 1.74 Å at 2.7 GPa) and angles ranging from 70 to 132° (compare to 104 – 115° at 2.7 GPa). Confirmation of such a strong polyhedral distortion by single-crystal HP-ADXRD measurements is advisable. It is worth to mention that the coexistence of the LP and HP1 phases would enable explaining two of the extra peaks observed between 3.5 and 5 GPa, as well as the apparent broadening of some reflections.

The zero-pressure volume and the compressibility of the HP1 phase have been estimated by fixing the pressure derivative B'$_0$ to 4: V$_0$ = 382(2) Å^3, B$_0$ = 69(3) GPa. This phase is a bit less compressible than the initial LP phase, the continuous decrease of the lattice parameters being shown in Fig. 4b.

Above 10 GPa, the diffraction peaks broaden significantly as a consequence of the loss of the quasi-hydrostatic conditions and the appearance of deviatoric stresses in the compressed sample[45] (see Fig. 3). These stresses could induce the second high-pressure phase (HP2) observed above 13 GPa. The limited quality of the x-ray patterns at these pressures avoids unequivocal indexation but the small amount of changes observed at the transition suggests either a slow process with coexistence of the HP1 and HP2 phases during a large pressure range or a low-symmetry distortion of the HP1 orthorhombic phase. Both high-pressure phase transitions are reversible and the LP phase is recovered after decompression with similar lattice constants.

4.- Lattice dynamics under compression

Group theoretical considerations[46] indicate that the *Pnma* structure of Ag$_2$CrO$_4$ has 36 Raman-active modes with the following mechanical representation $\Gamma = 11A_g + 7B_{1g} + 11B_{2g} + 7B_{3g}$, which can be also classified by factor group analysis as internal or external modes of the CrO$_4$ units so that there are 18 internal modes [2ν_1, 4ν_2, 6ν_3, 6ν_4] and 18 external modes [6 rotational (R) and 12 translational (T)][10]. Therefore, the 36 Raman-active modes can be classified as 11A$_g$ (ν_1,ν_2,2ν_3,2ν_4,R,4T) + 7B$_{1g}$ (ν_2,ν_3,ν_4,2R,2T) + 11B$_{2g}$ (ν_1,ν_2,2ν_3,2ν_4,R,4T) + 7B$_{3g}$ (ν_2,ν_3,ν_4,2R,2T). Up to now only 12 Raman modes were measured for Ag$_2$CrO$_4$ at ambient conditions, likely due to considerable overlapping of modes[10], while 28 out of 42 Raman modes were measured

for structurally-related alkaline-earth chromates[47,48] and 30 out of 36 Raman modes have been recently measured in monazite-type $PbCrO_4$ [49].

Figure 6 shows the Raman spectra of Ag_2CrO_4 at room temperature at selected pressures till 18.8 GPa. The Raman spectrum of the LP phase is similar to that reported earlier[10]. The most intense Raman modes are the stretching modes of the CrO_4 group in the high-frequency region between 750 and 900 cm^{-1} [10,47,48]. Of considerable smaller intensity are the bending modes of the CrO_4 group in the medium-frequency region between 300 and 400 cm^{-1}. Finally, translational and rotational lattice Raman modes in the low-frequency region below 150 cm^{-1} are the most difficult to identify. A change in the Raman spectrum can be clearly observed in both the medium- and high-frequency regions at 5 GPa. This change is in good agreement with the phase transition suggested by ADXRD measurements at similar pressures. A more important change in the Raman spectrum is observed above 14.8 GPa; thus confirming the phase transition reported around 14 GPa by ADXRD measurements. Raman measurements on downstroke at 12.8 and 0.1 GPa confirm the reversibility of both phase transitions.

Figure 7 shows the pressure dependence of the measured Raman mode frequencies in Ag_2CrO_4 at room temperature till 19 GPa. Experimental and calculated Raman modes for the LP phase are compared till 5 GPa and show a good agreement (see Table II). On the other hand, Table III summarizes the frequencies and pressure coefficients of the observed Raman modes for the HP1 and HP2 phases at 5 and 14 GPa, respectively. It can be observed that the frequencies of the stretching modes above 5 and 14 GPa are similar to those of the low-pressure phase, thus suggesting that there is no drastic change in coordination during the two phase transitions at least for the Cr atom. In this respect, the different pressure dependence of the Raman modes above 14 GPa do not suggest the coexistence of HP1 and HP2 phases in a region larger than 1 GPa.

Furthermore, the larger number of Raman modes observed in the HP2 phase with respect to HP1 suggests that HP2 could be a low-symmetry distortion of the HP1 phase.

5.- Optical absorption under compression

Figure 8 shows the optical absorption spectra of Ag_2CrO_4 at room temperature and at selected pressures up to 5.2 GPa. Absorption spectra of the LP phase show a steep absorption, characteristic of a direct bandgap, plus a low-energy absorption band, which overlaps partially with the fundamental absorption. This absorption band has been previously observed in related oxides and seems to be caused by the presence of defects or impurities. Its nature has been the subject of considerable debate and is beyond the scope of this work. Regarding the steep absorption edge, we found it exhibits an exponential dependence on the photon energy following the Urbach's law. Therefore, in order to determine the bandgap energy, E_g, we have analyzed the measured absorption spectrum assuming $\alpha = A_0 \exp[-(E_g - hv)/E_u]$. In this equation E_u is Urbach's energy, which is related to the steepness of the absorption tail, and $A_0 = k\sqrt{E_u}$ for a direct band gap, with k being a characteristic parameter. From the analysis of the spectra collected at ambient pressure we determined the bandgap to be 1.8 eV in good agreement with previous studies[50].

In Fig. 8 it can be seen that upon compression the absorption edge gradually red-shifts up to 4.7 GPa. At 5.2 GPa, an abrupt shift is detected, which produce the color change from brown-red to dark-brown, indicating the occurrence of a bandgap collapse. We associated this change to the first transition detected at similar pressure in diffraction and Raman experiments. At 5.2 GPa, the absorption spectrum also resembles that of a direct bandgap semiconductor. Unfortunately, at higher pressures we could not

perform experiments because the sample deteriorates likely due to increasing intergrain strains, which prevented the performance of accurate optical measurements.

In order to qualitatively analyze the pressure effects on the bandgap of the LP phase, we assumed that the LP and HP1 phases have a fundamental direct bandgap. Using the same method employed to determine E_g at ambient conditions, we obtained the pressure dependence of E_g. The inset of Figure 8 shows the variation of the E_g versus pressure up to 5.2 GPa. The LP phase shows a linear negative pressure coefficient of the bandgap energy (−30 meV/GPa) up to the phase transition pressure. From 4.7 to 5.2 GPa, E_g abruptly changes from 1.65 to 1.47 eV. Based upon present knowledge of the electronic structure of Ag_2CrO_4 at atmospheric pressure and the behavior of other chromates upon compression, a qualitative approach toward the understanding of the present results is suggested in the following. According to Ouyang et al.[50], the main contribution to the bottom of the conduction band in Ag_2CrO_4 results from the antibonding interaction between the Cr 3d orbitals and the Ag 5s5p orbitals, while the upper portion of the valence band results primarily from the interaction between Ag 4d and O 2p orbitals. Under compression, O 2p states shift toward high energies faster than the Cr 3d states because of the increase of the crystal field. This causes a reduction of the energy difference between the bottom of the conduction band and the top of the valence band, inducing the E_g reduction we observed up to 4.7 GPa. On the other hand, the collapse of E_g observed at 5.2 GPa could be caused by the structural change we found at similar pressures. Although the structural changes do not affect the global symmetry of the crystal, the crystal structure is highly distorted, affecting Cr-O and Ag-O bond angles and distances. These changes of the crystalline structure should be directly reflected in the electronic structure of Ag_2CrO_4, producing the collapse of E_g that we observed.

6.- First-principles calculations under compression

Total-energy (E) calculations as a function of volume were performed for five different high-pressure structural candidates of Ag_2CrO_4. The choice of these potential phases is justified by: (i) the expected analogy with the pressure-induced sequence in M_2X compounds (thenardite (Na_2SO_4-type, *Fddd*) and spinel (Na_2MoO_4-type, *Fd-3m*)), (ii) the expected analogy with pressure-induced transformations in olivine (wadsleyite (*Imma*), spinel) or (iii) possible structural similarities with chemically-related compounds (*Pnma* K_2CrO_4-type or *Pbnn* Na_2CrO_4-type).

After performing a full optimization of the lattice parameters and atomic positions, we found that, as expected, the initial *Pnma* phase is the structure of Ag_2CrO_4 with the lowest enthalpy at ambient pressure. A fit with a Birch-Murnaghan third-order equation of state (EOS) gives the following characteristic parameters in good agreement with experimental results: $V_0 = 408.2 \ Å^3$, $B_0 = 50.2$ GPa and $B'_0 = 5.7$ (see also Fig. 4). The equilibrium volume V_0 is overestimated by $\sim$ 4 %, as usual with the GGA approximation. Our first-principles calculations using the GGA approximation do not predict any volume collapse in the initial *Pnma* structure at high pressures. The addition of the on-site repulsion Hubbard term U to Ag and Cr atoms did not help either to reproduce the structural behavior of the orthorhombic Ag_2CrO_4 phase. Therefore, these experimental and theoretical evidences seem to indicate that a new structural and electronic description is required to model the properties of silver chromate. Low-symmetry subgroups of the initial Ag_2CrO_4 phase (space group Nrs. 31, 26, 19, 14 and 11) were also considered as HP candidates but, after relaxation of the lattice parameters and the atomic coordinates, all of them could be described within a *Pnma* space group.

Only the spinel-type structure has been found to be energetically competitive at high pressures for silver chromate (see Figure 9). The spinel-type structure, with cubic

symmetry, becomes more stable than the *Pnma* phase at a pressure of 11 GPa, after a first order phase transition with 2.7% decrease in the volume. The spinel phase, however, has not been found experimentally in the pressure range covered in our experiments. This may be caused by the presence of kinetic-energy barriers or temperature effects that avoid the transformation.

7.- Concluding remarks

Three different characterization techniques, i.e. X-ray diffraction, optical absorption and Raman spectroscopy, evidence the existence of two pressure-induced phase transitions in silver chromate, at 4 and 13 GPa. The first HP phase could be indexed into an orthorhombic cell similar to that adopted at ambient pressure, and the atomic coordinates of Ag and Cr atoms did not change significantly. Only a considerable distortion of the [CrO$_4$] seems to take place but the structure can still be described within the initial *Pnma* space group. Consequently, the transition can be considered as an isostructural transition. This collapse is mainly due to the drastic contraction of the *a* axis (~1.3%). We note that a similar rare transition was also recently observed in other chromate, the cubic perovskite PbCrO$_3$, which suffers a large volume collapse in an isostructural transition[51].

A second phase transition occurs at ~13 GPa, to an unknown structure which, Raman and x-ray diffraction data suggests could be a low-symmetry intimately-related polymorph. First-principles calculations have been unable to reproduce both phase transitions likely due to electronic considerations in Ag and Cr atoms and, in the case of the second transition, to the existence of non-hydrostatic conditions in the experiment. Instead, they predict a high pressure transformation to the spinel structure at 11 GPa,

which experimentally was not observed in the studied pressure range likely due to the existence of kinetic effects

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Table I.- Lattice parameters and Rietveld-refined fractional coordinates for the LP phase at ambient pressure and 2.7 GPa, and for the HP1 phase at 6.4 GPa.

	RP experiment	RP theory	2.7 GPa	6.4 GPa
a axis (Å)	10.065(4)	10.224	9.953(2)	9.682(3)
b axis (Å)	7.013(3)	7.025	6.9570(14)	6.862(2)
c axis (Å)	5.538(2)	5.653	5.4078(8)	5.3349(9)
Unit cell volume (Å^3)	390.9(4)	406.02	374.5(2)	354.4(3)
x_{Ag2}	0.1357(8)	0.1412	0.1364(9)	0.146(3)
z_{Ag2}	0.4916(14)	0.4827	0.5115(19)	0.522(3)
x_{Cr}	0.312(2)	0.3182	0.3130(19)	0.316(5)
z_{Cr}	1.003(3)	0.9633	0.983(5)	1.012(7)
x_{O1}	0.148(5)	0.1553	0.137(6)	0.149(19)
z_{O1}	0.919(8)	0.9051	0.974(13)	1.026(24)
x_{O2}	0.356(6)	0.3466	0.351(7)	0.389(11)
z_{O2}	0.265(9)	0.2558	0.270(12)	0.275(3)
x_{O3}	0.386(3)	0.3865	0.382(5)	0.441(7)
y_{O3}	0.442(4)	0.4429	0.454(5)	0.402(7)
z_{O3}	0.876(5)	0.8439	0.873(6)	0.940(9)

Table II.- Symmetries, zero-pressure frequencies, and pressure coefficients of the theoretical and experimental Raman-active modes of the LP phase of Ag_2CrO_4.

	ω_0 (th.) (cm^{-1})	a (th.) (cm^{-1}/GPa)	ω_0 (exp.) (cm^{-1})	a (exp.) (cm^{-1}/GPa)		ω_0 (th.) (cm^{-1})	a (th.) (cm^{-1}/GPa)	ω_0 (exp.) (cm^{-1})	a (exp.) (cm^{-1}/GPa)
B_{3g}	13.1(1)	0.7(1)			B_{1g}	320.8(3)	2.7(1)		
A_g	36.3(1)	1.0(1)			B_{3g}	321.0(2)	1.8(1)		
B_{1g}	40.4(3)	-1.3(2)			A_g	328.3(6)	0.6(2)		
B_{2g}	45.6(3)	1.1(1)			B_{2g}	330.0(3)	-0.9(1)		
A_g	51.2(1)	1.8(1)			B_{2g}	335.6(1)	1.9(1)	338(2)	1.4(2)
B_{2g}	61.0(1)	1.3(1)			B_{1g}	342.0(6)	1.2(2)		
B_{3g}	92.2(2)	4.7(1)			A_g	351.9(1)	0.13(4)		
A_g	104.6(7)	4.5(1)			B_{3g}	354.9(5)	1.5(1)	353(2)	2.9(3)
A_g	112.0(3)	4.8(1)	116(1)	2.6(1)	A_g	361.1(2)	2.4(1)	373(1)	2.7(2)
B_{2g}	117.6(5)	4.4(2)			B_{2g}	384.4(1)	2.1(1)		
B_{1g}	129.5(1)	2.9(1)			A_g	769.4(6)	3.3(2)	776(1)	5.5(2)
B_{2g}	139.4(5)	3.7(2)			B_{2g}	778.5(5)	1.4(2)		
B_{3g}	143.5(6)	3.7(2)			A_g	810.4(3)	1.7(1)	812(1)	0.9(1)
B_{2g}	148.8(2)	4.2(1)			A_g	830.0(3)	1.5(1)	826(2)	1.5(1)
B_{1g}	161.0(6)	6.4(2)			B_{3g}	839.6(5)	4.4(2)		
A_g	161.8(2)	3.7(1)			A_g	847.1(5)	4.3(2)	849(3)	3.8(2)
B_{1g}	216.6(3)	4.7(1)			B_{2g}	849.2(8)	-0.1(1)		
B_{3g}	225.5(4)	5.5(1)			B_{2g}	858.3(2)	2.4(2)	859(3)	2.6(1)

Table III.- Frequencies and pressure coefficients of the experimental Raman-active modes of the HP1 and HP2 phases of Ag_2CrO_4 at 5 and 14 GPa, respectively, after fit to equation $\omega = \omega_0 + a*P$.

Phase II (5 GPa)			Phase III (14 GPa)		
Mode	**ω_0 (exp.) (cm^{-1})**	**a (exp.) (cm^{-1}/GPa)**	**Mode**	**ω_0 (exp.) (cm^{-1})**	**a (exp.) (cm^{-1}/GPa)**
1	73(2)	0.8(1)	1	131(1)	0.8(1)
2	92(2)	0.8(1)	2	170(1)	-0.03(1)
3	119(2)	1.5(1)	3	214(1)	-0.9(1)
4	239(3)	4.4(2)	4	216(1)	1.6(1)
5	316(2)	-0.5(1)	5	243(1)	2.1(1)
6	345(2)	0.3(1)	6	351(2)	-3.9(1)
7	379(2)	2.1(2)	7	368(2)	-0.08(1)
8	808(1)	0.9(1)	8	385(2)	2.5(1)
9	823(1)	2.9(1)	9	415(9)	3.6(5)
10	853(1)	1.6(2)	10	816(1)	-1.0(1)
			11	819(1)	1.1(1)
			12	831(2)	1.6(1)
			13	852(2)	1.1(2)
			14	859(3)	4.7(2)

Table IV.- Lattice parameters and fractional coordinates for the spinel-type phase at 14.4 GPa, predicted from first-principles calculations above 11 GPa: S.G. Fd-3m (Nr. 227), origin choice 2.

Lattice parameter: $a = 8.759$ Å				
Unit cell volume: $V = 672$ Å^3				
Atom	Wyckoff position	x	y	z
Ag	16c	0	0	0
Cr	8b	0.375	0.375	0.375
O	32e	0.26508	0.26508	0.26508

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Figure captions

Figure 1.- (Color online) Projection along the c axis of the low-pressure olivine-like *Pnma* phase of silver chromate. Coordination polyhedra around the Ag and Cr atoms are depicted in gray and yellow, respectively.

Figure 2.- (Color online) X-ray powder diffraction patterns of Ag_2CrO_4 at three selected pressures below 10 GPa. The calculated profiles and the residuals of the Rietveld refinements at 2.7 and 6.4 GPa are represented as red and blue lines, respectively. Vertical marks indicate the Bragg reflections of the orthorhombic Pnma Ag_2CrO_4 structure and metallic copper, which was used as a second internal pressure calibrant. The asterisk marks the appearance of the most intense diffraction peak of the gasket.

Figure 3.- X-ray powder diffraction patterns of Ag_2CrO_4 at three selected pressures above 10 GPa. Vertical marks indicate the Bragg reflections of the orthorhombic Pnma Ag_2CrO_4 structure and metallic copper at 11.4 GPa.

Figure 4.- (Color online) Evolution of the volume (a) and the lattice parameters (b) of the low-pressure and the HP1 phases of Ag_2CrO_4 with pressure. Red, black and green symbols correspond to XRD data according to Xcalibur, Diamond and ALBA experiments. In (b), the a/2, b, and c axes are represented by squares, circles, and triangles, respectively. Dashed and solid lines correspond to fittings to our experimental data and results from theoretical calculations.
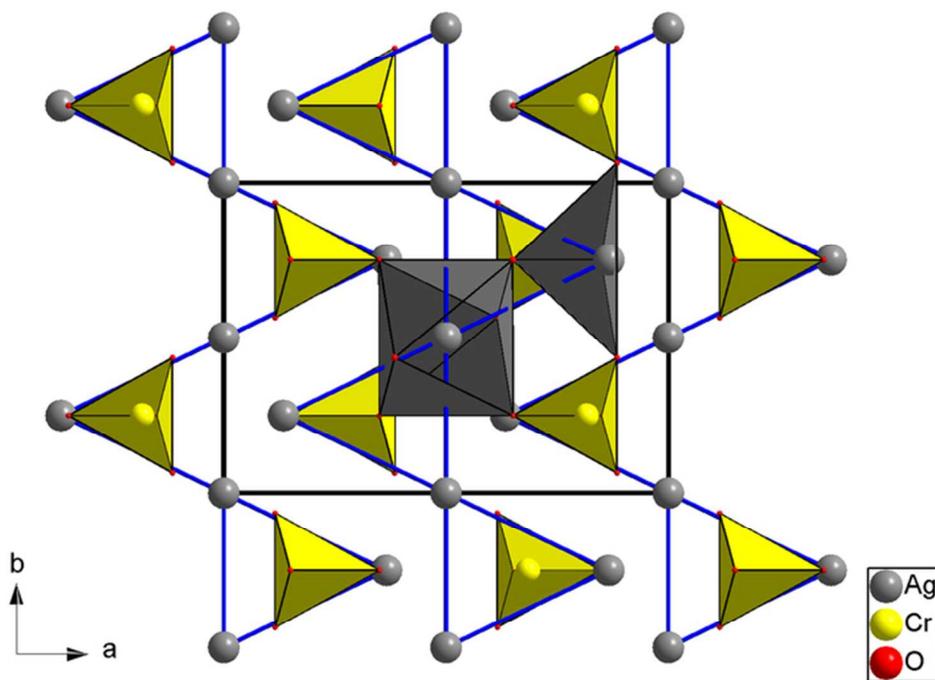
Figure 5.- (Color online) Projection along the c axis of the HP1 *Pnma* phase of silver chromate, to be compared to Fig. 1. As can be seen the cation Ag_2Cr subarray still adopts a Ni_2In-type structure, but the Ag and Cr coordination polyhedra are rather distorted.
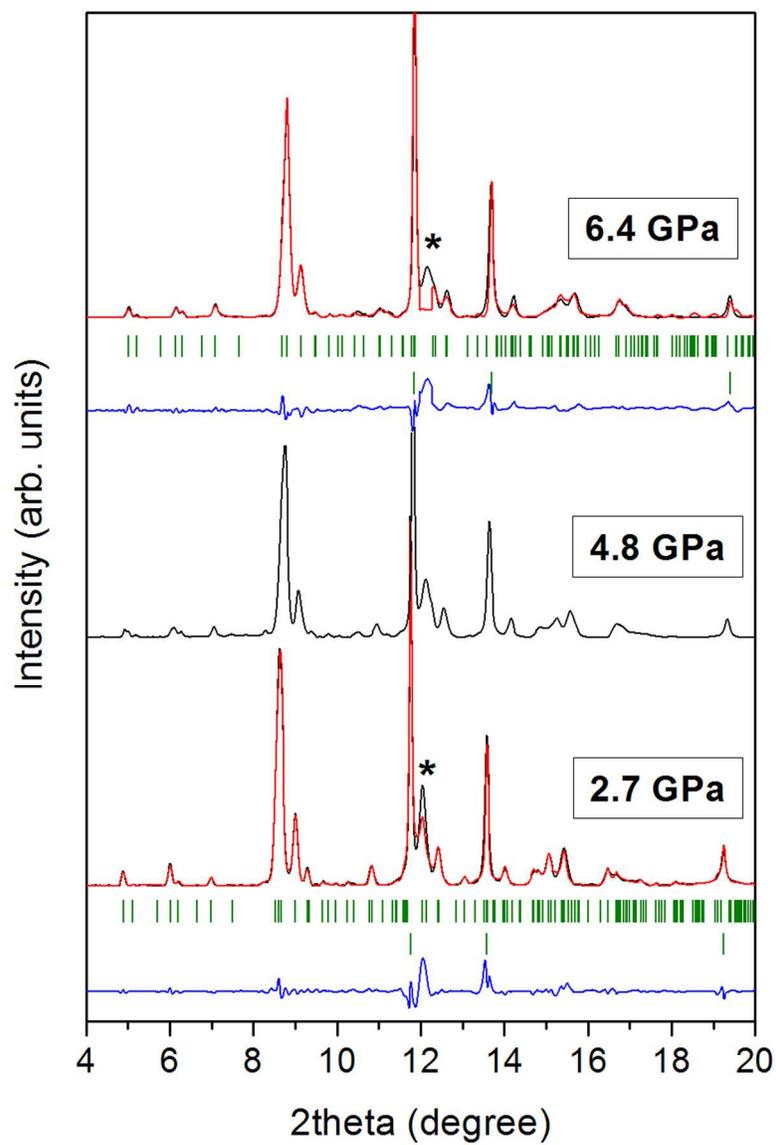
Figure 6.- Raman scattering spectra of Ag_2CrO_4 at selected pressures till 18.8 GPa on upstroke and down to ambient pressure on downstroke (d). Two reversible phase transitions around 5 and 14 GPa have been observed.

Figure 7.- (Color online) Pressure dependence of the Raman-active modes in Ag_2CrO_4. Red, blue, black, and pink black circles (experimental) and lines (theoretical) refer to A_g, B_{1g}, B_{2g}, and B_{3g} modes of the low-pressure phase, respectively. Raman-active modes of the HP1 and HP2 high-pressure phases above 5 and 14 GPa are noted with triangles and squares, respectively.

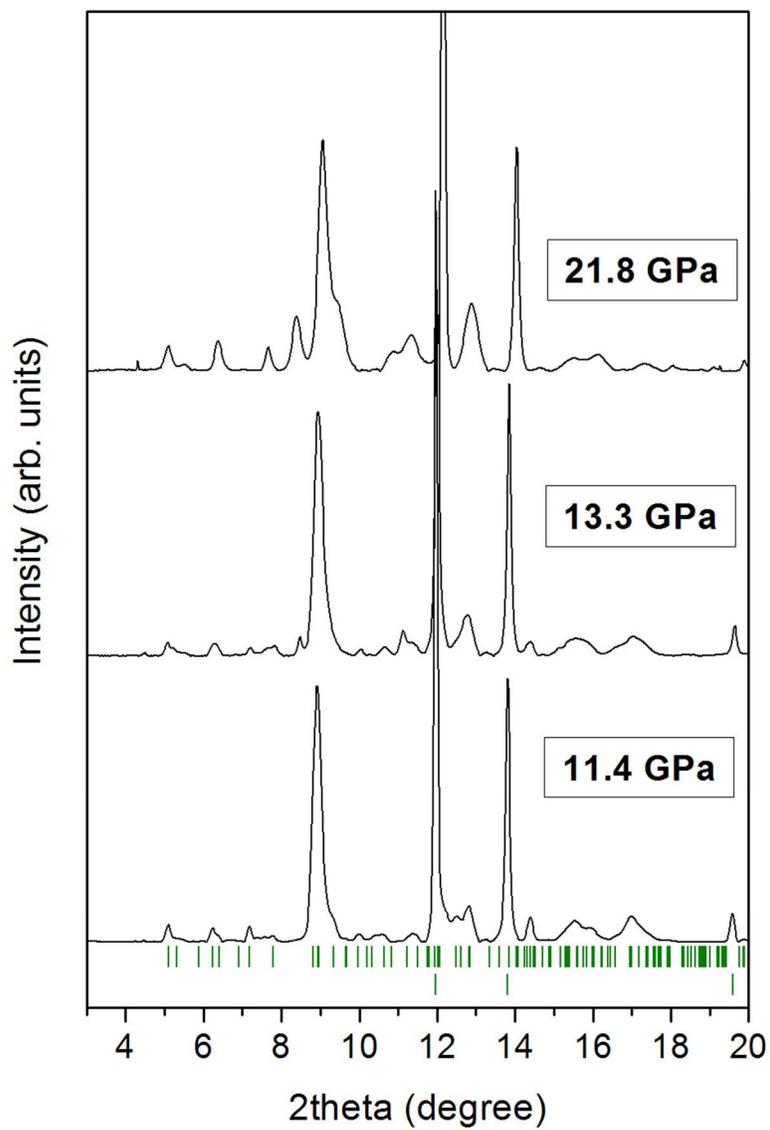**Figure 8**.- Optical absorption spectrum of Ag_2CrO_4 at selected pressures till 5.2 GPa. Inset shows the pressure dependence of the bandgap energy.

Figure 9.- Energy as a function of volume curves for the initial *Pnma* phase and the spinel-type phase. Both curves cross each other at a volume corresponding to a pressure of 11 GPa. Energy and volume are written per formula unit.

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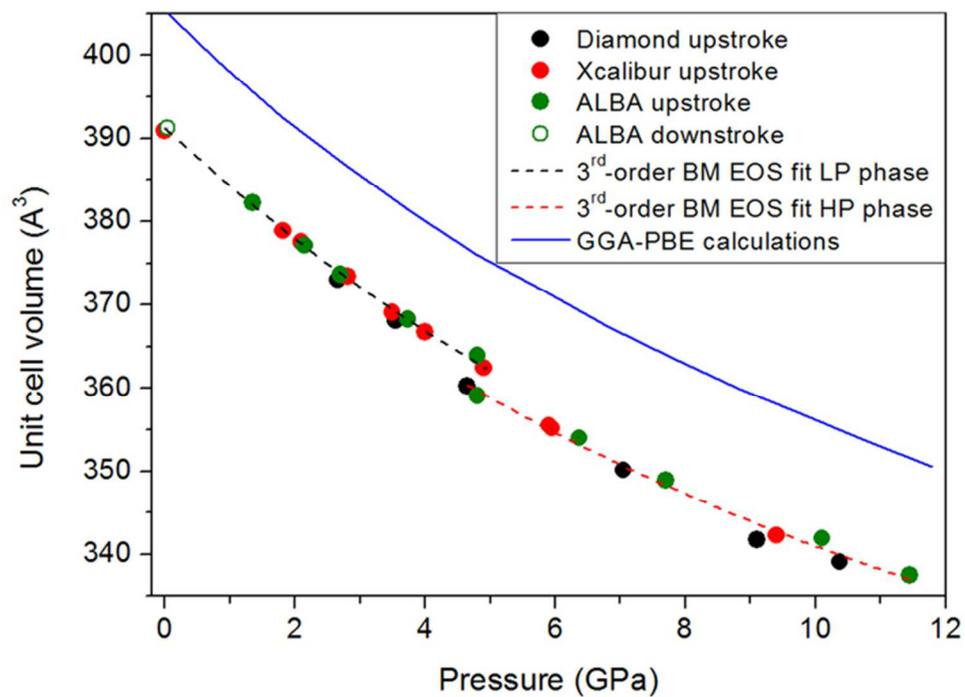2
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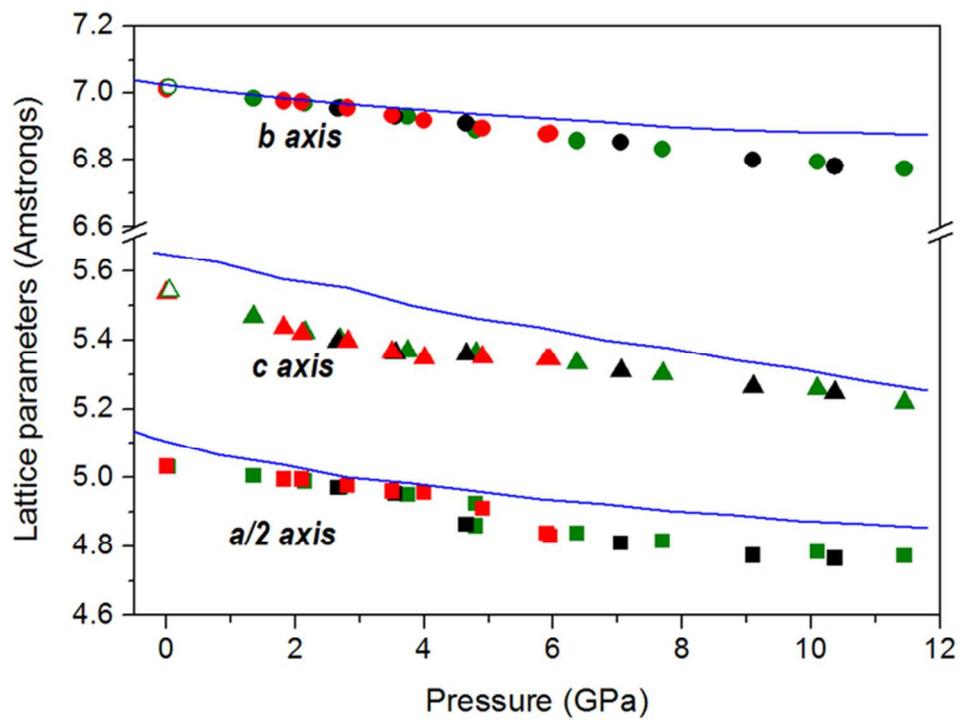41
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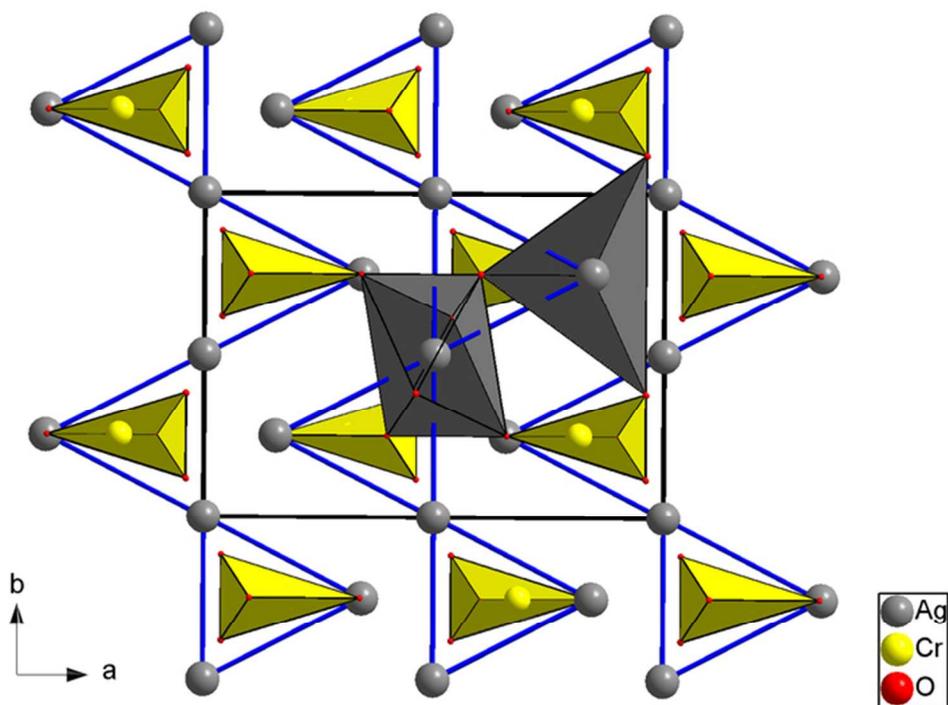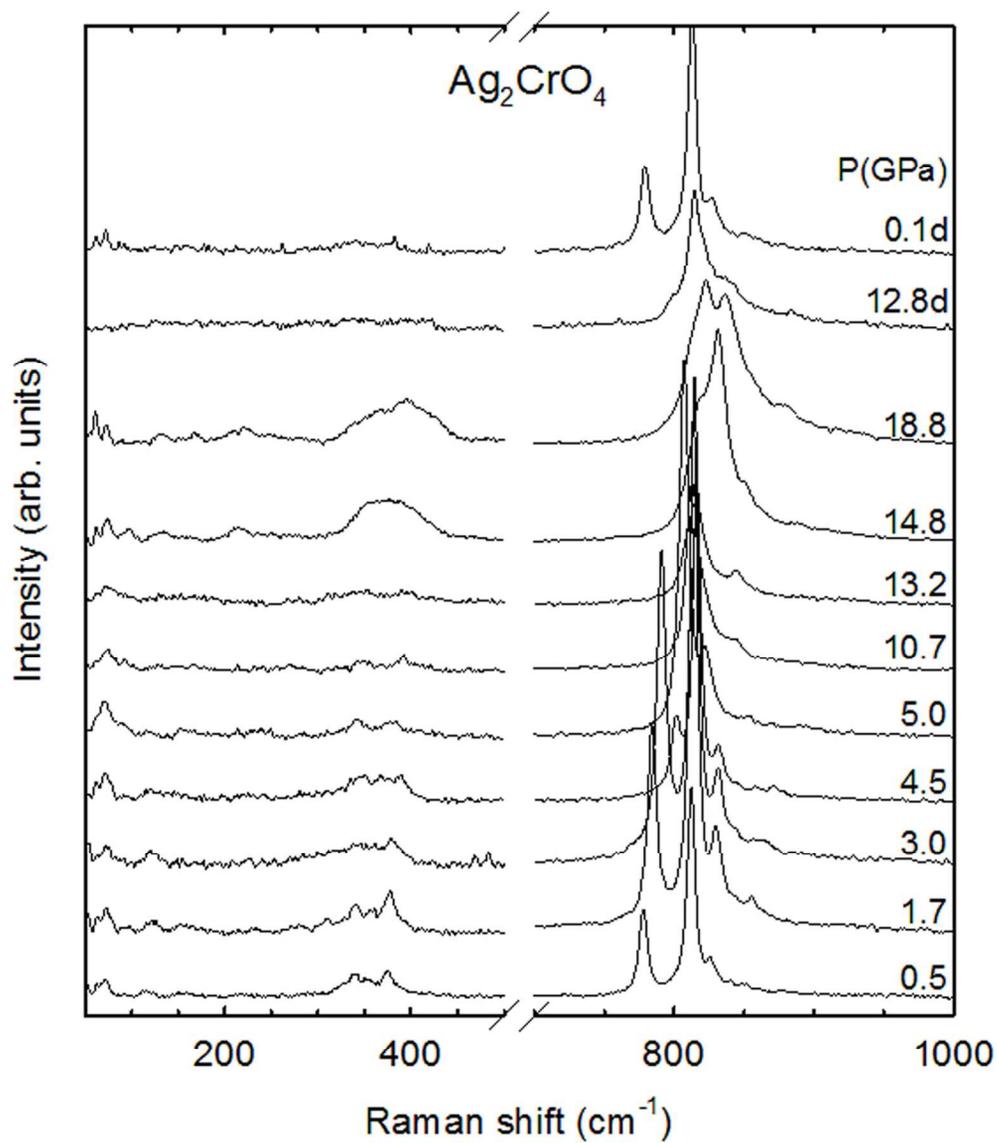63x48mm (300 x 300 DPI)

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