Gomis Hilario, O.; Vilaplana Cerda, RI.; Manjón, F.; Santamaría Pérez, D.; Errandonea, D.; Pérez González, E.; López Solano, J.... (2013). Crystal structure of HgGa2Se4 under compression. Materials Research Bulletin. 48:2128-2133. doi:10.1016/j.materresbull.2013.02.037.

Crystal structure of $HgGa_2Se_4$ under compression

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Abstract

We report on high-pressure x-ray diffraction measurements up to 17.2 GPa in mercury digallium selenide ($HgGa_2Se_4$). The equation of state and the axial compressibilities for the low-pressure tetragonal phase have been determined and compared to related compounds. $HgGa_2Se_4$ exhibits a phase transition on upstroke towards a disordered rock-salt structure beyond 17 GPa, while on downstroke it undergoes a phase transition below 2.1 GPa to a phase that could be assigned to a metastable zinc-blende structure with a total cation-vacancy disorder. Thermal annealing at low- and high-pressure shows that kinetics plays an important role on pressure-driven transitions.

Keywords:

A. Chalcogénides

C. High-pressure

C. X-ray diffraction

D. Crystal structure

D. Phase transitions

PACS numbers: 61.05.cp, 61.50.Ks, 62.50.-p, 64.70.kg

1. Introduction

Mercury digallium selenide ($HgGa_2Se_4$) is one of the less studied adamantine-type $A^{II}B_2^{III}X_4^{VI}$ ordered-vacancy compounds (OVCs). It crystallizes in the tetragonal defect-chalcopyrite (DC) structure with space group (SG) I-4, Z=2 [see **Fig. 1(a)**]. Adamantine OVCs are tetrahedrally-coordinated semiconductors which have an unoccupied cationic site **[1, 2]**. The presence of vacancies results in a complex physics and explains why OVCs have been scarcely studied. A common feature of them is that they have several non-equivalent tetrahedrally-coordinated cations resulting in a distortion of the crystal lattice from the cubic symmetry. This fact, their anisotropy, and their band-gap energies make them suitable for many technological applications **[3, 4].**

High-pressure (HP) studies on $A^{II}B_2^{III}X_4^{VI}$ compounds are receiving increasing attention in the last years **[3-20]**. In particular, ternary selenide compounds have been recently studied **[3, 4, 6 - 10, 12 - 20]**. However, to our knowledge, only one work has been devoted to $HgGa_2Se_4$ **[3]**, being focused on optical properties. In order to improve the knowledge of the HP behaviour of AGa_2Se_4 compounds, we report here synchrotron XRD measurements in $HgGa_2Se_4$. In particular, we show evidence of the presence of two new phases. They can be probably assigned to a disordered rock-salt (DR) structure (SG: Fm-3m, Z=1) [see **Fig. 1(b)**] and a disorder zinc-blende (DZ) structure (SG: F-43m, Z=1) [see **Fig. 1(c)**].

2. Experimental section

Single crystals of DC-$HgGa_2Se_4$ have been grown from its constituents HgSe and Ga_2Se_3 by chemical vapor transport method using iodine as a transport agent **[21]**. Chemical and structural analyses have shown the stoichiometric composition of the

crystals and no spurious phases have been observed. Ambient pressure x-ray diffraction and Raman spectroscopy confirmed that our sample has a DC-type structure.

We have carried out a HP angle-dispersive powder x-ray diffraction (XRD) experiment at room temperature. This experiment was performed up to 17.2 GPa at beamline ID27 of ESRF using a monochromatic beam (λ = 0.3738 Å) with a beam diameter of 5 μm full-width at half maximum. In this experiment samples were loaded in a modified Merrill-Basset diamond anvil cell (DAC) allowing access to an angular range of $2\theta = 25^{o}$. $HgGa_2Se_4$ powder was placed in the 150 μm-diameter hole of a stainless-steel gasket pre-indented to a thickness of 50 μm. XRD images were collected using a MARCCD detector located at 238 mm away from the sample and then integrated and corrected for distortions using FIT2D **[22].** The typical acquisition time was 10 s. In this case samples were loaded in the DAC with MgO which was used both as the pressure-transmitting medium (PTM) and as pressure marker using its equation of state (EOS): B_0 = 154.7 GPa, and B_0'= 4.69 **[23].** We select the use of this pressure medium because the non-hydrostatic conditions thus generated favor the occurrence of phase transitions **[24, 25]**. The indexing and refinement of the powder patterns were performed using the UNITCELL **[26],** POWDERCELL **[27]** and GSAS program packages **[28, 29].**

3. Results and discussion

Figure 2 shows selected XRD patterns of DC-$HgGa_2Se_4$ from ambient pressure till 17.2 GPa obtained in our experiment on increasing and decreasing pressure. Asterisks mark the peaks corresponding to MgO. **Table 1** summarizes the lattice parameters and atomic positions of DC-$HgGa_2Se_4$, obtained at 1 bar from a Rietveld

refinement of our XRD pattern. The refined parameters were: the scale factor, lattice parameters, profile coefficients, fractional coordinates of the Se anion, and the overall displacement factor. The background was subtracted previously. Our results agree with those of **Refs. 30** and **31** which are also shown in **Table 1** for comparison.

In **Fig. 2** diffractograms from 1 bar to 17.2 GPa on upstroke correspond to the low-pressure tetragonal DC phase and show that diffraction peaks move to higher angles as pressure increases, thus indicating that the interplanar distances decrease. It is also observed that peak widths of the DC-$HgGa_2Se_4$ phase increase gradually above 7 GPa which implies that hydrostatic conditions are deteriorating with increasing pressure. On the other hand, in general, $HgGa_2Se_4$ peaks move faster than those of MgO as can be seen from the (111) MgO Bragg reflection located at 8.93º at 7.1 GPa. This reflection is overtaken at 10.1 GPa by the (211) DC-$HgGa_2Se_4$ Bragg reflection located at 8.71º at 1 bar. This fact is a consequence of the different compressibility of MgO and $HgGa_2Se_4$. At 17.2 GPa all peaks broaden considerably and two new broad peaks appear (see + marks). We have interpreted this result as a signature of the onset of a non-reversible phase transition. In order to release strain in the sample at 17.2 GPa we annealed the sample (393 K during 1 hour) using an external heater **[32]**. After thermal treatment, pressure decreased slightly (16.2 GPa) and the new XRD pattern showed some remnant peaks from the initial DC phase and a major proportion of a new phase that can be assigned to the DR structure phase previously proposed for related compounds **[10, 16-19]**. According to the relation of intensities of Bragg peaks of both phases **[33]**, we can estimate that an 85% of the sample was transformed to the HP phase. Unfortunately, the DAC we used prevented us from going to higher pressures. A Rietveld refinement of the difractogram measured at 16.2 GPa at the upstroke which shows the coexistence of the DR and DC phases along with MgO is included in **Fig. 2**.

131 The multiphase Rietveld gives the same result for the amount of sample transformed to
132 the HP phase. **Table 2** summarizes the crystallographic parameters of DR-$HgGa_2Se_4$ at
133 16.2 GPa. The quality of the structural refinement is similar for the pattern collected at
134 16.2 GPa after annealing than for the pattern collected at 1 bar (see **Fig. 2** and residuals
135 in **Tables 1** and **2**).

136 On decompression we took several XRD patterns showing the coexistence of
137 DR and DC phases till 5.7 GPa, with the DR phase being in all cases the dominant one.
138 Below 5.7 GPa the peaks of the HP phase disappear and broad XRD peaks appear as
139 shown in the spectrum of **Fig. 2** at 2.1 GPa (solid line) on downstroke. As we will
140 discuss below, apparently the changes observed in the XRD pattern can be assigned to a
141 transition to a phase different than the low- and high-pressure phases previously
142 described. The XRD patterns of this new phase can be attributed to a DZ structure.
143 Again, in order to release strain, we annealed the recovered sample at 2.1 GPa (393 K
144 during 30 minutes). After thermal treatment, pressure decreased to 1.5 GPa and the new
145 XRD pattern showed a well-defined tetragonal structure, which proved to be similar to
146 the structure of the low-pressure phase, but with broader peaks that could evidence
147 some degree of disorder in the sample. A plausible hypothesis that can explain this
148 phenomenon is that the cation and vacancy disorder caused during the DC-to-DR
149 transition cannot be reordered upon decompression resulting in the appearance of a
150 metastable DZ phase on decompression. The additional energy provided by the thermal
151 annealing helps to reduce disorder and relax stresses favoring the recovery of the
152 thermodynamically stable low-pressure phase. A DZ structure has been already found in
153 $CdGa_2Se_4$ **[10]**, $CdAl_2Se_4$ **[17]**, $CdAl_2S_4$ **[19]**, and $HgAl_2Se_4$ **[19]** on decreasing pressure
154 from the DR structure.

As mentioned above, a detailed study of the XRD pattern obtained on downstroke at 2.1 GPa before annealing evidence the presence of a possible metastable phase with DZ structure. In **Figure 2** it is shown the comparison of the diffraction pattern measured upon decompression at 2.1 GPa (solid line) and the calculated pattern (dash-dotted line) for a DZ phase. A lattice parameter of 5.45(1) Å provides the best matching to the new peaks assigned to the DZ structure. To facilitate comparison of both diffractograms, the background was subtracted in the measured one and the simulated diffractogram was modeled with profile parameters obtained by comparison to the measured one using the Powdercell software. The resemblance of both experimental and calculated diffractograms is quite good. The broad aspect of the allowed zinc-blende diffraction Bragg reflections is likely to be a consequence of the complete disorder of cations and vacancies at the only cation site (4a Wyckoff position) in the metastable zinc-blende structure (see **Table 2**).

We would like to mention here that because of the broad bands of the diffraction pattern measured at 2.1 GPa and the fact that some of the Bragg peaks attributed to the DZ phase have quite a low intensity a structural refinement cannot be performed. Note also, that because the high symmetry of both the DR and DZ structures a maximum of 6 to 8 Bragg peaks of them can be detected working in a diamond-anvil cell even using short wavelength like in this work. This fact also precludes the performance of a kosher structural refinement even for simple structures like DR and DZ in which neither atom possesses any internal degree of freedom. In previous works, both phases have been identified in related compounds with less than six reflections, but not proper structural refinements were carried out **[10, 17, 19]** All these facts indicate that in the future it will be necessary to carry out single-crystal XRD experiments **[34]** in order to properly determine the crystal structure of the new HP phases observed in OVCs. Another

interesting issue to explore in the future is the role of kinetics. The fact that thermal annealing is requested for completion of the transitions triggered by compression or decompression shows that kinetical barriers could be relevant in the studied transitions. On the other hand, our observation of a tetragonal phase at 1.5 GPa after heating a decompressed sample with DZ structure at 2.1 GPa is compatible with previous studies that show a recrystallization of the DC structure in $Zn_{1-x}Mn_xGa_2Se_4$ after a moderate heating of samples with the defect stannite structure, which already has some degree of disorder, above 300ºC in vacuum and decreasing temperature in a controlled way **[35, 36]**.

Figure 3 shows the pressure dependence of the lattice parameters for DC-$HgGa_2Se_4$ from our experiment. The axial compressibilities for *a* and *c* axes at zero pressure, defined as $\kappa_x = \frac{-1}{x}\frac{\partial x}{\partial P}$ and obtained by fitting of a Murnaghan EOS to experimental data **[37],** are κ_a = 9(2)·10^{-3} GPa^{-1} and κ_c = 5(1)·10^{-3} GPa^{-1}. It can be observed that there is an anisotropy in the axial compression being the *a* axis more compressible than the *c* one. This result agrees with previous results for related compounds **[10, 16, 18, 19, 38]**.

Figure 4 shows the volume of the DC phase vs. pressure plot obtained from our experiment (circles). Experimental data for the DR phase on downstroke and the DZ phase at 2.1 GPa are shown as diamonds and squares, respectively. We have fitted our volume vs. pressure data for the DC phase with a third order Birch-Murnaghan EOS **[39]**. The fitting of the data of Fig. 4 (dashed line) with a volume at zero pressure fixed at a value of V_0= 352.70(16) $Å^3$ (the measured value at ambient pressure) and the bulk modulus pressure derivative at zero pressure fixed at a value of B_0' = 4 gives a bulk modulus of B_0= 52(2) GPa. The EOS parameters are summarized in **Table 3** together with parameters obtained from a different experiment carried out with a laboratory

diffractometer using methanol-ethanol as pressure transmitting medium to reduce deviatoric stresses and in a reduced pressure range (13.2 GPa) to avoid the influence of precursor effects **[40]** of the pressure-driven transition on the structure of the low-pressure phase **[38]**. If we compare the obtained value for B_0 when B_0' is fixed to 4 for both experiments, it can be seen that the B_0 for the experiment when MgO is used as PTM is about 16% greater than that B_0 obtained when methanol-ethanol is used as PTM. This result confirms the overestimation of B_0 under non-hydrostatic conditions noted in previous works **[24, 25, 41, 42, 43].** Finally, we note that the obtained value for B_0 in DC-$HgGa_2Se_4$ from our experiment with MgO as PTM is similar to that obtained for DC-$CdGa_2Se_4$ (B_0 = 41.5(2) GPa) **[10]**, DC-$MnGa_2Se_4$ (B_0 = 44(2) GPa) **[16],** DC-$CdAl_2Se_4$ (B_0= 52.1 GPa) **[17]**, and DS-$ZnGa_2Se_4$ (B_0 = 47(2) GPa) **[18]**.

As regards the DR phase, it can be observed from **Fig. 4** that it is less compressible than the DC phase. We have estimated a relative volume change per formula unit of -2.2% at 16.2 GPa, thus indicating that the DC to DR phase transition is a first-order phase transition of reconstructive nature. A fit of our experimental volume vs. pressure data for the DR phase with a Birch-Murnaghan EOS with B_0' fixed to 4 gives a bulk modulus of B_0 = 103(6) GPa and a volume at zero pressure V_0 = 159.9(8) $Å^3$. The greater value for the B_0 of the DR phase in comparison to that of the DC phase confirms the lower compressibility of the HP phase. The same result is found for other OVCs like $MnGa_2Se_4$, $CdAl_2S_4$ and $ZnGa_2Se_4$ **[16, 18, 19].** If we compare the normalized volumes of the DC, DR, and DZ phases at 2.1 GPa it is found that the volume of the DZ phase [324(2) $Å^3$] is between those of the DC [338(3) $Å^3$] and DR [314(2) $Å^3$] phases. In the comparison, the volume for the DR phase at 2.1 GPa has been extrapolated by using the EOS, and in the cases of the DR and DZ volume was normalized multiplying by two. The volume of the three phases decreases in the

sequence DC > DZ > DR which suggest that the compressibility of the DZ structure should be in between those of the other two phases since the packing efficiency of DZ is in between those of DC and DR.

Now we will analyze the evolution of the *c/a* ratio with pressure in DC-$HgGa_2Se_4$ since the tetragonal distortion, $\delta = 2 - c/a$, could give important information about the behavior of the sample on compression. Inset of **Fig. 4** shows the pressure dependence of the *c/a* ratio vs. pressure. It can be observed that *c/a* increases with increasing pressure from 1.89 at ambient pressure to 1.94 at 17.3 GPa. A similar experimental pressure dependence of the *c/a* ratio has been found in $CdGa_2Se_4$ **[10]**, $MnGa_2Se_4$ **[16],** $CdGa_2S_4$ **[18],** $HgAl_2Se_4$ **[19],** and in $HgGa_2Se_4$ **[38]** under better hydrostatic conditions than here. It is noteworthy that AGa_2X_4 compounds (*A*= Mn, Zn, Cd, Hg; *X*= S, Se) with tetragonal DC structure at ambient pressure have *c/a* values close to 1.90 **[10, 16, 38, 44]**, while those with tetragonal defect stannite structure like $ZnGa_2Se_4$ or $ZnGa_2S_4$, which have already some cation disorder, have *c/a* ratios close to 1.98 at ambient pressure **[18, 45]**. Furthermore, a *c/a* ratio very close to 2, or equivalently a very small tetragonal distortion of the tetragonal phase, has been considered up to now as a measure of complete cation-vacancy disorder **[31, 44]**. Therefore, our results show that DC-$HgGa_2Se_4$, like other DC compounds **[4, 10, 16],** tends to a more symmetrical structure on compression prior to undergoing the phase transition to the DR structure at 17.2 GPa.

To conclude we would like to comment on the different coordination found on the DC, DR, and DZ structures shown in **Fig 1**. The low pressure DC phase has four-fold coordination where cations are tetrahedrally-coordinated while anions are surrounded by three cations and a vacancy. The high pressure DR phase has six-fold coordination where cations and anions are octahedrally-coordinated. In this way, the

phase transition implies an increase of the symmetry of the crystal and is accompanied by a change of coordination of the cations from tetrahedral to octahedral. On the other hand, the metastable DZ phase has again four-fold coordination as the original DC phase.

4. Summary

We have performed XRD measurements in defect chalcopyrite $HgGa_2Se_4$ under compression. The experiments show that the pressure dependence of the volume and lattice parameters of DC-$HgGa_2Se_4$ behaves in a similar way to other adamantine OVCs. The axial compressibilities and the equation of state of $HgGa_2Se_4$ have been obtained for the tetragonal DC structure under non-hydrostatic conditions. It is observed that the tetragonal structures of OVCs tend to become more symmetric under compression irrespective of the conditions of hydrostaticity. A non-reversible phase transition to the disordered rock-salt phase on increasing pressure has been found. On decreasing pressure the sample was found to undergo a phase transition to a metastable structure that might be attributed to a disordered zinc-blende structure. Apparently kinetics plays an important role on the occurrence of the reported phase transitions. This is evidenced by the fact that thermal annealing favors the occurrence of phase transitions.

Acknowledgements

This study was supported by the Spanish government MEC under Grants No: MAT2010-21270-C04-01/03/04 and CTQ2009-14596-C02-01, by the Comunidad de Madrid and European Social Fund (S2009/PPQ-1551 4161893), by MALTA Consolider Ingenio 2010 project (CSD2007-00045), and by the Vicerrectorado de Investigación y

279 Desarrollo of the Universidad Politécnica de Valencia (UPV2011-0914 PAID-05-11
280 and UPV2011-0966 PAID-06-11). E.P-G., J.L-S., A.M., and P.R-H. acknowledge
281 computing time provided by Red Española de Supercomputación (RES) and MALTA-
282 Cluster.

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Table 1. Experimental crystallographic parameters of tetragonal (I-4, Z=2) $HgGa_2Se_4$ at room conditions. The residuals for the Rietveld refinement are R_p= 11% and R_{wp} =16.4%.

	X-ray diffraction[a]	X-ray diffraction[b]	X-ray diffraction[c]
a (Å)	5.711(1)	5.715	5.693(1)
c (Å)	10.814(1)	10.78	10.826(4)
Hg site: 2*a*	x=0 y = 0 z =0	x=0 y = 0 z =0	x=0 y = 0 z =0
Ga(1) site: 2*b*	x = 0 y = 0 z = 0.5	x = 0 y = 0 z = 0.5	x = 0 y = 0 z = 0.5
Ga(2) site: 2*c*	x = 0 y = 0.5 z = 0.25	x =0 y = 0.5 z =0.25	x = 0 y = 0.5 z = 0.25
Vacancy site: 2*d*	x = 0 y = 0.5 z = 0.75	x = 0 y = 0.5 z = 0.75	x = 0 y = 0.5 z = 0.75
Se site: 8*g*	x =0.270(2) y = 0.245(5) z =0.1315(6)	x = 0.25 y = 0.25 z = 0.125	x =0.273(1) y = 0.2582(8) z =0.1382(6)

[a] Our XRD experiment. [b] Reference **30**. [c] Reference **31**.

Table 2. Experimental crystallographic parameters of DR (Fm-3m, Z=1) $HgGa_2Se_4$ at 16.2 GPa. The lattice parameter is a = 5.2048(5) Å. The residuals for the Rietveld refinement are R_p = 9.8% and R_{wp} = 13.4%. We also include the atomic positions used to simulate DZ-$HgGa_2Se_4$ (F-43m, Z=1) at 2.1 GPa with a = 5.45(1) Å.

	DR-$HgGa_2Se_4$		DZ-$HgGa_2Se_4$	
	Wyckoff position	Site occupancy factor (S.O.F.)	Wyckoff position	Site occupancy factor (S.O.F.)
Hg	4a (0,0,0)	0.25	4a (0,0,0)	0.25
Ga	4a (0,0,0)	0.5	4a (0,0,0)	0.5
Vacancy	4a (0,0,0)	0.25	4a (0,0,0)	0.25
Se	4b (1/2,1/2,1/2)	1	4c (1/4,1/4,1/4)	1

387 **Table 3:** Experimental (exp.) volume (V_0), bulk modulus (B_0), and its pressure
388 derivative (B_0') for DC-$HgGa_2Se_4$ at ambient pressure. Values were obtained by fitting
389 data to a third-order Birch-Murnaghan EOS with B_0' fixed to 4 and V_0 fixed to the
390 value measured at 1 bar. Data from **Ref. 38** are also included for comparison.
391

	V_0 (Å^3)	B_0 (GPa)	B_0'	References
exp.	352.70	52(2)	4 (fixed)	This work
exp.	352.9(6) 351.4(5)	39(2) 44.9(7)	5.2(4) 4 (fixed)	**38**

392
393

394 **Figure captions**

395

396 **Figure 1. (Color online)** (a) Structure of the defect chalcopyrite (DC) $HgGa_2Se_4$, (b)
397 defect rock salt (DR) $HgGa_2Se_4$, and (c) defect zinc blende (DZ) $HgGa_2Se_4$. Big light
398 atoms are Hg, medium dark atoms are Ga, and small dark atoms are Se. To distinguish
399 between nonequivalent atoms in the DC structure, the Wyckoff sites are given in
400 parenthesis.

401 **Figure 2.** XRD patterns of $HgGa_2Se_4$ on upstroke up to 17.2 GPa and downstroke to 1.5
402 GPa. The diffractogram measured at 1 bar at the upstroke is shown as solid circles. The
403 calculated pattern at 1 bar obtained from a Rietveld refinement along with the residuals
404 are shown as solid lines. A Rietveld refinement of the difractogram measured at 16.2
405 GPa at the upstroke showing the coexistence of the DR and DC phases along with MgO
406 is included. The residuals are $R_p = 9.8\%$ and $R_{wp} = 13.4\%$. In the pattern collected at 2.1
407 GPa on downstroke, we show the comparison of the measured pattern (solid line) and
408 the calculated diffractogram using Powdercell software for the defect zincblende (DZ)
409 phase (dash-dotted line). Vertical marks indicate the Bragg reflections for the DC phase
410 at 1 bar at the upstroke, for the DR and DC phases and MgO at 16.2 GPa at the
411 upstroke, and for the DZ phase at 2.1 GPa at the downstroke. Plus (+) symbols refer to
412 reflections attributed to the disordered rocksalt phase and MgO reflections are marked
413 with * symbols.

414 **Figure 3.** Lattice parameters of the DC phase of $HgGa_2Se_4$ as a function of pressure.
415 Solid and empty circles refer to data from our XRD experiment on increasing and
416 decreasing pressure, respectively. Solid lines are a guide to the eye.

Figure 4. Volume of the DC (circles) and DR (diamonds) phases as a function of pressure. The volume of the DZ phase at 2.1 GPa is included as square symbols. Full symbols are used for upstroke and empty symbols for downstroke. Note that for comparison of the three structures we have plotted twice the volume of the DR and DZ phases since the unit cell of DC phase has Z = 2 while that of the DR and DZ phases has Z=1. Dashed and dash-dotted lines are the result of the EOS fit for the DC and DR phases of our experiment. Inset: Evolution of the c/a ratio of the DC phase as a function of pressure for our experiments (circles). Dashed line is a linear fit to experimental data.

Figure 1.

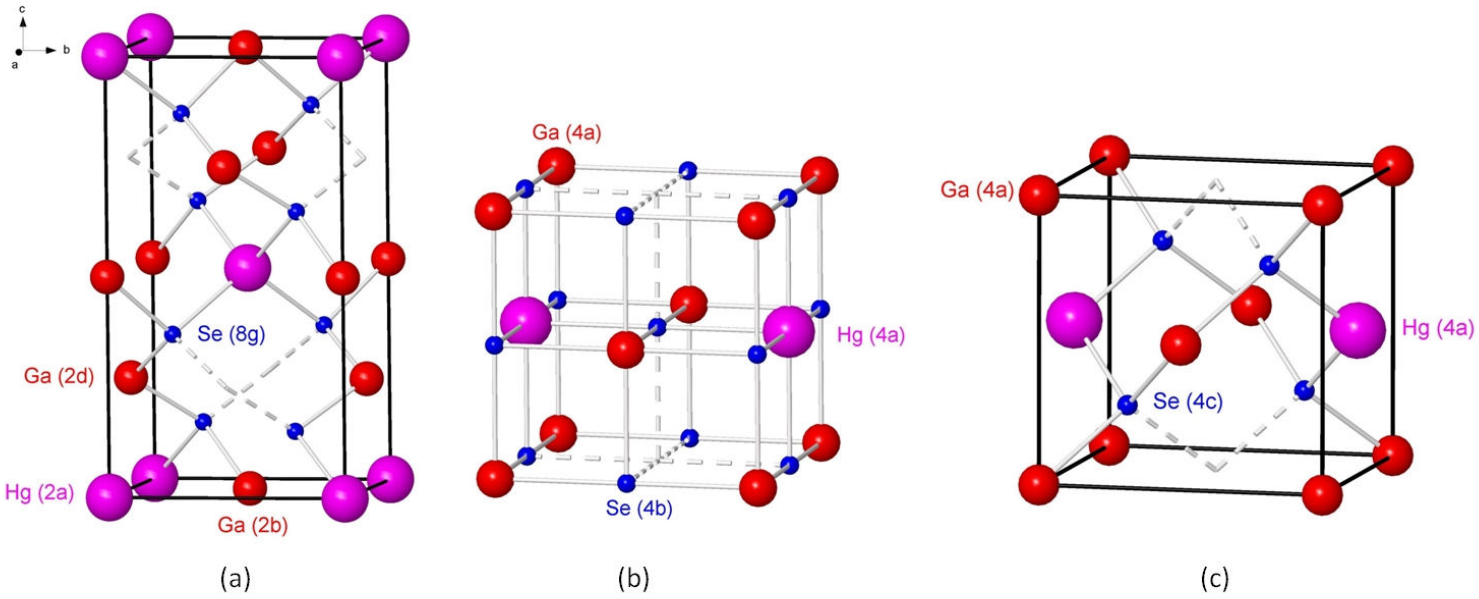

Figure 2

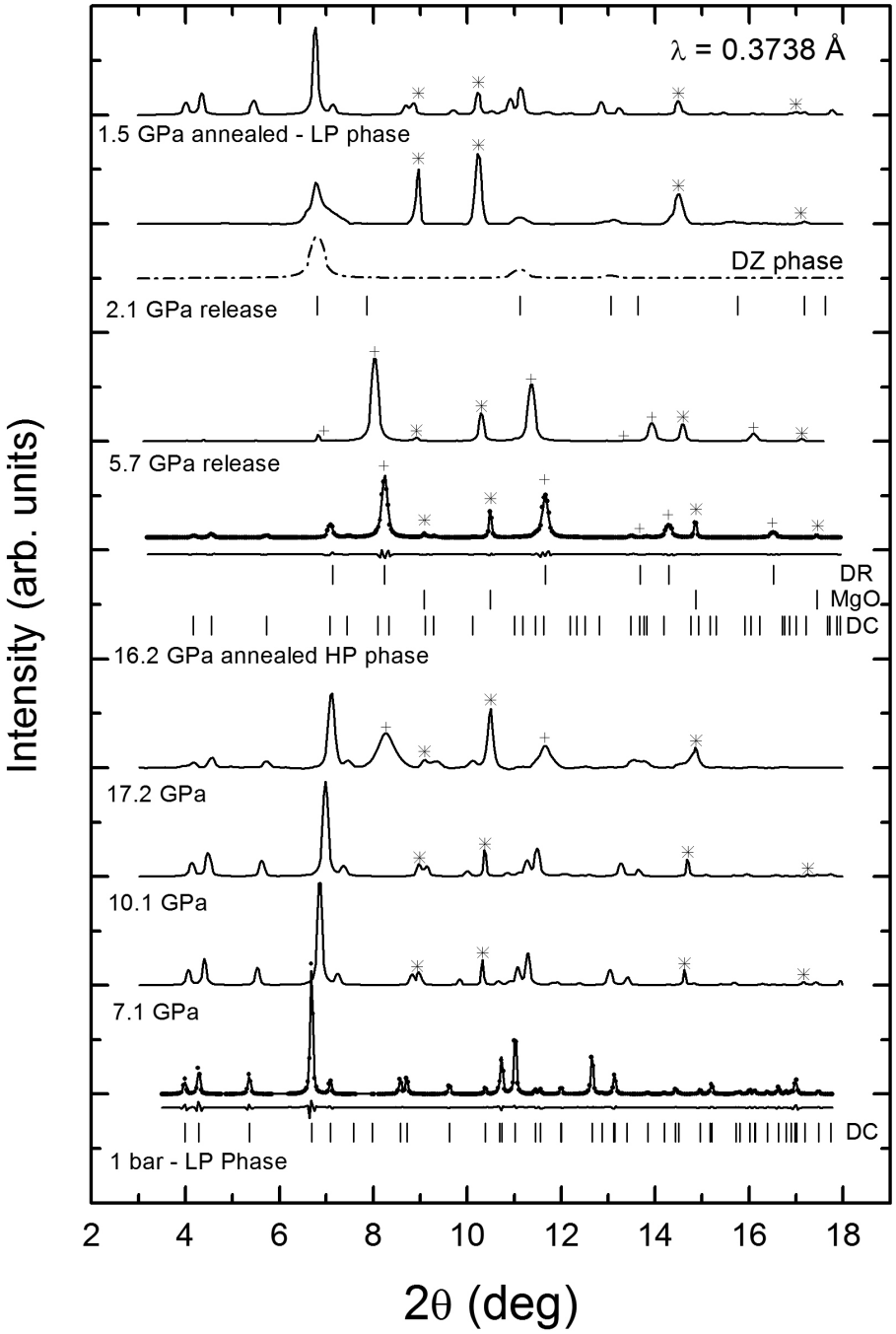
λ = 0.3738 Å
1.5 GPa annealed - LP phase
DZ phase
2.1 GPa release
5.7 GPa release
DR
MgO
DC
16.2 GPa annealed HP phase
17.2 GPa
10.1 GPa
7.1 GPa
DC
1 bar - LP Phase
Intensity (arb. units)
2
4
6
8
10
12
14
16
18
2θ (deg)

Figure 3

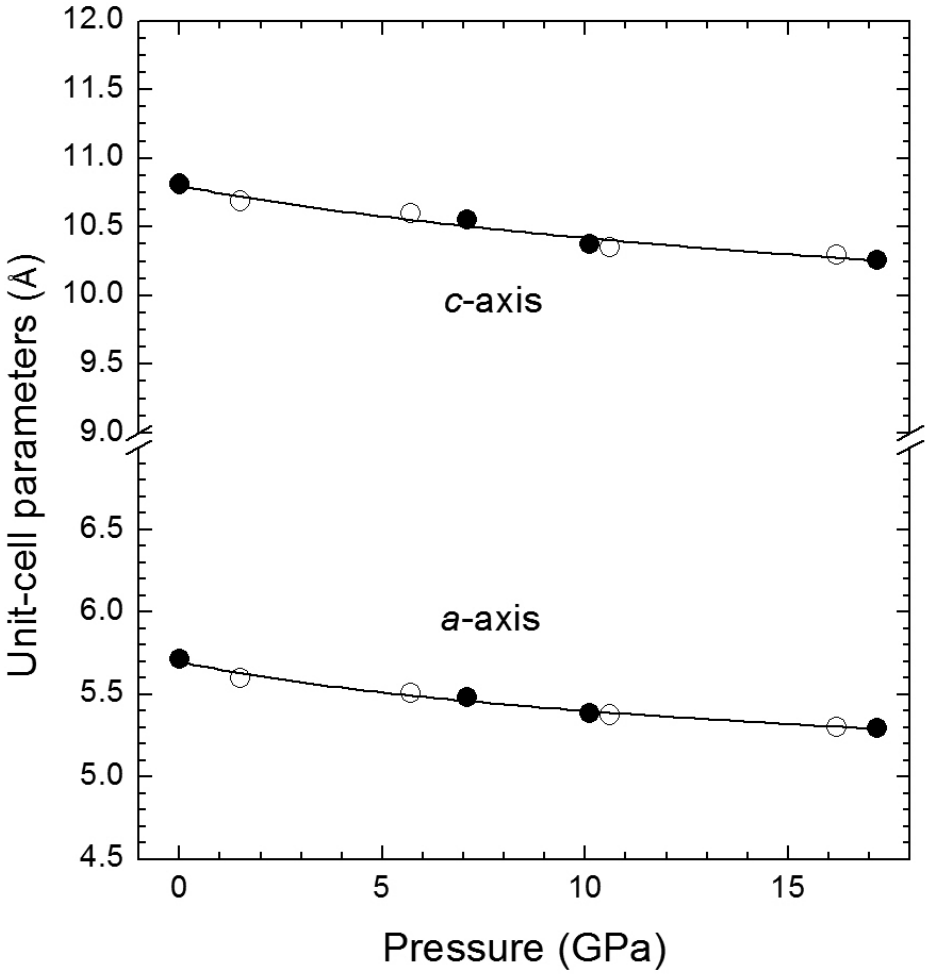
12.0
11.5
11.0
10.5
10.0
9.5
9.0
6.5
6.0
5.5
5.0
4.5
Unit-cell parameters (Å)
c-axis
a-axis
0
5
10
15
Pressure (GPa)

Figure 4