

Synthesis of ternary compound in H-S-Se system at high pressures

Xiao Zhang(张晓)

Citation: Chin. Phys. B, 2021, 30 (**12**): 127801. DOI: 10.1088/1674-1056/abf7aa
Journal homepage: http://cpb.iphy.ac.cn; http://iopscience.iop.org/cpb

What follows is a list of articles you may be interested in

Signal-to-noise ratio of Raman signal measured by multichannel detectors

Xue-Lu Liu(刘雪璐), Yu-Chen Leng(冷宇辰), Miao-Ling Lin(林妙玲), Xin Cong(从鑫), and Ping-Heng Tan(谭平恒)
Chin. Phys. B, 2021, 30 (**9**): 097807. DOI: 10.1088/1674-1056/ac1f06

Achieving high-performance multilayer $MoSe_2$ photodetectors by defect engineering

Jintao Hong(洪锦涛), Fengyuan Zhang(张丰源), Zheng Liu(刘峥), Jie Jiang(蒋杰), Zhangting Wu(吴章婷), Peng Zheng(郑鹏), Hui Zheng(郑辉), Liang Zheng(郑梁), Dexuan Huo(霍德璇), Zhenhua Ni(倪振华), and Yang Zhang(张阳)
Chin. Phys. B, 2021, 30 (**8**): 087801. DOI: 10.1088/1674-1056/abea8b

SnS_2 quantum dots: Facile synthesis, properties, and applications in ultraviolet photodetector

Yao Li(李尧), Libin Tang(唐利斌), Rujie Li(李汝劼), Jinzhong Xiang(项金钟), Kar Seng Teng, Shu Ping Lau(刘树平)
Chin. Phys. B, 2019, 28 (**3**): 037801. DOI: 10.1088/1674-1056/28/3/037801

Raman scattering under extreme conditions

Feng Jin(金峰), Yang Yang(杨洋), An-Min Zhang(张安民), Jian-Ting Ji(籍建葶), Qing-Ming Zhang(张清明)
Chin. Phys. B, 2018, 27 (**7**): 077801. DOI: 10.1088/1674-1056/27/7/077801

Effect of pressure on the semipolar GaN (10-11) growth mode on patterned Si substrates

Liu Jian-Ming, Zhang Jie, Lin Wen-Yu, Ye Meng-Xin, Feng Xiang-Xu, Zhang Dong-Yan, Steve Ding, Xu Chen-Ke, Liu Bao-Lin
Chin. Phys. B, 2015, 24 (**5**): 057801. DOI: 10.1088/1674-1056/24/5/057801

Synthesis of ternary compound in H–S–Se system at high pressures*

Xiao Zhang(张晓)[1,2,†]

[1] Key Laboratory of Materials Physics, Institute of Solid State Physics, HFIPS, Chinese Academy of Sciences (CAS), Hefei 230031, China
[2] University of Science and Technology of China, Hefei 230026, China

(Received 13 February 2021; revised manuscript received 8 April 2021; accepted manuscript online 14 April 2021)

The chemical reaction products of elemental sulfur (S), selenium (Se), and molecular hydrogen (H_2) at high pressures and room temperature are probed by Raman spectroscopy. Two known compounds H_2S and H_2Se can be synthesized after laser heating at pressures lower than 1 GPa. Under further compression at room temperature, an H_2S–H_2Se and an H_2S–H_2Se–H_2 van der Waals compounds are synthesized at 4 GPa and 6 GPa, respectively. The later is of guest–host structure and can be identified as $(H_2S)_x(H_2Se)_{(2-x)}H_2$. It can be maintained up to 37 GPa at least, and the stability of its H_2Se molecules is extended: the H–Se stretching mode can be detected at least to 36 GPa but disappears at 22 GPa in $(H_2Se)_2H_2$. The pressure dependence of S–H and Se–H stretching modes of this ternary compound is in line with that of $(H_2S)_2H_2$ and $(H_2Se)_2H_2$, respectively. However, its hydrogen subsystem only shows the relevance to $(H_2S)_2H_2$, indicating that this ternary compound can be viewed as H_2Se-replaced partial H_2S of $(H_2S)_2H_2$.

Keywords: hydride, high pressure, Raman spectroscopy

PACS: 78.30.–j, 82.40.Fp, 74.70.–b **DOI:** 10.1088/1674-1056/abf7aa

1. Introduction

Metallic hydrogen[1] attracts a lot interest due to its charming properties, especially room-temperature superconductivity.[2] However, the enormous pressure required makes such a state of hydrogen remain a challenge. Chemical precompression in hydrides has been proposed to facilitate metallization of hydrogen.[3] Based on this, many hydrides are predicted to be candidates for high temperature superconductors.[4–6] Moreover, high temperature superconductivity of hydrides is proved in H_3S which shows a remarkably high superconducting transition temperature T_C of 203 K at 150 GPa.[7] Since then, a lot of new hydrides are synthesized[8–10] and record of the highest T_C is broken by hydrides in rapid succession.[11–13]

As H_3S is the first material to demonstrate such a high temperature superconductivity, the investigation into mechanism of the high T_C of H_3S has been a hot topic and fruitful.[14–17] It was suggested that superconductivity of H_3S can be attributed to conventional phonon-mediated mechanism as it exhibits strong covalent bonds giving rise to large electron–phonon couplings.[14,18] Improving the covalent characteristics of the sulfur-hydrogen bond by replacing S atoms with mixtures of chalcogens or other atoms is a good choice to further enhance superconducting properties of H_3S.[19] Several ternary hydrides based on the H_3S structure were predicted to exhibit high-T_C behavior.[19–22] Recently, a carbonaceous sulfur hydride exhibited room-temperature superconductivity.[13] However, superconductivities in other doping systems are still to be confirmed experimentally. It is of fundamental importance to investigate the synthesis conditions of these hydrides.

Superconducting H_3S is of cubic Im-3m structure.[16,23] It can be considered as being stoichiometrically disproportionate H_2S[7,24] or synthesized by the directly laser-heated elements.[25] Besides, a molecular host–guest compound $(H_2S)_2H_2$ with the same stoichiometry as H_3S was found at low pressures,[26] and it remained stable at up to 160 GPa.[27,28] The room-temperature superconductor, carbonaceous sulfur hydride, was suggested to have a similar host–guest structure $(CH_4)_x(H_2S)_{(2-x)}H_2$ based on its Raman spectra,[13,28] but different from H_3S.[29] On the other hand, owing to similar kinetic diameters of H_2S, CH_4, and H_2Se, it is possible to expect a similar van der Waals compound in H–S–Se system by substituting H_2S for H_2Se. Moreover, this ternary compound of H–S–Se promises to be achieved by using a similar route carbonaceous sulfur hydride.[13,29]

Here in this work, the ternary compound in H–S–Se system at high pressures is synthesized. This compound has a molecular host–guest structure and can be named $(H_2S)_x(H_2Se)_{(2-x)}H_2$ ($0 < x < 2$). The ternary compound can be maintained at up to 37 GPa at least. The pressure dependence of S–H and Se–H stretching modes of this ternary compound are excellently corresponding to that of $(H_2S)_2H_2$[28] and $(H_2Se)_2H_2$,[8] respectively. But its hydrogen subsystem only shows the relevance to $(H_2S)_2H_2$. Moreover, unlike $(H_2Se)_2H_2$[8] and pure H_2Se,[30] H_2Se molecule has the stabil-

*Project supported by the National Natural Science Foundation of China (Grant Nos. 51672279, 51727806, 11874361, and 11774354), the Science Challenge Project, China (Grant No. TZ2016001), the CAS Innovation Fund (Grant No. CXJJ-19-B08), and the CASHIPS Director's Fund (Grant No. YZJJ201705).

†Corresponding author. E-mail: xiaozhang@issp.ac.cn

© 2021 Chinese Physical Society and IOP Publishing Ltd

ity that can be extended in this ternary system as H–Se stretching mode can be detected in the whole pressure range.

2. Experimental methods

Symmetric diamond anvil cells (DACs) equipped with anvils with central culets of 250 μm in diameter were employed in the experiments. Small pieces of S and Se were positioned close to a hole in a rhenium gasket and filled with H_2 gas at $\sim$ 200 MPa. Two samples (A and B) were used in this experiment.

Because H_2S solifies at a low pressure of about 1.1 GPa,[26] in order to get fluid H_2S and H_2Se, laser heating are performed at pressures lower than 1 GPa. Samples A and B were heated at 0.9 GPa and 0.4 GPa, respectively. Laser sharply focused on a spot of 2 μm–3 μm in diameter irradiated two solids alternatingly for a few seconds and moved back and forth. The 532-nm solid state laser at power about 460 mW was used in laser heating to melt S and Se. Synthesis of H_2S and H_2Se are judged from Raman spectra measured. Once the mixture of H_2S, H_2Se, and H_2 became fluids, the DAC was compressed up to 37 GPa at room temperature.

Pressure was determined by using the ruby fluorescence.[31] For the Raman experiments, a backscattering geometry was adopted for confocal measurements with an incident laser wavelength of 532 nm.[32] The Raman notch filter is of a very narrow bandpass (Optigrate), allowing Raman measurements down to 10 cm^{-1} in the Stokes and anti-Stokes. One of these notch filters was used as a beam splitter to inject the laser into the optical path.

3. Results and discussion

After being heated by laser, both solid S and Se melt as observed visually. The transparent region looks uniform without boundary of fluids. Meanwhile, Raman spectra measured at different positions in H_2 region all show two new sharp peaks at about 2350 cm^{-1} and 2620 cm^{-1} (Fig. 3). These two peaks can be assigned to Se–H[33] and S–H[5] stretching modes, respectively. The S–H stretching mode has higher intensity than Se–H stretching mode. Summing up the above, fluids H_2S and H_2Se are synthesized and mix well with each other and also together with H_2. The two samples A and B show similar outcomes in the further experiment. However, some different phenomena are observed. It is worthwhile to describe the changes in two samples respectively.

In sample A, at 6.8 GPa, H_2 region is filled with punctate black solids (Fig. 1(a)). However, they are too small to be characterized by Raman spectra. On the other hand, high-intensity S–H and Se–H stretching modes can be detected simultaneously at boundary of S and Se, along with an additional Raman peak at lower frequency in H–H vibron. Although there are some peaks in lattice region at about 200 cm^{-1}, no peak can be attributed to S–Se bond.[34] The Raman spectrum measured shows the coexistence of molecular H_2S, H_2Se, and prolonged H_2, indicating the formation of van der Waals S–Se–H ternary hydride like $(H_2S)_2H_2$[26,28] and $(H_2Se)_2H_2$.[8] On the other hand, owing to similar kinetic diameters of H_2S and H_2Se,[8] the substitution of H_2Se for H_2S is possible and it is a good choice to describe this new ternary compound as $(H_2S)_x(H_2Se)_{(2-x)}H_2$ $(0 < x < 2)$. No further change is observed in image of compression later. But at pressures above 27 GPa, Raman spectra are degraded, making the peaks hard to distinguish.

When pressure decreased to 9.5 GPa, three transparent single crystals emerge (Figs. 1(b) and 2(a)). These crystals have similar spectra to ternary compound at boundary of S and Se (Figs. 1(a) and 1(b)). Some differences including no sharp peak at about 200 cm^{-1} are caused by measurement relatively far from S and Se. These transparent single crystals can be recognized as being different form of $(H_2S)_x(H_2Se)_{(2-x)}H_2$. At 3.7 GPa, $(H_2S)_x(H_2Se)_{(2-x)}H_2$ turns into H_2S–H_2Se van der Waals compound which does not have prolonged H_2 molecules (Fig. 2(b)). Meanwhile, small punctate black solids disappear. Finally, DAC is successfully decompressed to 0.6 GPa. At this pressure, all kinds of crystals decompose. Instead, some scale-like vesicles spatially separated appear in chamber (Fig. 2(c)), figuring out immiscibility of fluid H_2S, H_2Se, and H_2. Furthermore, after being exposed to the laser, the transparent part quickly turns into a uniform three-fluid mixture.

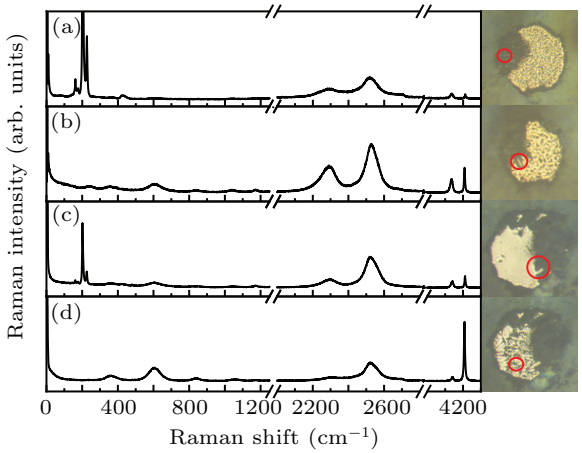


Fig. 1. Microscopic images and Raman spectra of $(H_2S)_x(H_2Se)_{(2-x)}H_2$ in different forms at about 6 GPa, showing (a) compound at boundary of S and Se, (b) single-crystalline compound obtained on decompression, (c) crystal attached on Se, and (d) mall black solid compound. Spectra are measured at positions marked as red circles.

In sample B, van der Waals compound of H_2S and H_2Se is also observed on compression at 4.1 GPa. This compound grows up gradually as a transparent crystal adjoining Se approaches to fluid H_2 region. Its Raman spectrum is shown in Fig. 3.

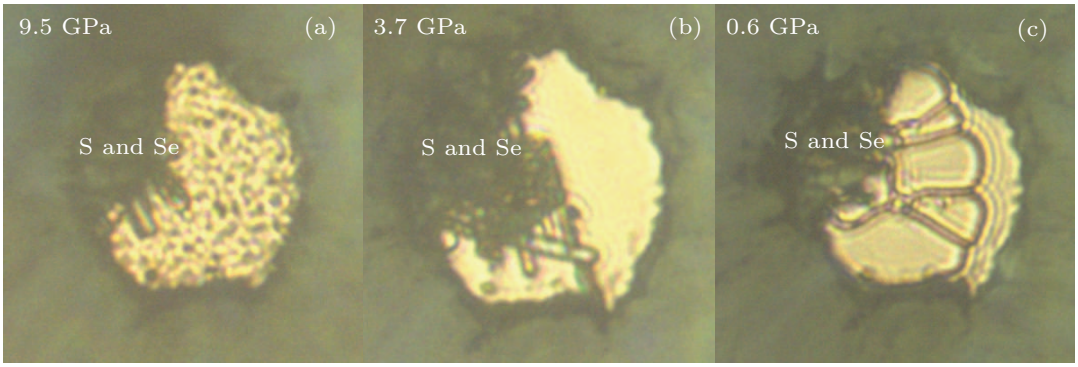


Fig. 2. Microscopic images of sample A at different pressures on decompression, showing (a) growing-out crystalline $(H_2S)_x(H_2Se)_{(2-x)}H_2$, (b) emerging H_2S–H_2Se van der Waals solid, (c) immiscibility of fluid H_2S and H_2Se with H_2.

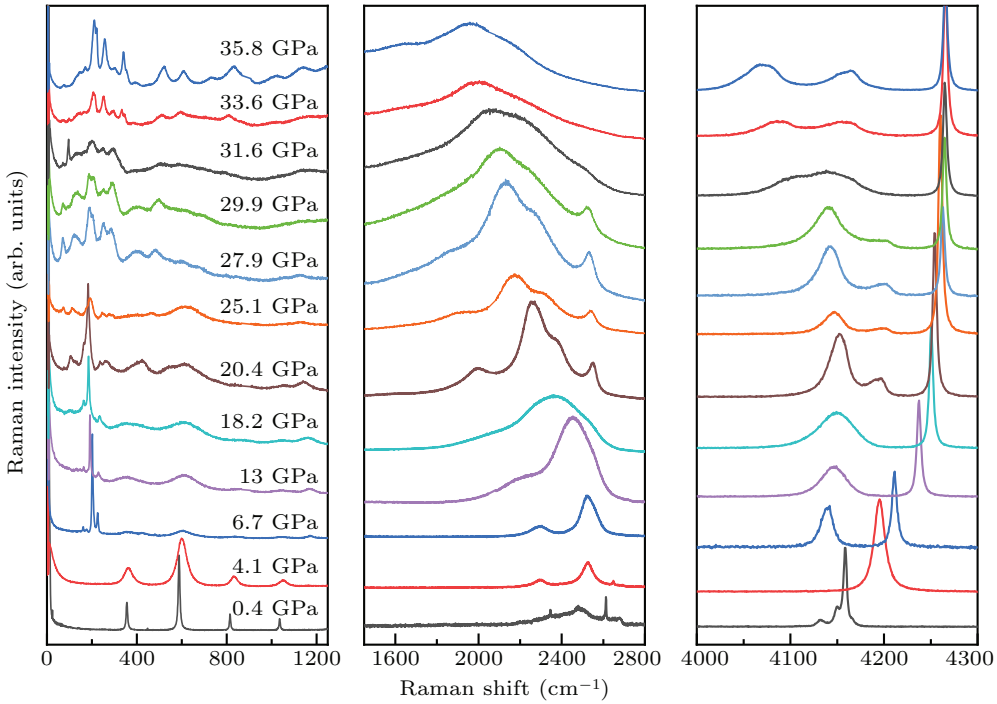


Fig. 3. Raman spectra of H–S–Se compounds in sample B at different pressures.

At 6.1 GPa, the van der Waals compound of H_2S and H_2Se disappears. Instead, the same small black solids which are present in sample A emerge in H_2 region (Fig. 1(d)). These solids are much bigger on this occasion. Their Raman spectra are in common with spectra of single-crystalline $(H_2S)_x(H_2Se)_{(2-x)}H_2$ obtained on decompression (Figs. 1(b) and 1(d)). Besides, spectra with S–H and Se–H stretching modes and extra H–H vibron are detected at boundary of S and Se, as done in sample A. These two spectra figure out that the H–S–Se ternary compound $(H_2S)_x(H_2Se)_{(2-x)}H_2$ is also synthesized in sample B. And H–S–Se ternary compound is in the form of small black solid. To obtain bigger crystalline solid for high-quality spectra, sample B is decompressed to 5.3 GPa. At this point, small black solids disappear, and the ternary compound cannot be detected on S or Se either. Meanwhile, fluid H_2S comes back and shows a sharp peak at about 2650 cm^{-1}. When compressing sample again to 6.7 GPa, ternary compound regains as a black solid at edge of Se where H_2S–H_2Se van der Waals solid was located before. It is not big but shows a good Raman spectrum with high-intensity Raman characteristic peaks (Figs. 1(c) and 2).

At 20.4 GPa, a new component of stretching mode appears at 2600 cm^{-1} (Figs. 3 and 4). This splitting of S–H Raman vibrational stretching mode is due to strengthening of H bonding between neighboring H_2S molecules. The same clues can also be found in $(H_2S)_2H_2$[26,28] and pure H_2S.[35,36] Besides, the H–H vibron splitting observed in $(H_2S)_2H_2$ is also observed in ternary compound at 2.4 GPa. But the pressure of peak splitting is hysteretic in comparison with $(H_2S)_2H_2$. The later material finishes this phase transition at 16.7 GPa. Because some peaks at about 200 cm^{-1} arise from S and Se, the lattice modes of compound cannot be distinguished well. But orientational ordering of H_2S molecules which are concurrent with splitting of S–H stretching mode and H–H vibron in $(H_2S)_2H_2$ disappear at 20.4 GPa in $(H_2S)_x(H_2Se)_{(2-x)}H_2$.

Above 29.9 GPa, Se–H stretching becomes weak but

can still be resolved. Its lifespan has been prolonged while $(H_2Se)_2H_2$[8] and pure H_2Se[30] are not stable at room temperature and chemically decomposes above 22 GPa. Even though this binary compound is stable at low temperature, its Raman signal will lose above 29 GPa. Above 31.6 GPa, stretching modes turns into a broad band. Meanwhile, two peaks of H–H vibron belonging to compound are equal in intensity.

Without regard to different initiate or terminate pressures, the pressure dependence of S–H and Se–H stretching modes of $(H_2S)_x(H_2Se)_{(2-x)}H_2$ is in line with that of $(H_2S)_2H_2$[28] and $(H_2Se)_2H_2$,[8] respectively (Fig. 4). These correspondences indicate that H_2S and H_2Se exist in the same coordinate as their binary guest–host compounds. Because of similar structure of $(H_2S)_2H_2$ and $(H_2Se)_2H_2$, with the addition of similar kinetic diameters of H_2S and H_2Se, substitution of H_2Se for H_2S or *vice versa* is possible to form H–S–Se ternary compound.

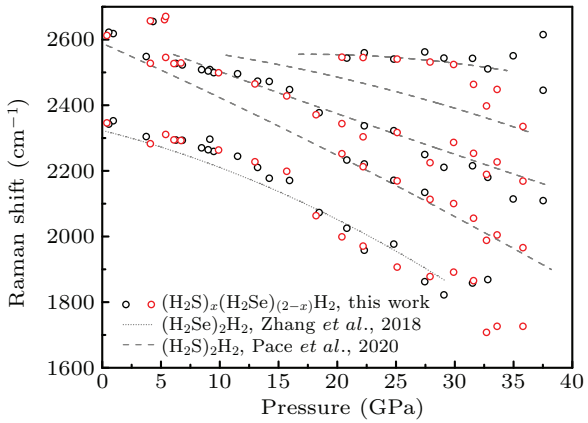


Fig. 4. The pressure-dependent S–H and Se–H stretching modes of $(H_2S)_x(H_2Se)_{(2-x)}H_2$ in comparison with those of $(H_2S)_2H_2$[28] (dashed lines) and $(H_2Se)_2H_2$[8] (dotted line), respectively.

From pressure-dependent H–H vibron (Fig. 5), the transition of H_2 subsystem in $(H_2S)_x(H_2Se)_{(2-x)}H_2$ only conforms to that of $(H_2S)_2H_2$,[28] while H_2 molecule in $(H_2Se)_2H_2$ are abandoned. It is shown that the ternary compound has $(H_2S)_2H_2$ as framework and the substitution of H_2Se for H_2S has more chances. In addition, no contribution of H_2Se in H_2 subsystem provides a clue to certifying the formation of ternary compound. If ternary compound does not exist, but the mixture of two binary compounds $(H_2S)_2H_2$ and $(H_2Se)_2H_2$ participates in Raman measurement, the H–H vibron mode of $(H_2Se)_2H_2$ should be detected.

Although the earlier theoretical studies predict that the S–Se–H ternary hydride should be based on a cubic structure in $Im\bar{3}m$ phase with a strong covalent character through atomic substitution,[20,21] our experiments suggest the synthesized S–Se–H ternary compound is a van der Waals compound with guest–host structure like C–S–H room temperature superconductor.[13,29] The new S–Se–H ternary hydride is also possible to be a superconductor with high transition temperature driven by strong electron–phonon coupling to high-frequency hydrogen phonon modes.[38,39] To further reveal the structural and superconducting properties of the S–Se–H ternary hydride, synchrotron x-ray diffraction and charge transport studies are needed in future.

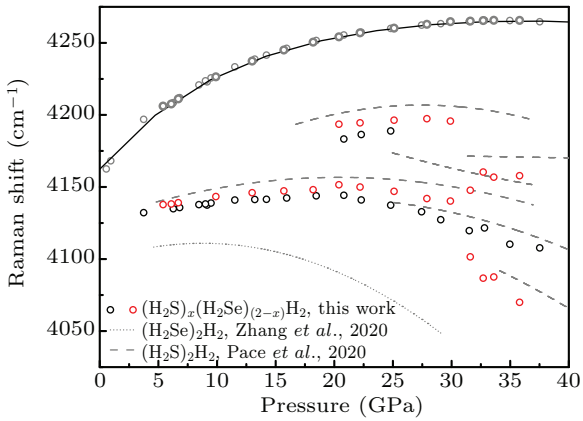


Fig. 5. Pressure-dependent H–H vibron of $(H_2S)_x(H_2Se)_{(2-x)}H_2$ in comparison with $(H_2S)_2H_2$[28] (dashed lines) and H_3Se[8] (dotted line). Solid line refers to literature data for H_2.[37]

4. Conclusions

Chemical transformations in H–S–Se system are detected with Raman spectroscopy in this experiment. The H_2S and H_2Se can combine into a van der Waals solid at about 4 GPa. More importantly, a ternary van der Waals compound of H_2S–H_2Se–H_2 is synthesized at about 6 GPa. This compound has a guest–host structure and can be identified as $(H_2S)_x(H_2Se)_{(2-x)}H_2$ because H_2Se replaces partial H_2S in $(H_2S)_2H_2$. This compound is stable at up to 37 GPa at least and down to 3.6 GPa. The changes in properties of this material with pressure are very well consistent with the behavior of $(H_2S)_2H_2$. Moreover, the stability of H_2Se molecule is improved in this ternary system, besides the decomposition in $(H_2Se)_2H_2$ and pure H_2Se. These results pave the way to studying the properties of this material at higher pressures and are conducive to the study of other ternary hydrides.

References

[1] Wigner E and Huntington H B 1935 *J. Chem. Phys.* **3** 764
[2] Ashcroft N W 1968 *Phys. Rev. Lett.* **21** 1748
[3] Ashcroft N W 2004 *Phys. Rev. Lett.* **92** 187002
[4] Duan D, Liu Y, Tian F, Li D, Huang X, Zhao Z, Yu H, Liu B, Tian W and Cui T 2014 *Sci. Rep.* **4** 6968
[5] Li Y, Hao J, Liu H, Li Y and Ma Y 2014 *J. Chem. Phys.* **140** 174712
[6] Liu H, Naumov, Ii, Hoffmann R, Ashcroft N W and Hemley R J 2017 *Proc. Natl. Acad. Sci. USA* **114** 6990
[7] Drozdov A P, Eremets M I, Troyan I A, Ksenofontov V and Shylin S I 2015 *Nature* **525** 73
[8] Zhang X, Xu W, Wang Y, Jiang S, Gorelli F A, Greenberg E, Prakapenka V B and Goncharov A F 2018 *Phys. Rev. B* **97** 064107
[9] Geballe Z M, Liu H, Mishra A K, Ahart M, Somayazulu M, Meng Y, Baldini M and Hemley R J 2018 *Angew. Chem. Int. Ed. Engl.* **57** 688
[10] Semenok D V, Kvashnin A G, Ivanova A G, Svitlyk V, Fominski V Y, Sadakov A V, Sobolevskiy O A, Pudalov V M, Troyan I A and Oganov A R 2020 *Mater. Today* **33** 36

[11] Drozdov A P, Kong P P, Minkov V S, Besedin S P, Kuzovnikov M A, Mozaffari S, Balicas L, Balakirev F F, Graf D E, Prakapenka V B, Greenberg E, Knyazev D A, Tkacz M and Eremets M I 2019 *Nature* **569** 528
[12] Somayazulu M, Ahart M, Mishra A K, Geballe Z M, Baldini M, Meng Y, Struzhkin V V and Hemley R J 2019 *Phys. Rev. Lett.* **122** 027001
[13] Snider E, Dasenbrock-Gammon N, Mcbride R, Debessai M, Vindana H, Vencatasamy K, Lawler K V, Salamat A and Dias R P 2020 *Nature* **586** 373
[14] Errea I, Calandra M, Pickard C J, Nelson J, Needs R J, Li Y, Liu H, Zhang Y, Ma Y and Mauri F 2015 *Phys. Rev. Lett.* **114** 157004
[15] Komelj M and Krakauer H 2015 *Phys. Rev. B* **92** 205125
[16] Einaga M, Sakata M, Ishikawa T, Shimizu K, Eremets M I, Drozdov A P, Troyan I A, Hirao N and Ohishi Y 2016 *Nat. Phys.* **12** 835
[17] Bernstein N, Hellberg C S, Johannes M D, Mazin I I and Mehl M J 2015 *Phys. Rev. B* **91** 060511
[18] Errea I, Calandra M, Pickard C J, Nelson J R, Needs R J, Li Y, Liu H, Zhang Y, Ma Y and Mauri F 2016 *Nature* **532** 81
[19] Heil C and Boeri L 2015 *Phys. Rev. B* **92** 060508(R)
[20] Liu B, Cui W, Shi J, Zhu L, Chen J, Lin S, Su R, Ma J, Yang K, Xu M, Hao J, Durajski A P, Qi J, Li Y and Li Y 2018 *Phys. Rev. B* **98** 174101
[21] Amsler M 2019 *Phys. Rev. B* **99** 060102
[22] Chang P H, Silayi S, Papaconstantopoulos D A and Mehl M J 2020 *J. Phys. Chem. Solids* **139** 109315
[23] Duan D, Huang X, Tian F, Li D, Yu H, Liu Y, Ma Y, Liu B and Cui T 2015 *Phys. Rev. B* **91** 180502
[24] Goncharov A F, Lobanov S S, Kruglov I, Zhao X M, Chen X J, Oganov A R, Konopkova Z and Prakapenka V B 2016 *Phys. Rev. B* **93** 174105
[25] Goncharov A F, Lobanov S S, Prakapenka V B and Greenberg E 2017 *Phys. Rev. B* **95** 140101
[26] Strobel T A, Ganesh P, Somayazulu M, Kent P R C and Hemley R J 2011 *Phys. Rev. Lett.* **107** 255503
[27] Guigue B, Marizy A and Loubeyre P 2017 *Phys. Rev. B* **95** 020104(R)
[28] Pace E J, Liu X D, Dalladay-Simpson P, Binns J, Peña-Alvarez M, Attfield J P, Howie R T and Gregoryanz E 2020 *Phys. Rev. B* **101** 174511
[29] Bykova E, Bykov M, Chariton S, Prakapenka V B, Glazyrin K, Aslandukov A, Aslandukova A, Criniti G, Kurnosov A and Goncharov A F 2021 *Phys. Rev. B* **103** L140105
[30] Pace E J, Binns J, Pena Alvarez M, Dalladay-Simpson P, Gregoryanz E and Howie R T 2017 *J. Chem. Phys.* **147** 184303
[31] Mao H K, Xu J and Bell P M 1986 *J. Geophys. Res.* **91** 4673
[32] Goncharov A F 2012 *International Journal of Spectroscopy* **2012** 617528
[33] Paldus B A, Schlueter S A and Anderson A 1992 *J. Raman Spectrosc.* **23** 87
[34] Ward A T 1968 *J. Phys. Chem.* **72** 4133
[35] Shimizu H, Yamaguchi H, Sasaki S, Honda A, Endo S and Kobayashi M 1995 *Phys. Rev. B* **51** 9391
[36] Loveday J S, Nelmes R J, Klotz S, Besson J M and Hamel G 2000 *Phys. Rev. Lett.* **85** 1024
[37] Mao H K and Hemley R J 1994 *Rev. Mod. Phys.* **66** 671
[38] Kim D Y, Scheicher R H, Mao H K, Kang T W and Ahuja R 2010 *Proc. Natl. Acad. Sci. USA* **107** 2793
[39] Tanaka K, Tse J S and Liu H 2017 *Phys. Rev. B* **96** 100502