

Compression of klockmannite, CuSe

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Copper selenide (CuSe) was compressed in a diamond anvil cell at room temperature up to a pressure of 52 GPa and studied using energy dispersive x-ray diffraction and Raman spectroscopy. CuSe is nearly isostructural with copper sulfide (CuS), and a previous study indicates that copper sulfide undergoes reversible pressure-induced amorphization at 18 GPa. The intensity of the x-ray diffraction peaks for CuSe decrease slowly, however, they never completely disappear up to a pressure of 52 GPa. The third-order Birch–Murnaghan equation of state fit to the data yields $K_0 = 96.9 \pm 5.3$ GPa and $K'_0 = 4.1 \pm 0.5$. Vinet's universal equation of state yields essentially identical parameters. Raman spectroscopy demonstrates that upon compression, the S–S bond in CuS compresses differently than the Se–Se bond in CuSe, possibly accounting for the different high pressure behavior of these two very similar compounds. © 1998 American Institute of Physics. [S0021-9606(98)01926-6]

INTRODUCTION

CuSe is a slate-gray mineral that is commonly referred to as klockmannite. Klockmannite is similar to covellite (CuS) in structure and composition. Extensive studies done by Earley and Berry established that klockmannite is isostructural with covellite.^{1,2} Both CuS and CuSe have a hexagonal crystal structure with trigonal-planar CuX_3 units surrounded by tetrahedral CuX_4 units.^{3,4} Therefore, the crystal is composed of layers of CuX_4 – CuX_3 – CuX_4 , which are held together by covalent bonding between X atoms from each layer.⁵ The only difference between CuSe and CuS is that CuSe has a hexagonal superstructure of 13 CuS-type subshells which is caused by inexact positioning of certain copper atoms in the trigonal-planar layer.

It has been reported that CuSe undergoes two phase transitions with increased temperature. The first phase transition occurs at 323 K from the hexagonal to an orthorhombic symmetry. Further increase in temperature leads in a transition to another hexagonal structure at 393 K, where no superlattice reflections are observed.⁶ Isostructural CuS shows pressure-induced amorphization under high pressure, at 18 GPa.⁷ Thus, we wanted to observe the effect of compression on the CuSe lattice.

We report here the study of CuSe at high pressure with x-ray diffraction and Raman spectroscopy using a diamond anvil cell. While increasing the pressure, the intensity of the x-ray diffraction patterns for CuSe decrease, but do not completely disappear up to 52 GPa. The diffraction data for CuSe were fit with Birch–Murnaghan and Vinet's universal equa-

tions of state to obtain zero-pressure isothermal bulk moduli and pressure derivatives for CuSe. The difference in the Raman spectra of CuS and CuSe at high pressure, is evidence that the compression mechanisms of these two compounds are not identical.

EXPERIMENT

CuSe samples (99.5%, Johnson Matthey Electronics, lot# D25A22) were loaded into a Mao–Bell⁸ type diamond anvil cell at ambient temperature. The culets of the diamonds were about 250 μm in diameter. Gaskets made of 127 μm thick Inconel, were drilled with holes 150 μm in diameter. After the gasket and hole were preindented to about 90 μm in thickness and 80 μm in diameter, a sample of crushed CuSe was loaded inside the gasket hole. Each sample was loaded in air with a few specs of gold (Au) powder mixed in as an internal pressure standard.

Synchrotron x-ray diffraction patterns were obtained with an energy dispersive Ge detector at beamline X17C of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. The detector was calibrated using the K_α lines of Cu, Rb, Mo, Tb, Ba, and Ag. X-ray spectra were collected for 5–18 min with the detector at a 2θ angle of 15° from the incident beam. With the detector at this angle, a value of $E-d$ (derived from $E=h\nu$ and Bragg's law $\lambda=2d \sin \theta$) is 47.546 84 keV Å. The energy (E) of each of the diffraction peaks in each spectrum was estimated by fitting a Gaussian curve to each peak. The 6–20 CuSe diffraction peaks were indexed according to the Joint Committee on Powder Diffraction Standards (JCPDS) card numbers 6-0427 and 20-1020. The unit cell volume was calculated using the average cell parameters of a hexagonal

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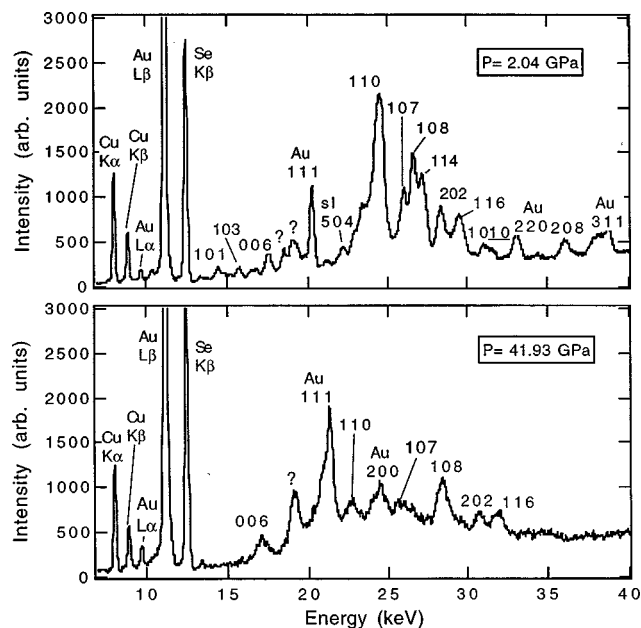


FIG. 1. X-ray diffraction spectra of CuSe at two different pressures. Both spectra are scaled to the intensity of the Cu K_{α} peak.

crystal structure. Pressures were determined by calculating the gold unit cell volume from gold diffraction peaks and using a standard equation of state for gold.⁹

Raman spectra was obtained for two samples of CuSe at the Argonne National Laboratory up to a pressure of 50 GPa. The Raman system was in a nearly backscattered geometry with an incident angle of about 30° . Two separate lenses were used to focus the incident and scattered beams. Spectra was obtained using the 476.2 nm excitation of a Kr ion laser, a JY T64000 triple spectrometer, and a Princeton Instruments CCD array. Both samples were loaded with a methanol:ethanol:water (16:4:1) mixture as a pressure medium. Pressure was determined by using the *in situ* ruby fluorescence method¹⁰ with Raman spectroscopy.

RESULTS

X-ray diffraction patterns obtained at 2.04 GPa and at 41.93 GPa, are shown in Fig. 1. All the spectra included many fluorescence lines of Au, Cu, and Se. In this figure, we have used the Cu K_{α} fluorescence line to scale the intensity of the two spectra presented. This scaling ensures that the compared intensities result from the same quantity of CuSe, eliminating any effect on intensity due to sample thinning during compression, and allowing a real comparison of intensity of the diffracted lines. The spectrum at 2.04 GPa has more peaks than the spectrum at 41.93 GPa. As pressure is increased, the 101, 103, 110, 1010, and 208 CuSe diffraction peaks lose intensity up to 52 GPa, while the peaks 006, 107, 108, 202, and 116 maintain almost consistent intensity. In Fig. 1, the 110 peak shows the most significant decrease in intensity; at 41.93 GPa it is only 30% of the intensity at 2.04 GPa. Upon decompression of the sample, all but the 107 and 1010 CuSe diffraction peaks regain intensity. The x-ray data that were obtained have been published elsewhere.¹⁵

There are three peaks (marked with “?”) on the spectra presented in Fig. 1. We were unable to index these peaks to any CuSe lattice or superlattice lines, and we believe that these peaks are possibly due to an impurity in the commercially obtained samples. The initial lot of CuSe powder sent was more contaminated or was a different composition of CuSe than stoichiometric 1:1. All the data presented here was obtained from a second batch of CuSe sent by Johnson Matthey, and electron microprobe analysis was performed to ensure correct stoichiometry, and minimum impurities.

Elastic parameters were calculated by fitting Birch–Murnaghan¹¹ and Vinet’s¹² universal equations of state to the diffraction data. The second order Birch–Murnaghan (BM) equation of state yields a bulk modulus of 98.48 ± 1.59 GPa, where K'_0 is held at a constant of 4.0. The third order BM equation of state, where K'_0 is allowed to vary gives a statistically better fit, yielding a bulk modulus of 96.9 ± 5.3 GPa and a pressure derivative of 4.14 ± 0.47 . Vinet’s universal equation of state yields a bulk modulus of 97.81 ± 5.67 GPa, with a pressure derivative of 4.24 ± 0.55 .

The Raman spectra obtained for CuSe at ambient pressure concurs with Iishi.¹³ However, the peak at 17 cm^{-1} was not observed because the detector was saturated by the Rayleigh peak below 35 cm^{-1} . Spectra obtained at 2.37 GPa, 16.63 GPa, and 39.67 GPa are presented in Fig. 3, and they contain many krypton laser plasma lines and Ar calibration lines. The peaks due to Raman scattering by CuSe are labeled in the 2.37 GPa spectrum. The peak at 263 cm^{-1} (labeled as 270 in Fig. 3) at 2.37 GPa, moves to a slightly higher frequency upon compression. At 16.63 GPa the peak splits in two, and starts to lose intensity. By 39.67 GPa, the double peak is still visible, but with very low intensity. The peak at 44 cm^{-1} overlaps with the Kr plasma peak and appears at 55 cm^{-1} as a very intense peak. Upon compression, the intensity of this peak increases. The small peak at 207 cm^{-1} is also overshadowed by the Kr peak at 215 cm^{-1} .

DISCUSSION

Although CuSe and CuS are similar in composition and structure, our studies have shown that as pressure increases, each compound behaves in a different manner. The bulk modulus for CuSe is 96.92 ± 5.31 GPa with a pressure derivative of 4.14 ± 0.47 . In comparison, the bulk modulus of CuS is 89 ± 10 GPa with a pressure derivative of -2 ± 2 .⁷ The higher the bulk modulus, the less compressible the compound. Therefore, CuSe is a more rigid structure than CuS, possibly due to the higher covalency of Cu–Se bonds in comparison with Cu–S bonds. The compression curve of CuSe (Fig. 2) is typical of many minerals, where K'_0 has a value close to 4. However, CuS has a negative K'_0 value, which indicates that it is thermodynamically unstable at high pressures, and compression to 18 GPa results in amorphization of CuS. In addition, though both CuSe and CuS have identical symmetry, CuSe also has a superstructure due to inexact positioning of copper atoms in the trigonal-planar layer. These facts, together with the larger size of the Se atoms in comparison to S atoms, help us understand the differences in the compression of these two compounds.

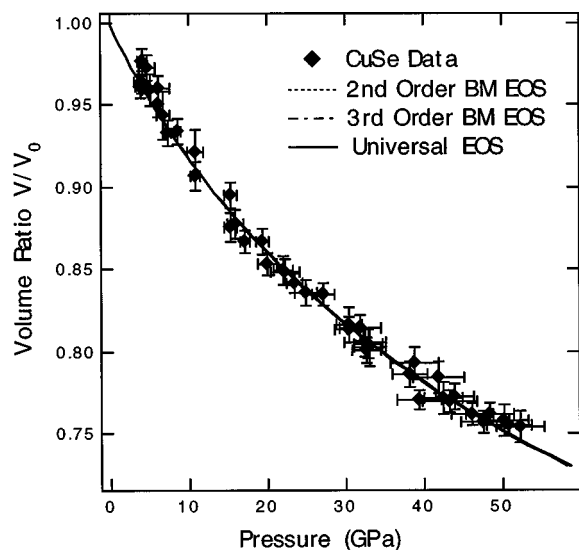


FIG. 2. Pressure vs V/V_0 , where $V_0 = 231.059 \text{ \AA}^3$, using CuSe compression data. Birch–Murnaghan and Vinet's universal equations of state fitted to the data are the dotted and solid lines.

Upon compression, diffraction experiments show a loss of intensity of certain CuSe peaks. The decrease in intensity due to the thinness of the sample is accounted for by scaling the spectra in Fig. 1 according to the $\text{Cu } K_\alpha$ peak. However, up to 52 GPa, there are CuSe peaks that remain in the x-ray diffraction spectrum that can be indexed to the ambient pressure CuSe structure. Therefore, CuSe does not completely amorphize to 52 GPa, unlike CuS. Instead the loss of intensity of certain peaks may also imply some preferred orientations within the lattice or a minor phase change.

Pressure-induced amorphization is considered to be a transition from a stable to an unstable phase. CuS undergoes a transition to an orthorhombic phase at a temperature of 55 K.¹⁴ Since the effect of low temperature is thermodynamically similar to increased pressure, the mechanism by which CuS goes amorphous has been discussed as a kinetically hindered transition to the low temperature orthorhombic phase.⁷ CuSe undergoes a similar transition to an orthorhombic phase, but at 323 K, a temperature higher than room temperature.⁶ This transition then is due to an expansion effect as opposed to the effect of compression. Thus, if the loss of CuSe diffraction intensity does result in amorphization at a pressure higher than 52 GPa, the mechanism for amorphization would be different to that of the amorphization of CuS.

According to Iishi¹³ the peak labeled 270 (in Fig. 3) in the Raman spectra of CuSe is assigned the Se–Se stretch. Upon compression, this peak splits into two, but retains a position close to the ambient pressure position of 263 cm^{-1} . The peak splitting indicates that there are two different Se–Se bond lengths at high pressure. This observation suggests that the structure is undergoing a minor phase transformation to another crystalline phase. However, because this

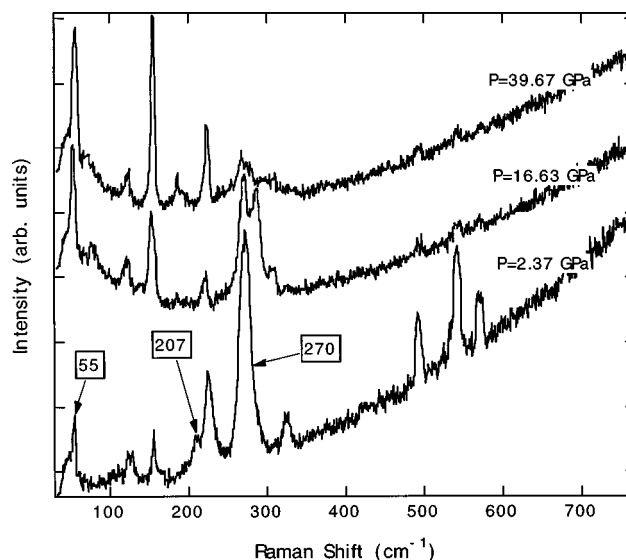


FIG. 3. Raman spectra of CuSe. The peaks due to Raman scattering from CuSe are labeled according to their position at 2.37 GPa.

peak also loses intensity by 39 GPa, implying the breakdown of this Se–Se bond vibration, the amorphization of CuSe at a pressure higher than 52 GPa is also a relevant possibility.

CONCLUSION

We have performed x-ray diffraction experiments on CuSe while compressing the sample in a diamond anvil cell. As pressure increases, the intensity of a number of CuSe peaks decrease. The equations of states calculated for CuSe yielded an average bulk modulus of $97.25 \pm 5.49 \text{ GPa}$ with an average pressure derivative of 4.19 ± 0.51 . Raman spectroscopy of CuSe indicates that the Se–Se bond splits in two suggesting different Se–Se bond lengths. These observations can be explained by either pressure-induced amorphization or a crystalline–crystalline phase transition in CuSe at a pressure higher than 52 GPa.

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