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X-ray diffraction measurements on CuGeO_3 under high pressures to 81 GPa using synchrotron radiation and imaging plates

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Abstract

Angle-dispersive x-ray diffraction measurements using CuGeO_3 (I) and CuGeO_3 (III) as the starting materials were carried out to 81 and 31 GPa, respectively, at room temperature. Data for phase (I) show that phase transitions occur at ~ 7 , ~ 14 , and ~ 22 GPa, respectively, corresponding to (I) \rightarrow (II), (II) \rightarrow (II'), and (II') \rightarrow (VI) transitions, as reported previously. The tetragonal phase (VI) was found to be stable up to 81 GPa, the highest pressure determined in this study. The volume changes at the transition pressures are estimated to be of $\sim 5\%$, $\sim 0\%$, and $\sim 14\%$ for (I) \rightarrow (II), (II) \rightarrow (II'), and (II') \rightarrow (VI) transitions, respectively. Data from measurements where phase (III) was the starting material show that phase (III) first changes to phase (IV) at ~ 7 GPa and then to (IV') at 13.5 GPa, and finally to phase (V) at ~ 18 GPa, with volume changes of 1.5%, 0%, and 20%, respectively, at the transition pressure. The volume change of 20% at 18 GPa is consistent with the pyroxene–perovskite transition.

1. Introduction

Recent Raman spectroscopic measurements and optical microscopic observations on single-crystal samples of CuGeO_3 at high pressures have revealed novel phase transitions such that a different pathway is followed depending critically not only on the hydrostaticity of the pressure medium used in the experiment [1–3], but also on the starting material used [4]. As a result, with an alcohol mixture or helium as the pressure medium, the phase transition sequence is (I) \rightarrow (II) \rightarrow (VI) at 7 and 8 GPa, respectively, whereas with other pressure media such as H_2O , Ar, and KBr, it is (I) \rightarrow (III) \rightarrow (IV) at 7, 8, 20 GPa, respectively. When phase (III) is used as the starting material with an alcohol mixture or helium as the pressure medium,

the transition sequence has been found to be (III) \rightarrow (IV) \rightarrow (IV') \rightarrow (V) at 8, 12.5, and 18 GPa, respectively [4]. A downward shift by about 300 cm^{-1} was observed in one of the Raman modes in phase (V), indicating octahedral coordination for Ge, which suggests a perovskite-like phase for phase (V) [4].

Recently, Ming *et al* carried out energy-dispersive x-ray diffraction measurements on CuGeO_3 (I) using a methanol/ethanol mixture as the pressure medium and reported three high-pressure phases (i.e., the orthorhombic phase (II), the monoclinic phase (II') and the tetragonal phase (VI)) at 7, 20, and 32 GPa respectively [5]. This is generally in accord with previous Raman measurements.

To further characterize the nature of each transition observed, we have carried out angle-dispersive x-ray diffraction measurements using both phase (I) and phase (III) as the starting materials. The results thus obtained are presented and discussed in relation to previous x-ray diffraction and Raman measurements.

2. Experimental methods

A modified Bassett-type diamond-anvil cell (DAC) was used in both studies. The cell consists of a pair of gem quality anvils of 1/3 carat with a culet of $400\text{ }\mu\text{m}$ and a gasket (T301, fully hardened, 10 mm thick) with a $100\text{ }\mu\text{m}$ hole serving as the sample chamber. A 4:1 methanol-ethanol mixture was used as the pressure medium and the sample pressure was determined by the ruby fluorescence method. X-ray diffraction experiments were carried out at the Photon Factory at the National Laboratory for High Energy Physics (KEK), Japan, using an imaging plate and monochromatic radiation from a bending magnet beamline (BL-18C).

Two separate experiments were performed. In the first experiment, we used CuGeO_3 (I) as the starting material, which is the same material as was used in our previous energy-dispersive x-ray diffraction measurements. In the second experiment, CuGeO_3 (III) was used as the starting material. A powder sample of CuGeO_3 (III) was synthesized by compressing CuGeO_3 (I) to 7 GPa at room temperature in a large-volume press at Osaka University and then unloaded to atmospheric pressure. The recovered sample was blue in colour and was confirmed by powder x-ray diffraction to be pure phase (III), an orthorhombic phase with lattice parameters $a = 10.0541 \pm 0.0073\text{ }\text{\AA}$, $b = 8.1965 \pm 0.0076\text{ }\text{\AA}$, $c = 5.7950 \pm 0.0045\text{ }\text{\AA}$.

These values are in excellent agreement with those obtained from single-crystal measurements ($a = 10.05\text{ }\text{\AA}$, $b = 8.19\text{ }\text{\AA}$, $c = 5.79\text{ }\text{\AA}$) [4].

3. Results and discussion

In the first experiment, a sample of CuGeO_3 (I) was gradually compressed to 81 GPa. X-ray diffraction patterns show clearly changes at 9.7, ~ 14 , and ~ 22 GPa indicating strongly that the phase transitions have taken place at these pressures. The high-pressure phases thus observed in this study are in accord with phases (II), (II'), and (VI) as reported previously [5]. On the basis of the high-quality diffraction data obtained in this study and those for a single crystal at 6.5 GPa [6], we revised phase (II) to having a monoclinic unit cell and phase (II') to being orthorhombic. The x-ray diffraction patterns between 22 and 81 GPa can be explained by a tetragonal unit cell, indicating that the tetragonal phase (VI) is stable to 81 GPa. The good quality of the spectrum obtained at 81 GPa (shown in figure 1) probably indicates that the sample is well crystallized at this pressure.

Molar volumes thus calculated for each phase at different pressures are plotted in figure 2, showing a good agreement between the data obtained using the angle-dispersive method in this study and those obtained previously with energy-dispersive methods.

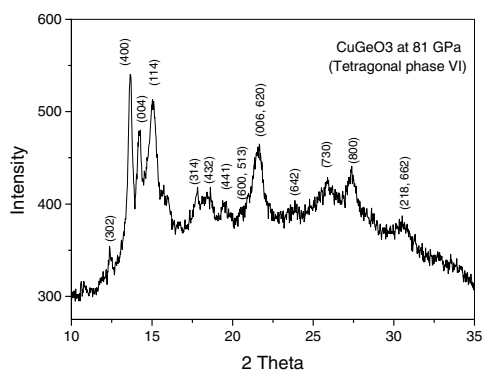


Figure 1. An angle-dispersive x-ray diffraction pattern of CuGeO_3 obtained at 81 GPa and room temperature.

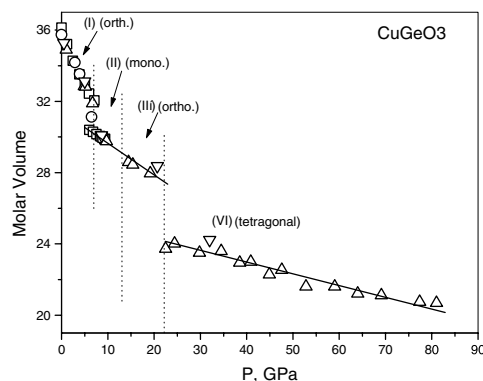


Figure 2. The effect of pressure on the molar volumes of phases (I), (II), (II'), and (VI) in CuGeO_3 , where downward-pointing triangles, circles, and squares show data from [5–7], respectively. Upward-pointing triangles show results from this study.

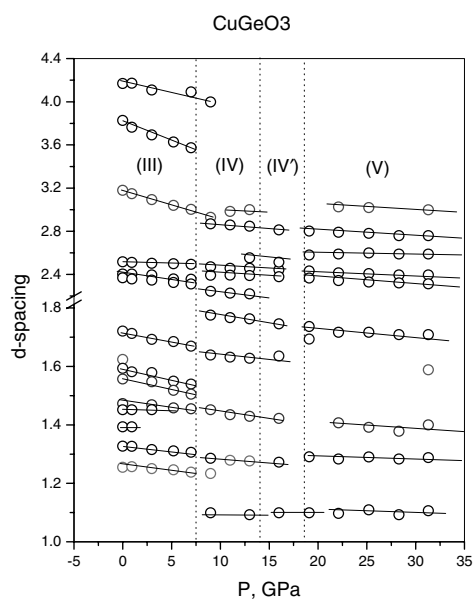


Figure 3. The effect of pressure on the d -spacing of CuGeO_3 at room temperature.

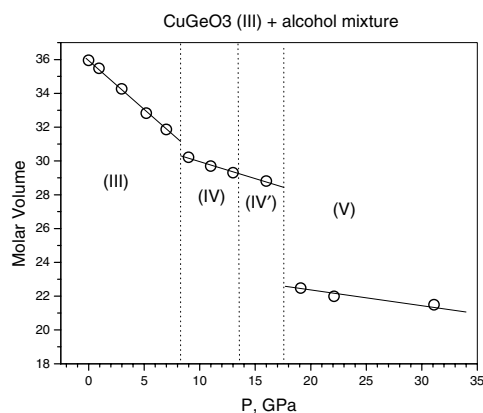


Figure 4. The effect of pressure on the molar volumes of phases (III), (IV), (IV'), and (V) in CuGeO_3 .

The volume changes for (I)–(II), (II)–(II'), and (II')–(VI) transitions are estimated as 5%, $\sim 0\%$, and 14%, respectively, at their respective transition pressure. The 14% change in the (II')–(VI) transition is consistent with the pyroxene–garnet transition as observed in CaGeO_3 [8].

In the second experiment, CuGeO_3 (III) was compressed gradually to 30 GPa. X-ray diffraction data are given in figure 3, where the d -spacings obtained are plotted against the pressure. Changes can easily be observed around 7.5, 13.5, and 18 GPa from the disappearance or appearance of the peak(s), or from the change of the slope in the plot.

These changes indicate the phase transitions that have taken place in CuGeO_3 (III) and correspond well with (III)–(IV), (IV)–(IV'), and (IV')–(V) transitions, respectively, as observed in Raman measurements. The x-ray diffraction data for phase (IV) obtained in this study are the same as those obtained in a quasihydrostatic environment [8]. Both phases (IV') and (V) are found to be orthorhombic, yet with different unit cells.

The molar volumes of phases (III), (IV), (IV'), and (V) obtained at different pressures are plotted in figure 4, showing the changes at the transition pressure, estimated to be 1.5%, 0%, and 20%. The volume change of 20% at 18 GPa is consistent with the pyroxene–perovskite transitions as reported for CaGeO_3 [7], CaSiO_3 [9], FeGeO_3 [10], MgGeO_3 [11], and $\text{CaMgSi}_2\text{O}_6$ [12].

References

- [1] Jayaraman A, Wang S Y, Ming L C and Cheong S-W 1995 *Phys. Rev.* **75** 2345
- [2] Jayaraman A, Sharma S K, Wang S Y and Cheong S-W 1996 *Curr. Sci.* **71** 306
- [3] Goni A R, Zou T, Schwarz U, Kremer R K and Syassen K 1996 *Phys. Rev. Lett.* **77** 1079
- [4] Jayaraman A, Shieh S R, Sharma S K, Ming L C and Wang S Y 2001 *J. Raman Spectrosc.* **32** 167
- [5] Ming L C, Shieh S R, Jayaraman A, Sharma S K and Kim Y H 1999 *J. Phys. Chem. Solids* **60** 69
- [6] Yoshiasa A, Yagyu G, Ito T, Yamanaka T and Nagai T 2000 *Z. Anorg. Allg. Chem.* **626** 36
- [7] Ming L C, Kim Y H, Chen J-H, Vaughan M, Shieh S R, Jayaraman A and Sharma S K 2001 *J. Phys. Chem. Solids* **62** 1185
- [8] Ross N L and Navrotsky A 1988 *Am. Mineral.* **73** 1355
- [9] Wang Y and Weidner D 1994 *Geophys. Phys. Lett.* **21** 895
- [10] Hattori T, Matsuda T, Tsuchiya T, Nagai T and Yamanaka T 1999 *Phys. Chem. Minerals* **26** 212
- [11] Leivenweber K, Wang Y, Yagi T and Yusa H 1994 *Am. Mineral.* **79** 197
- [12] Kim Y, Ming L C and Manghnani M H 1994 *Phys. Earth Planet. Interiors* **83** 67