

Researchers discover pressure-induced polyamorphism in dense sulfur dioxide

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Some substances are known to exist in several different structurally disordered solid states, a phenomenon known as polyamorphism.



The first and perhaps most celebrated example of polyamorphic behavior was discovered in water ice in 1984 by Mishima et al. Two different forms of amorphous water ice were identified, known as low-density amorphous and high-density amorphous ices. Later on, similar phenomena were also observed in other important systems such as Si, SiO_2 , and GeO_2 .

In condensed matter physics, polyamorphism is a very interesting but poorly understood phenomenon.

Recently, a team of Chinese scientists and their collaborators at the Institute of Solid State Physics of the Hefei Institutes of Physical Science examined polyamorphism in the molecular substance SO₂.

While exploring phase transition in dense SO_2 , they found pressureinduced amorphization in dense SO_2 and a reversible pressure-induced structural transformation between the molecular amorphous and polymeric amorphous forms of SO_2 . This work was published in *PNAS* on April 4, 2020.

 SO_2 plays a significant part in chemistry research and in the physics of the Earth and atmosphere. While properties of similar solid molecular systems such as CO_2 or N_2 at high pressures have been extensively studied, more research on dense SO_2 , especially its behavior and properties, still needs to be done.

In this study, scientists took a closer look at this simple molecule through a combined experimental and computational effort that tried to describe some new and unexpected phenomena.

By using experimental techniques of Raman spectroscopy and X-ray diffraction at high pressures, they compressed SO_2 up to 60 GPa with a diamond anvil cell and explored the <u>phase transitions</u> and structures of



 SO_2 up to 60 GPa and at temperatures ranging from 77-300 K.

At 77 K and below 16 GPa, <u>sulfur dioxide</u> was crystalline. When compressed to 16 GPa, the sulfur dioxide in the crystalline phase went through pressure-induced amorphization and entered the amorphous phase of the molecular state. When further compressed to above 26 GPa, a phase transition occurred from the molecular amorphous phase (twocoordinated sulfur) to the chain polymeric amorphous phase (threecoordinated sulfur).

The researchers studied several different temperature paths and found that the phase transition path in dense SO_2 proceeded from the crystalline to the molecular amorphous phase and then to the polymeric amorphous phase over the entire temperature range of 77-300 K. They also discovered that the phase transition path was reversible.

Furthermore, the amorphization pressure changed with temperature, ranging from 10-16 GPa across the 77-300 K <u>temperature</u> range.

To test their observations, the team used molecular dynamics simulations and the same phenomenon was also observed. In particular, the <u>highpressure</u> polymeric amorphous form was found to consist mainly of disordered polymeric chains made of three-coordinated <u>sulfur</u> atoms connected via oxygen atoms, and few residual intact molecules.

The amorphous molecular to amorphous polymeric transition identified in this research may also suggest the possible existence of a similar transition in the liquid state.

More information: Huichao Zhang et al, Pressure-induced amorphization and existence of molecular and polymeric amorphous forms in dense SO₂, *Proceedings of the National Academy of Sciences* (2020). DOI: 10.1073/pnas.1917749117



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