

# Exploration of pressure-induced phase transition to the post-PbCl<sub>2</sub> structure in dioxides

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## Introduction

Materials transform to denser phases under high pressure inside the Earth and planets. The densest structure of dioxides reported so far is the PbCl<sub>2</sub> type in which each cation is surrounded by 9 oxygens (9-fold coordinated). Many dioxides with large cations are known to have the PbCl<sub>2</sub> structure under high pressure, but any phase transition to the structure with a higher coordination number, namely the post-PbCl<sub>2</sub> structure, has not been reported. The purpose of this study is to explore the post-PbCl<sub>2</sub> structure of dioxides. Since lead is in the same group of carbon and silicon and PbO<sub>2</sub> is known to have the PbCl<sub>2</sub> structure under high pressure, CO<sub>2</sub> and SiO<sub>2</sub>, which are important compounds in Earth and planetary science, may have the PbCl<sub>2</sub> and/or the post-PbCl<sub>2</sub> structure at ultimately high pressures. At present, pressures above 200 GPa are difficult to achieve in laboratory. Since there is an inverse correlation between cation radius and transition pressure, it is better to choose a dioxide with a larger cation to explore the post-PbCl<sub>2</sub> structure in a limited pressure range. The cation radius of TeO<sub>2</sub> is even larger than those of the dioxides reported to have the PbCl<sub>2</sub> structure. We have studied the pressure-induced phase transition in TeO<sub>2</sub> by Raman scattering and X-ray diffraction.

## Experiment

The diamond-anvil cell was used to generate high pressure. TeO<sub>2</sub> (paratellurite, six-fold coordinated) powder was packed and loaded in a hole of Re gasket without pressure medium. The sample was heated using Nd:YAG laser. Pressure was measured with the edge frequency shift of the T<sub>2g</sub> Raman mode of the diamond anvil (Akahama et al., 2004). The Raman scattering experiments were carried out with a 500 mm focal-length imaging spectrometer and a cooled CCD detector. The 488 nm line from Ar ion laser was used for excitation. Angle-dispersive synchrotron X-ray diffraction experiments were carried out with an imaging-plate detector at BL-13A and BL-18C of PF, KEK (Tsukuba, Japan).

## Results and Discussion

Raman spectrum and X-ray diffraction pattern changed dramatically at about 25 GPa. The similar change in Raman spectrum has been measured by Jayaraman et al. (1991). They inferred that TeO<sub>2</sub> transformed to the PbCl<sub>2</sub> structure. In deed, our X-ray diffraction pattern is well explained with the PbCl<sub>2</sub> structure. The PbCl<sub>2</sub> phase of TeO<sub>2</sub> contracted rather isotropically with increasing pressure, similar to the PbCl<sub>2</sub> phases of other dioxides (e.g., TiO<sub>2</sub>, ZrO<sub>2</sub>, PbO<sub>2</sub>). In contrast, the PbCl<sub>2</sub> phases of dihalides contract quite anisotropically and then transform to the post-PbCl<sub>2</sub> structures. This suggests that the mechanism of the phase transition to the post-PbCl<sub>2</sub> structure in dioxides might be different from that of dihalides. A fit of pressure-volume data to the second-order Birch-Murnaghan equation of state gave the zero-pressure bulk modulus of about 140 GPa for the PbCl<sub>2</sub> phase of TeO<sub>2</sub>. This value is as small as (or smaller than) about a half of those of other PbCl<sub>2</sub>-structured dioxides. This indicates that the PbCl<sub>2</sub> phase of TeO<sub>2</sub> is more sensitive to pressure than other PbCl<sub>2</sub>-structured dioxides and may transform to the post-PbCl<sub>2</sub> structure at a lower pressure. At about 100 GPa, Raman signals became hardly detected. New peaks appeared in X-ray diffraction pattern, while the peaks of the PbCl<sub>2</sub> phase decreased in intensities. These changes strongly suggest the occurrence of the phase transition, possibly to the post-PbCl<sub>2</sub> structure. We are now trying to clarify the nature of this phase transition.