X-ray Diffraction of Anatase Titanium Dioxide under High Pressures

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Introduction

Three crystalline modifications of titanium dioxide, rutile, anatase and brookite, have networks composed of differently connected TiO_6 octahedra. This leads to different optical, electrical and structural properties. Although many investigations have been carried out for rutile, anatase has been given less attention. It is necessary to conduct a systematic study of all the crystalline phases for the investigation of structural dependence of TiO_2. In this report, anatase single crystal under high pressure is investigated by X-ray diffraction in order to obtain structural information.

Experimental

The X-ray powder diffraction under high pressures was measured at the BL-18C operating λ=20 keV. The powder specimens were made by grinding single crystals of anatase grown by the chemical vapor transport method [1, 2], because we have to obtain pure and well-crystallized powder of anatase better than that on the market. A small ruby tip was introduced with the powder in the sample chamber of a preindented stainless steel gasket using a 4:1 mixture of methanol and ethanol as the pressure medium. The X-ray diffraction pattern was obtained by digital integration of Debye-Scherrer ring recorded on an imaging plate. The pressures were determined by the frequency shifts of the ruby R_1 fluorescence line.

Results and Discussion

Figure 1 shows change of X-ray diffraction spectra depending on the pressure. The curve (a) measured at 0.53 GPa shows typical pattern of the anatase powder of good quality. The diffraction lines of anatase are marked by triangles. The spectra (b) and (c) measured at 3.3-4.1 GPa show that some additional lines are observed. When the pressure reaches to 5.2 GPa, another additional lines were observed, as shown in spectrum (d). Here, the pressure was released to 0.17 GPa. Some of the additional lines disappear in the spectrum (e), so that the additional lines could be classified into two groups. Group 1 is observed only when the sample is compressed under the high pressures and group 2 involves irreversible phase transition, which are marked by open and solid rhombuses, respectively. Our previous study concluded that the irreversible phase transition from anatase to the high-pressure phase (HP), which has isostructure with α-PbO_2, is induced in the pressure range from 4.3-4.6 GPa [3]. The lines of the group 2 can be attributed to the HP. The lines of group 1 will be indexed using lattice parameters, $a'=2a$ and $c'=2c$. This involves that the pressure induces a distortion of the crystal lattice

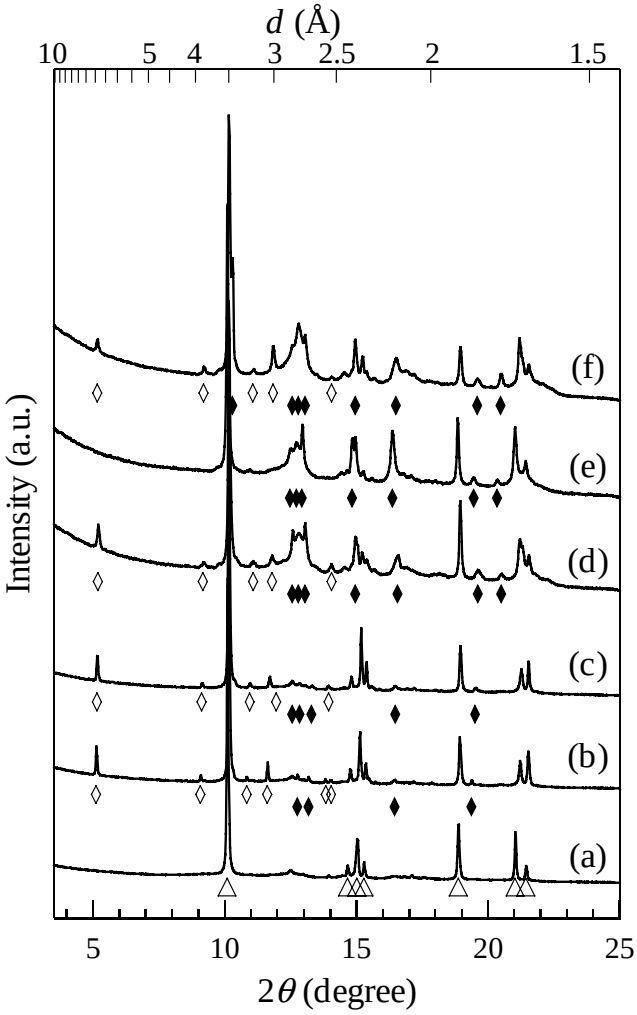

Fig. 1 X-ray diffraction spectra of anatase at (a) 0.53, (b) 3.3, (c) 4.1and (d) 5.2 GPa. The spectrum (e) was recorded when the pressure released to 0.17 GPa. (f) After (e), the sample was compressed to 5.2 GPa, again.

resulting in the formation of superstructure. The spectrum (d) indicates that anatase phase is still present in spite of the compression at pressure higher than the critical one. It is necessary to perform further investigation to elucidate this

References

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