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On the transformation pathways of α-PbO_2-type TiO_2 at the twin boundary of rutile bicrystals and the origin of rutile bicrystals

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Abstract: Extraction and electron irradiation (under transmission electron microscopy) of an epitaxial nanometer-thick α-PbO_2-type TiO_2 slab between twinned rutile bicrystals in ultra-high pressure metamorphic rock caused phase changes into a modified fluorite-type and then an amorphous phase. This martensitic-type transition process accounts for the dislocations and stacking faults of the slab and disordering of Ti in the adjoined rutile bicrystals. Additional hydrothermal experiments of sol-gel TiO_2-Al_2O_3 performed at 8.5–9 kbar and 675–800°C in the piston-cylinder apparatus indicated that twinned rutile bicrystals were shaped in mirror image without the formation of α-PbO_2-type TiO_2 slab at the twin boundary and with no other planar defects for the bicrystals. The twinned bicrystals can be rationalized by growth and/or coalescence processes. Accordingly, it is not justified to assume a precursor phase of α-PbO_2-type structure for twinned rutile bicrystals when there is no such relic. Rutile, unless exsolved epitaxially from a host mineral such as garnet, does not constitute evidence for unusually deep burial for ultra-high pressure terranes.

Key-words: α-PbO_2-type TiO_2, transformation path, twinned rutile, ultra-high pressure, metamorphism.

Introduction

There are a number of high-pressure TiO_2 polymorphs having a higher density than rutile (space group $P4_2/mnm$). Static compression coupled with laser heating indicated the existence of a hexagonal-like structure of TiO_2, which may be related to the fluorite type and which reverts to the α-PbO_2 structure upon release of pressure (Liu, 1978). Later static compression studies at ambient temperature or up to 1527°C by laser heating showed the compression path rutile → α-PbO_2 type (space group *Pbcn*) → baddeleyite type (MI, space group $P2_1/c$) → orthorhombic OI structure (space group *Pbca*) → cotunnite type (OII, space group *Pnma*) (Sato *et al.*, 1991; Dubrovinskaia *et al.*, 2001; Dubrovinsky *et al.*, 2001). Recently, Nd-YAG-laser pulse irradiation of Ti target under oxygen background gas for the combined effects of oxidation and very rapid radiant heating/cooling was used to synthesize α-PbO_2-type (Chen & Shen, 2002) and fluorite-like TiO_2 condensates partly transformed into baddeleyite-type structure (Chen & Shen, 2004). Spherical TiO_2 nanocondensates were found to transform martensitically into baddeleyite-type and then α-PbO_2-type structures with accompanied transformation twinning, shearing and shape change into ellipsoid upon electron irradiation. The relatively large particles followed the same transformation path yet with alternative lattice correspondence and additional multiple deformation twinning of the baddeleyite type (Chen & Shen, 2004). The existence of a cubic fluorite-like TiO_2 was further supported by the most recent static compression coupled with laser heating at a pressure of 48 GPa and temperatures between 1900 and 2100 K (Mattesini *et al.*, 2004).

α-PbO_2-type TiO_2 can be transformed directly from rutile and the phase transformation pressure is lower for nanophase material (~4 GPa and 900°C for the transformation of 10 nm-size particles) than for the bulk (~6 GPa and 850°C) (Olsen *et al.*, 1999). This knowledge gives indicative P-T constraints on the natural occurrence of α-PbO_2-type TiO_2, recently identified by analytical electron microscopy as an epitaxial nanometer-thick slab between twinned rutile bicrystals included in almandine-rich garnet of diamondiferous quartzo-feldspathic rocks in the ultra-high pressure (UHP) metamorphic terrane of Saxonian Erzgebirge, Germany (Hwang *et al.*, 2000). [UHP refers to metamorphic pressure above 2.5 to 2.7 GPa for the production of coesite (Liou *et al.*, 1998).] The Saxonian Erzgebirge continental crustal rocks were therefore suggested to have been buried to a depth of at least 200–130 km (Hwang *et al.*, 2000).

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