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Twining and inclusions in chrysoberyl from Pratinhas, Brazil

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Chrysoberyl (BeAl_2O_4) is a rare mineral usually found in metamorphosed pegmatites, granites and silicic volcanoclastic rocks [1]. It is orthorhombic with unit-cell parameters $a = 5.481\text{Å}$, $b = 9.415\text{Å}$ and $c = 4.428\text{Å}$. Besides single crystals, contact twins and cyclic twins on $\{130\}$ planes are common. The most famous chrysoberyl twin occurrences are in phlogopite mica matrix in Russia (Urals) [2] and in pegmatite matrix or in alluvial or colluvial gravels in Brazil (Bahia, Corrego Alegre, Espirito Santo) [3]. The reasons for the formation of chrysoberyl twins were not studied before. In our previous analyses of growth twins and related planar defects in various synthetic materials [4] and natural minerals [5,6] we showed that the formation of such defects is not accidental, but chemically triggered already in the nucleation stage of the crystal growth. In order to reveal the reasons for the formation of chrysoberyl twins, we studied contact $\{130\}$ twins in natural crystals from Pratinhas locality in Bahia (Brazil) by electron microscopy methods. A typical heart-shape contact twin, as used for our studies, is shown in Figure 1a. The crystal is oriented along the $[001]$ orientation and the $\{130\}$ boundary, which divides the crystal into two equivalent halves, is clearly visible. For transmission electron microscopy (TEM) analyses, a block of 2×2 mm was cut from the crystal centered across the twin boundary parallel to the $[001]$ direction. The block was inserted and glued into a brass ring, which was subsequently cut into about $500\ \mu\text{m}$ thick slices. The slices were thinned down to $100\ \mu\text{m}$, dimpled down to $20\ \mu\text{m}$ in the centre and perforated using Ar ions (PIPS, Gatan, Netherlands). The samples were analyzed with TEM (JEM-2100, Jeol, Japan) equipped with a detector for energy-dispersive spectroscopy (EDS).

A low-magnification image of the $\{130\}$ twin boundary in chrysoberyl oriented along the $[001]$ zone axis is shown in Figure 1b. In this orientation, the twin boundary is usually a straight interface, occasionally interrupted by short steps to nearby parallel planes. Diffraction patterns were recorded in both crystal domains and across the twin boundary (Figures 1c-d). The common $\{260\}$ reflections (marked in Fig. 1e) confirm that the twin lies parallel to the $\{130\}$ planes of the chrysoberyl structure. A typical HRTEM image of the twin boundary was taken in a thin part of the TEM sample (Fig. 1f). The contact between the two twin domains is sharp and no secondary phase was observed on the contact, as expected in analogy to the $\{301\}$ twins in rutile [5]. Besides the twin boundary, we also observed numerous nano-sized precipitates in bulk chrysoberyl. The density of precipitates was similar in all regions of the analyzed TEM sample. HRTEM analysis of the precipitates (Figure 2) revealed that they lie parallel to the two equivalent $\{120\}$ planes of chrysoberyl, which intersect at an angle of 98.7° . These precipitates are probably the reason for the origin of 4-ray asterism in rare and precious chrysoberyl gems. We performed also some preliminary EDS analyses in bulk chrysoberyl, across the precipitates and at the twin boundary (Figure 3). The results reveal that bulk chrysoberyl contains a small amount of iron, which is a common impurity in natural chrysoberyl crystals. The spectrum taken across the precipitate revealed that it is enriched in Ti. In combination with structural analysis, the precipitates could be rutile or some high-pressure TiO_2 polymorph. Ti and Fe enrichment was detected also in the region near the twin boundary as a consequence of diffusion and segregation processes.

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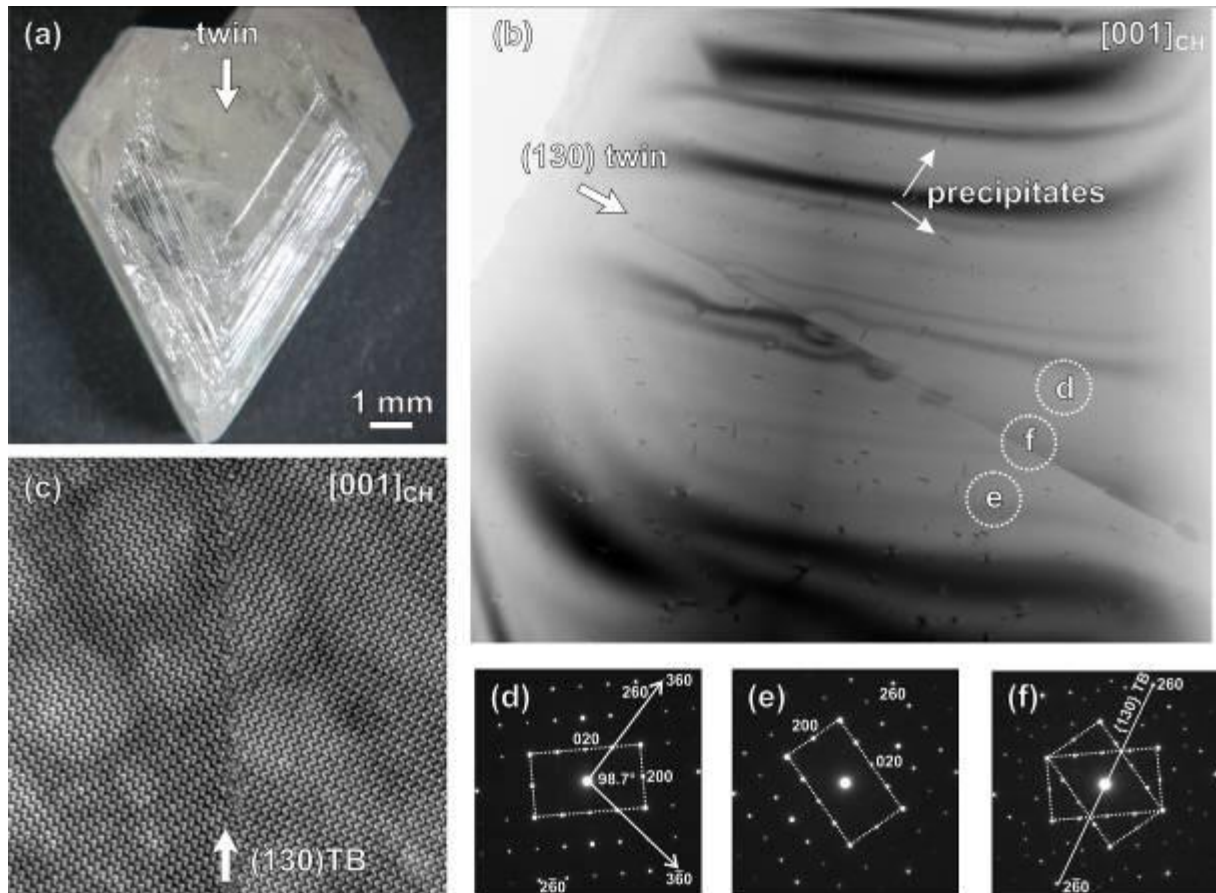


Figure 1. (a) Chrysoberyl with a well-defined contact twin boundary. (b) Low magnification TEM image of the twin boundary in chrysoberyl. Many nano-sized inclusions following two directions are visible in the bulk chrysoberyl. (c-e) Diffraction patterns taken in both crystal domains and across the twin boundary confirm that it lies parallel to $\{130\}$ planes of the structure. (f) HRTEM image of the twin boundary.

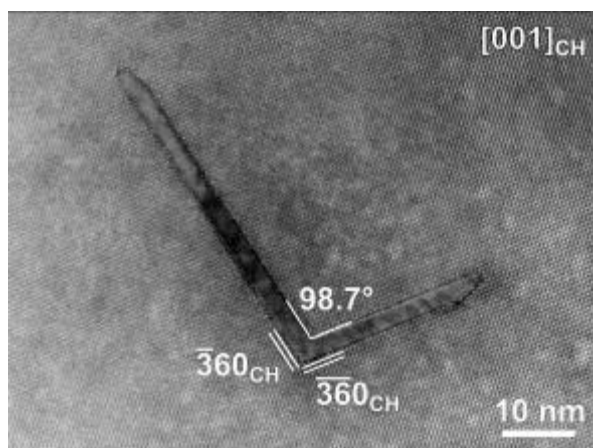


Figure 2. HRTEM image of a typical knee-shaped precipitate in chrysoberyl. The edges of the precipitate lie parallel to $\{120\}$ planes of chrysoberyl, which form an angle of 98.7° .

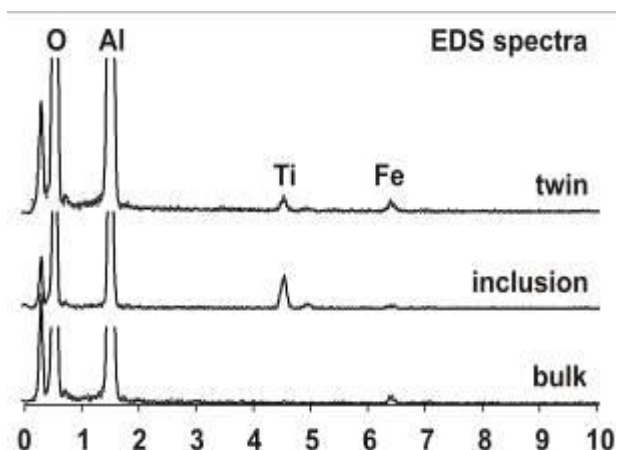


Figure 3. EDS spectra taken in bulk chrysoberyl, across the inclusion and across the $\{130\}$ twin boundary reveal that bulk chrysoberyl contains some Fe, the inclusion is enriched in Ti, while the region near the twin boundary contains increased amount of Ti and Fe.