We studied (130) twins of natural chrysoberyl (BeAl$_2$O$_4$) crystals from Pratinhas, Brazil. To determine the local structure of twin boundaries, powder X-ray diffraction analysis (XRD), transmission electron microscopy (TEM) methods and density functional theory (DFT) calculations were used. Chrysoberyl has a slightly distorted hexagonal close-packed (hcp) O-sublattice with Al$^{3+}$ and Be$^{2+}$ ions partially occupying octahedral and tetrahedral interstices. The crystal structure was refined by Rietveld analysis (Topas-Academic V4) using our experimental XRD data collected on finely ground bulk material, starting with the atomic coordinates determined by Hazen (1987). The structure of chrysoberyl was refined in the orthorhombic s.g. 62 (Pmnb) with unit cell parameters: $a = 5.4825(1)$, $b = 9.4163(2)$, $c = 4.4308(1)$ and $R_{wp} = 7.8\%$. The refined structure was then used for interpretation of electron diffraction patterns and lattice images obtained by TEM (JEM2100, Jeol). The specimens were investigated in [001]-projection, where the (130) twin boundaries are viewed edge-on (Fig. 1). EDS measurements show $\sim$1% Fe in bulk chrysoberyl, suggesting an average composition of BeAl$_{1.99}$Fe$_{0.01}$O$_4$. The increase of Ti at the twin boundary suggest a transient Ti-exsolution that took place after the twin formation. The twin boundary appears to be coherent, making occasional steps to parallel (130) planes. Following the interface, we observe that the periodicity is attained after every $\sim$1.9 nm, roughly corresponding to 4·[110] interplanar distances. HRTEM images recorded at the defocus value of -60 nm are very sensitive to the positions of Be-atoms, which alternate form one to another side of the O-chains (Fig. 2). Image simulations, based on simple mirror-twin model, match the general contrast features, whereas the interface is not well reproduced and needs some reconstruction. A close look at the interface shows two distinct features, which are a result of different occupation of coordination polyhedra accompanied by some relaxation. Calculations within the framework of the density functional theory (DFT), using pseudo-potential method, suggested that the atomic Cluster-I undergoes a significant relaxation of interfacial Be$^{2+}$ and O$^{2-}$ positions, whereas in Cluster-II the interfacial Be$^{2+}$ sites are shifted to neighboring tetrahedral interstices, further away form the boundary. The local charge balance involved with this operations remains unchanged. whereas the contrast of the simulated image based on the DFT relaxed atomic model, shows correct tendency in the interface contrast compared to experimental HRTEM images. Further analysis of (130) twin boundaries will be necessary to verify the possibility of chemically-induced twinning in chrysoberyl (Takeuchi 1997).

Acknowledgement: References:
Fig. 1: HRTEM image of (130) boundary in natural chrysoberyl crystals (inset) with the corresponding SAED pattern showing the twin operation. EDS analysis indicates the presence of Ti on the twin boundary.

Fig. 2: Refinement of the atomic model, based on HRTEM image simulations and DFT calculations. Major differences occur in atomic clusters I and II, outlined in the HRTEM image.