The structural study of (111) twin of natural spinel crystals from Mogok (Burma) suggested that tetrahedrally coordinated Mg\(^{2+}\) ions, linked to the twin-forming hcp stacking, are probably replaced by Be\(^{2+}\). It has been also proposed that incorporation of Be during crystal growth triggers tropochemical twinning in spinel and the formation of modulated compounds of the taaffeite Be\(_{x}\)Mg\(_{y}\)Al\(_{2(x+y)}\)O\(_{4(x+y)}\) homologous series [Daneu et al. 2007]. This hypothesis has been experimentally supported by liquid-phase assisted reactive sintering of primary oxides, where the addition of BeO triggered abundant twinning of spinel, whereas no twins formed in pure Al\(_2\)O\(_3\)–MgO system [Drev et al. 2013]. Atomic-resolution HAADF-STEM images of (111) twin boundaries indicated a distinctive dark contrast at the boundary tetrahedral sites (Fig. 1), but spectroscopic evidence for a single atomic layer of Be was still lacking to confirm the tropochemical origin of twinning. To produce such an evidence, we designed analytical strategy for accurate measurement of Be on the twin boundary, using a probe-corrected field-emission gun transmission electron microscope with the scanning unit (jeol-ARM). First, EELS spectra were collected from synthetic chrysoberyl (BeAl\(_2\)O\(_4\)) and taaffeite (BeMg\(_3\)Al\(_8\)O\(_{16}\)) samples, where Be\(^{2+}\) ions are in a similar structural environment as in the (111) twin boundary in spinel. The material is quite sensitive to high electron doses and spectral imaging (ESI) was out of question. As opposed to the (111) twin boundary in spinel, where we have only one situation per crystal, in taaffeite structure there are multiple situations where the analytical approach could be tested. Therefore the spectra were collected from (0001) planes of taaffeite using short acquisition times and a narrow rectangular window of approx. dimensions of 20 x 0.2 nm\(^2\), containing only Be atoms in hcp layers of the structure. The width of the stripe was limited by the neighboring Al-rich kagome layers, which could cause overshadowing of Be-K edge (111 eV) by the tails of the Al-L\(_{2,3}\) edge (79 eV). To avoid collecting energy losses from neighboring atomic layers the spectra were recorded form thin crystal parts. The same analytical approach was then implemented on the (111) twin boundaries in spinel, where the presence of Be was successfully confirmed. Based on experimental HAADF-STEM images supercell models containing 336 atoms were constructed for simulations and twin-boundary energy calculations within the frame of density-functional theory (DFT). The calculated boundary energy for Mg\(^{2+}\) occupying the interfacial tetrahedral sites is one order of magnitude larger than if the sites are occupied by Be\(^{2+}\). Continued in Acknowledgement ...

Acknowledgement: ... Comparison of the twin boundary energy to bulk spinel suggests that the twinning is more favorable than a fault-free structure (Fig. 2), which explains anisotropic growth of (111) twins after their nucleation [Drev et al. 2013].

References:
Fig. 1: Z-contrast image of (111) twin with EELS spectra for chrysoberyl, taaffeite and (111) twin boundary in spinel. 

Fig. 2: Comparison of simulated and experimental HAADF-STEM images of (111) twin. DFT calculations indicate that Be-rich boundary has the lowest energy. Intensity maxima correspond to atomic columns of overlaid models.