Structure, composition and bonding at grain boundary and interfaces affect the sintering process, the microstructure control and the thermo-mechanical properties of advanced ceramics. TEM has always played the leading role in pursuit of grain boundary nature: in the pre-C$_s$ time, equilibrium amorphous film was found at grain boundaries in Si$_3$N$_4$; in the beginning of C$_s$ era, rare-earth cations were directly imaged at specific sites of intergranular films, which opened the door of detailed study of chemical bonding. However, between structure and bonding, the composition of grain boundaries was not sufficiently studied as compared either on scale or quality. Here I would like to present a comprehensive approach to probe chemical composition and bonding based on a combined EELS methodology [1]. The resultant quantitative knowledge on grain boundary chemistry may help us to gain deeper insights into the nature of ceramic materials.

Difference in ELNES characters between the probed grain boundary film and the adjacent grains allow the overlapping spectrum to be separated in a systematic procedure, which is based on the “spatial difference” method combined with the principle of “Multiple-variant Statistic Analysis”. Indeed the ~1nm thick amorphous film is made of silicate, hence the SiO$_4$ bonding must be quite different from the Si-N$_4$ bonding. As illustrated in Fig. 1, this approach separates not only the specific ELNES for grain boundary film, but also the associated volume, which results in corresponding chemical width and composition for the grain boundary film [1]. This is effectively an orthogonization process to find two independent vectors in the vector-space of EELS spectra. This indirect approach could even obtain atomic level EELS spectrum in the pre-C$_s$ era in a suitable case [2].

The exclusive EELS spectrum reveals that the amorphous film is made of silicon oxynitride instead of silicate. Ratio of N:O remains close to 1:2 in several doping systems, but it could vary when the sintering could not fully densify [3]. More detailed study reveals further that dopant cations segregated to the grain boundary film in a trend different from the film composition, and the grain surfaces play also a role in the structure and chemistry of amorphous films [4]. The ELNES separation could also be applied to phase boundary to reveal the exclusive spectrum corresponding to the boundary width [1]. It leads to finding amorphous double-layer film at the boundary between a grain and a devitrified triple pocket phase in a doped Si$_3$N$_4$ (Fig. 2). More details and implication of such a phenomenon will come soon.

Fig. 1: ELNES separation results in the specific spectrum of grain boundary film that contains no overlapping signal from the adjacent grains, thanks to their difference in bonding nature [1].

Fig. 2: EELS line-scan across triple pocket in a La₂O₃-doped Si₃N₄ to reveal the double-layer for amorphous film at the two-phase boundary. The EELS spectra were processed according to their ELNES differences between both phases as described in [1].