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Detection and imaging of light elements in Mg-Al-spinel

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$MgAl_2O_4$ is considered a promising material for optical applications and hence object to research for more than 40 years worldwide [1-3]. The densification mechanism of $MgAl_2O_4$ (hereafter termed spinel) doped with lithium fluoride (LiF) as transparent ceramic has been intensively studied.

Optical transparency requires densification to a value near the theoretical density since residual porosity, which acts as scattering source, has to be eliminated. In addition, impurities and secondary phases have to be removed to avoid scattering or absorption of the transmitted radiation (i.e. visible or IR light). LiF greatly reduces the sintering temperature and facilitates enhanced densification at low temperatures. However, the basic mechanisms behind the sintering process are still not fully understood, as neither LiF nor an additional secondary phase is detectable in the final product.

Based on individual studies Reimanis, Kleebe and Rozenburg [4-6] postulated three major processes during sintering of spinel with LiF including (i) Enhanced volume diffusion by incorporation of O-vacancies (ii) Dissolution – Reprecipitation and (iii) Wetting – Dewetting: At this early stage of sintering, the densification mechanism can be described by a classical liquid phase sintering process facilitating particle rearrangement. At temperatures above 1000°C, no secondary phase is detectable along grain boundaries. In a recent work it was shown that these mechanisms occur simultaneously interacting with each other [7], however, the verification was made by indirect methods as for example the double fringe technique introduced by D.R. Clark [8] for the wetting-dewetting mechanism as shown in Figure 1. In this presentation we will show exemplarily the reason for the twice changing mean inner potential creating the double Fresnel fringes as an example of the high potential of probe-corrected microscopes in the applied transmission electron microscopy and material science. Using an ARM 200F operating at 200kV a series of high resolution STEM-EELS investigations were performed at a polycrystalline spinel sample, sintered at 900°C, consistently showing an incorporation of fluorine in the first two atomic layers near the grain boundaries as depicted in Figure 2. This means that a) the double Fresnel fringes cannot only be created by an amorphous layer of a secondary phase but also by additional incorporated elements and b) the wetting mechanism occurs much earlier in the sintering process then postulated.

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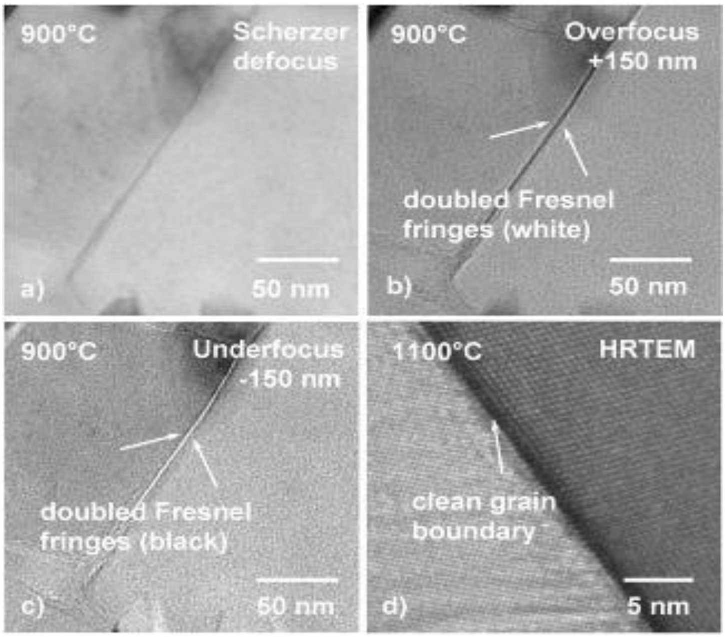

Figure 1. Defocus series of a spinel-spinel grain boundary. The material was sintered at 900°C [a,b,c] and 1100°C [d]. The double fringes occurring at 900°C indicate a twice changing mean inner potential which was interpreted as a wetting of the grain boundary. At higher temperatures no wetting was observed.

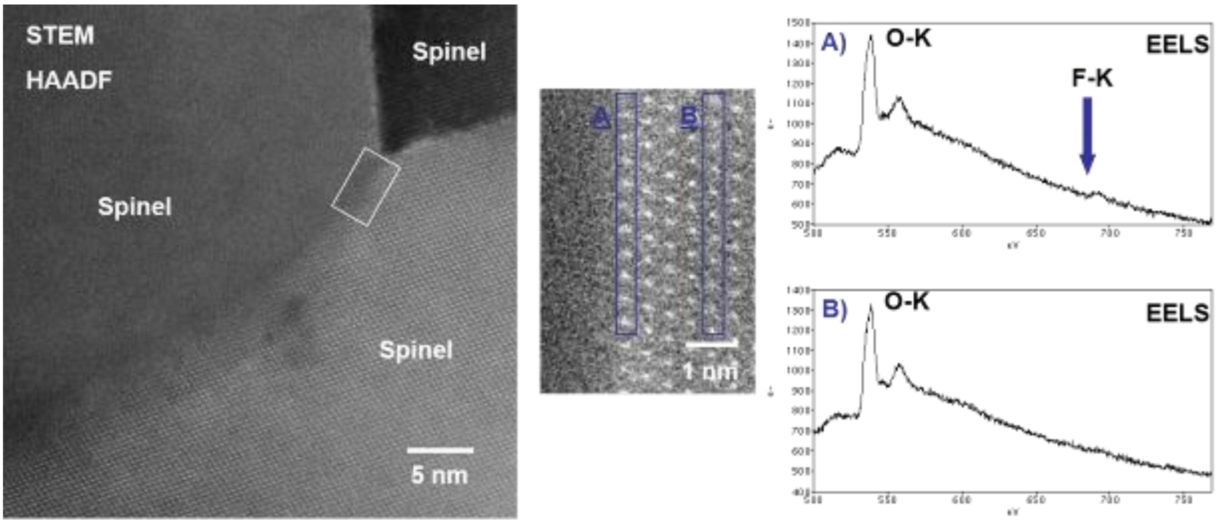

Figure 2. HR-STEM image of a spinel-spinel grain boundary. When applying the defocus technique double Fresnel fringes occurred but even in highest magnification no wetting could be shown. Instead, by using STEM EELS techniques, an incorporation of fluorine in the first two atomic layers was observed at a sintering temperature of 900°C.