Type of presentation: Poster

IT-5-P-3376 Comparison of the silicon/phosphorus ratio in natural and synthetic nagelschmidtite for possible use as standard for microanalysis based on X-ray lines of Si and P

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Quantitative chemical microanalysis by energy-dispersive X-ray spectroscopy (EDXS) in a (scanning) transmission electron microscope (STEM) relies on the use of accurate *k*-factors. The most commonly used reference line is Si K.

For semiconductor research, standards for elemental semiconductors and for III/V compound semiconductors including elements from groups III and V of the periodic table are required. For the arsenides we have published results on X-ray quantification based on standards of InGaAs [1]. InAs and InP can be used to link arsenides and phosphides. However, the nominal *k*-factor for the P K-line in the ISIS software of *k*=1.000 indicates that this has probably not been measured at all.

Here, we use a natural and a synthetic sample of the mineral nagelschmidtite, a calcium silico-phosphate (ideal formula $Ca_7(SiO_4)_2(PO_4)_2$ [2]), to evaluate the Si/P ratio from EDXS.

The natural mineral stems from the Hatrurim formation [3] and was cut from a thin section by a focused ion beam to produce an electron transparent specimen for TEM. Electron probe microanalysis (EPMA) of a larger inclusion of nagelschmidtite yielded an atomic ratio of Si/P=3.15. Results from TEM-EDXS are displayed in green.

The synthetic mineral was prepared in the laboratory of C Wu, Shanghai Institute of Ceramics [4]. Its chemical analysis using a Spectro Cirus Vision ICP-OES spectrometer gave a Si/P ratio of 0.36 (by at%), i.e. an almost inverted ratio. (S)TEM-EDXS results from these particles are displayed in dark blue.

Figure 1 shows that, for the detector setting used the deadtime of the detector is linearly related to the count rate up to a max of ~2500 counts/second or 50%, above which the detector runs into saturation.

Figures 2 and 3 plot atomic ratios as obtained from ISIS without absorption correction. The synthetic compound (blue) clearly reveals a higher P/Si ratio than the natural mineral (green) in Fig.2.

If the chemical concentration x_n of an element n is proportional to the product of X-ray intensity I_n, *k*-factor $k_{n,Si}$ (for weight%) and absorption factor a_n, divided by the atomic weight A_n, then we can calculate an effective *k*-factor [5]:

$k^{eff}_{P,Si} = k_{P,Si}\ a_{P,Si} = (I_{Si}\ x_P\ A_P) / (I_P\ x_{Si}\ A_{Si})$

This is plotted in Fig.4. While the data scatter is rather large, a linear fit to the spectra that gave reasonable densities (≤ 3.5 gcm^{-3}) as determined by ISIS allows us to determine the thin-film *k*-factor by extrapolation to zero count rate. The result is $k_{P,Si}=1.16\pm0.45$ ($R^2=0.287$).

[1] T Walther, Proc EMAG2009, J Phys Conf Ser **241** (2010) 012016

[2] G Nagelschmidt, J Chem Soc **1** (1937) 865

[3] M Fleischer, LJ Cabri, GY Chao, A Pabst, Am Mineral **63** (1978) 424

[4] Y Zhou, C Wu, Y Xiao, Acta Biomaterialia **8** (2012) 2307

[5] Y Qiu et al, Proc EMC2008, **2** (2008) 643

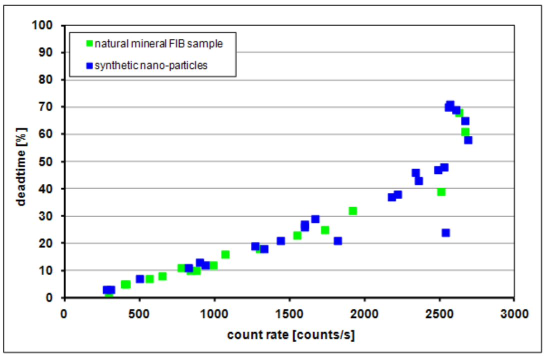

Figure 1. *Plot of deadtime vs count rate*

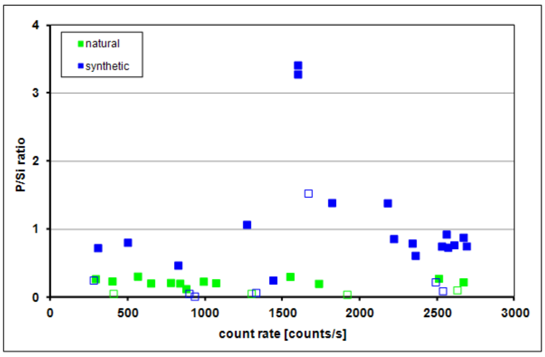

Figure 2. *Plot of P/Si ratio from (S)TEM-EDXS*

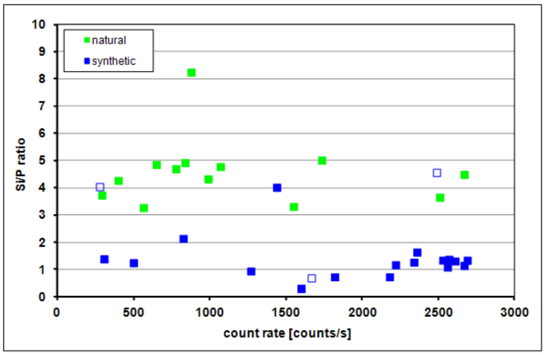

Figure 3. *Plot of Si/P ratio from (S)TEM-EDXS*

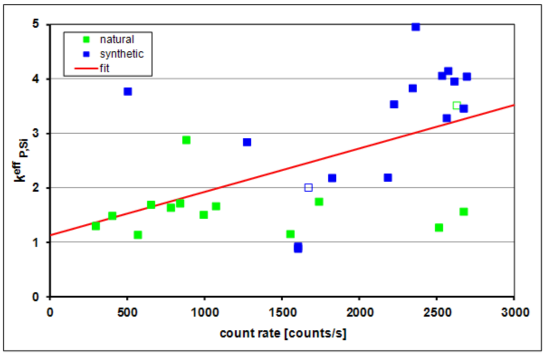

Figure 4. *Plot of effective k-factor vs count rate*

Fig. 1: