Phase Identification by EBSD Analysis of Non-Metallic Crystallites

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Material characterization techniques constitute a major part in exploratory synthesis in many fields like energy storage and conversion, biomaterials, chemical catalysis, aerospace, electronics, etc. for crystalline materials phase identity plays the ultimate role in material function as applications are highly structure dependent.

There are a variety of well-established, complementary techniques for phase identification of crystalline solid-state materials including single crystal X-ray diffraction, powder X-ray diffraction, neutron diffraction, low-energy electron diffraction, selected area electron diffraction and electron backscattered diffraction (EBSD).

Currently, EBSD is used routinely for phase and crystallites orientation mapping and studying the grain boundary of metallic and alloy samples [1]; this is partially due to the well-suited nature of these sample types for EBSD as they show no charging effect and can be polished smoothly to provide a good diffraction path from specimen surface back to EBSD camera. On the other hand, though not greatly investigated, EBSD can be applied to non-conducting, individual single crystals of micron and *sub-micron* sizes. Here the purpose is to use EBSD for phase identification of powdered samples composed of small crystallites for which the usual sample preparation methods is not applicable.

In this work EBSD technique has been used successfully for phase confirmation of two sample types: 1) A new insulator, poly-anion metal framework compound with formula $Li_5Fe_2PO_4F_8$ which may finds applications as solid-state electrolyte for Li-ion batteries and, 2) Iron Tavorite, LiFePO4F, which finds applications as cathode material for Li-ion batteries [2]. For the latter case, to the best of the author's knowledge there is no structural information from *single-crystal* diffraction due to the lack of large single-crystals and the proposed structures are based on X-ray or neutron diffraction from bulk, powdered samples and Hence EBSD was used to check the validity of LiFePO$_4$F structure.

The crystal structure of $Li_5Fe_2PO_4F_8$ was solved first with single-crystal X-ray diffraction. For LiFePO$_4$F, crystal information was taken from Inorganic Crystal Structure Database (ICSD crystal # 167611). For both specimens the obtained crystal data were feed into Twist software (Channel 5) for generation of hkl reflector list which is subsequently used for indexing the diffraction pattern of some small crystallites. The crystals of interest were mounted on carbon dot and carbon coated for 5 sec as both compounds exhibit extremely low conductivities. Image acquisition was performed with a Helios NanoLab 600 FESEM at 30.0 kV and 11 nA. The scope was equipped with an Oxford Instruments HKL EBSD detector. EBSPs acquisition and indexing was done with Channel 5 Flamenco software.

Electron micrograph of the $Li_5Fe_2PO_4F_8$ crystallite is shown in Figure 1.a and as it can be seen there is a minimal charging effect. Figures 1.b and 1.c illustrate the acquired and indexed EBSPs of the sample, respectively. The indexing is done perfectly with a mean angle deviation (MAD) value of 0.48° which is an indication of goodness-of-fit of the indexing process. Roughly a MAD value below 1° is assumed as an acceptable indexing.
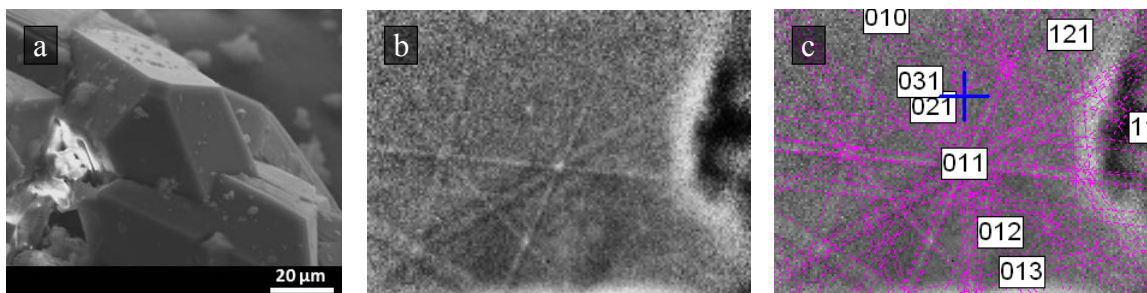
Figure 1. a) Acquired electron micrograph of $Li_5Fe_2PO_4F_8$; b) Raw EBSP and, c) indexed EBSP. The pattern center is marked with a cross (binning: 4x4).

The SEM image along with the raw and indexed EBSPs for $LiFePO_4F$ are shown in Figure 2.a, 2.b and 2.c, respectively. It should be noted that the EBSP is composed of Kikuchi lines from two adjacent single-crystals and only one of the diffraction patterns has been used for indexing. The MAD value for indexing is 0.948°. This value indicates that the suggested backbone for $LiFePO_4F$ structure is generally consistent with the observed EBSP, but some modifications are required.
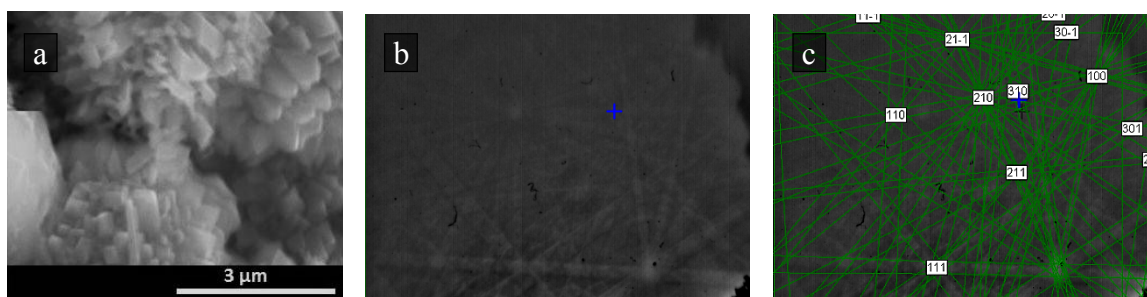

Figure 2. a) Acquired electron micrograph of $LiFePO_4$; b) Raw EBSP and, c) indexed EBSP. The pattern center is marked with a cross (no binning).

It worth mentioning that for each sample only some crystal faces are oriented in a way that the backscattered diffracted electrons can be directed toward the detector and therefore examination of different faces is required in order to find the optimum results; but generally it is possible to find such conditions with a few tries.

The results shown above propose the opportunity to use EBSD for routine phase identification and confirmation of small crystallites. Also in cases where a structure is proposed from solving a powder pattern, it can be used as a confirmatory tool. Except for carbon coating, no extensive sample preparation is required. Having a very accurate geometrical calibration is vital for successful indexing. The specimen charging can be problematic but still it may be possible to get an EBSP from a charged sample.

References:

[1] F J Humphreys, Journal of Material Science **36** (2001), p. 3833.
[2] T N Ramesh, K T Lee, B L Ellis and L F Nazar, Electrochemical and Solid-State Letters **13** (2010), p. A43.
[3] The author acknowledges CSMMS, specially Tommi White, Paul Carpenter and Clarissa Wisner for supporting this work.