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MS-5-P-1576 Element/Site-Selective Local Ligand Analysis using High-Angular Resolution Electron Channeled Fluorescent Spectroscopy

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The current state-of-the-art scanning transmission electron microscope (STEM) equipped with aberration correctors allows it handy for atomic scale imaging and elemental/electronic structural analysis, due to its high-brightness electron source and highly focused subatomic probe size available. The technique inevitably leads to a drawback associated with a high density of focused electron probe and its small illuminating area (i.e., a small number of sampling points), so that the probe can drill the sample or otherwise the obtained data may contain high level noise accordingly. We have hence been engaged in an alternative microanalysis method, instead of exploiting the atomic resolution in real space, using inelastic scattering by channeled electrons in a crystal [1]. We have developed an ‘integrated electron spectroscopic STEM’, where electron energy-loss spectroscopy (EELS), energy/wavelength dispersive x-ray spectroscopy (E/WDXS) and cathode-luminescence (CL) are implemented in a single STEM.

The incident electron beam is rocked about a pivot point on a sample, acquiring the spectroscopic intensity data as a function of the incident beam direction (and the momentum transfer vector in EELS) (Ionization channeling pattern: ICP). The sample orientation and beam direction is monitored by the rocking image recorded by the ADF detector. The present method exploits site selective information of the material associated with different electron densities propagating along the specific atomic planes/columns by varying Bloch wave symmetries excited in the crystalline sample.

We have examined Eu/Y doped Ca_2SnO_4 with red emissions associated with f-f transitions: Eu(Y) occupies the Ca and Sn sites by the ratio of 7:3 (3:7) determined by EDXS (cf., Fig. 1), both taking the tri-valent state by EELS [2] and the Ca site with the asymmetric ligand as the active light emitting site by CL (Fig. 2). It is noted that the electric dipole transition (615 nm: $_5D^0$-$_7F^2$) changed in its intensity with the diffraction condition, while the magnetic dipole transitions ($_5D^0$-$_7F^1$, $_5D^1$-$_7F^2$) were independent of the diffraction condition. The present results directly support the conventional idea [3] that Eu^{3+} occupying the asymmetric Ca site is a primary light emitting specie induced by the enhanced electric dipole moment.

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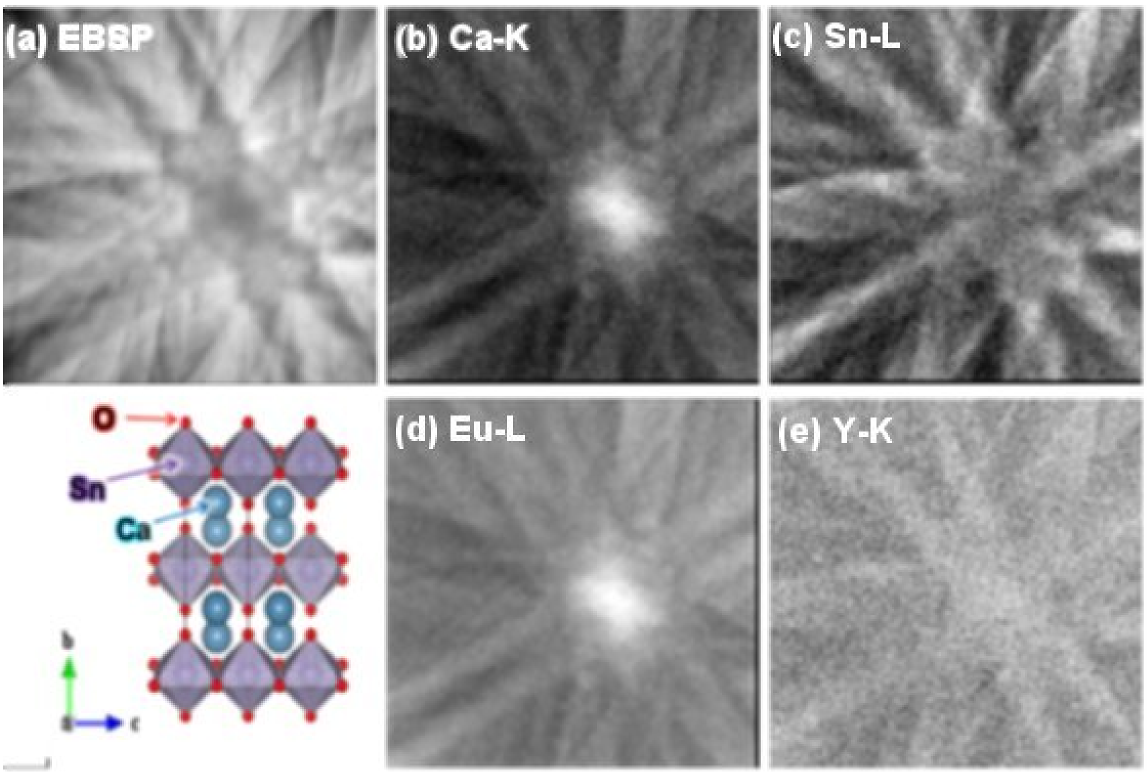

Fig. 1: Electron beam rocking pattern (a) and ICPs of Ca-K(b), Sn-L(c), Eu-L(d) and Y-K(e) characteristic x-ray emissions from Eu/Y doped Ca_2SnO_4 near [100]. It is seen that Eu(Y) mainly occupies the Ca(Sn) site. The crystal structure of Ca_2SnO_4 is inset lower left corner.

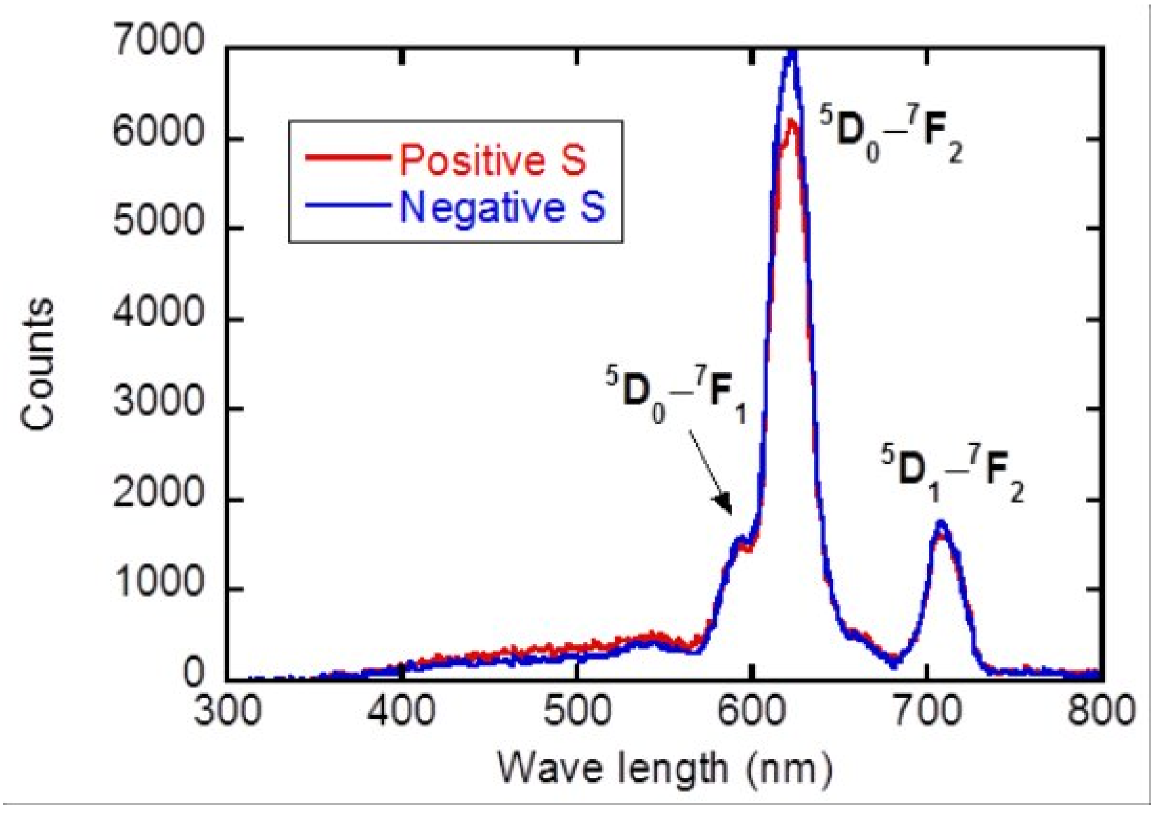

Fig. 2: CL spectra from Ca_2SnO_4 with the excitation error S of 100 reflection positive (red) and negative (blue).