Development of New Specimen Holder for Cathodoluminescence Measurement in TEM and Its Application to Site-Selective Electron Transition Analysis of Rare Earth-Doped Phosphor Materials

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We have been developing an integrated electron spectroscopic S/TEM, putting EELS, WDX(EDX) and CL (cathodoluminescence) together into a single S/TEM for obtaining element- and site-selective electronic structure information over the entire band scheme around the Fermi level from the single common spot, as schematically shown in Figs. 1 and 2.

We once manufactured a prototype of TEM-CL system with the light collecting/guiding parts integrated on the specimen holder [1], unlike the most common TEM-CL systems equipped with an ellipsoidal or parabolic reflector within the gap of the objective lens pole piece. The design enabled the system compatible with the EDX/WDX and EELS at the same time, and also allowed large angle sample tilt. The main disadvantage of the holder was a significant background level: one comes from the thermal glow of the electron gun, and the other from the light emission of the light-guiding optical fiber itself, excited by the electrons scattered or reflected from the specimen and holder components [1].

We have newly designed the TEM-CL specimen holder, not only overcoming the difficulties above but also improving the light-collecting efficiency by two orders of magnitude, as shown in Fig. 2. The reflectors and optical fiber are placed away from the TEM optical axis. The light-collecting solid angle is approximately 1.3 strad, approximately 100 times larger than that of the prototype. The overall light collection efficiency depends however on the quality of the mirrors, the optical alignment, and the transmission properties of the fiber. A small cylindrical sample is mounted at the end of the metal wire, the position of which can be adjusted to the focal point of the primary mirror by the piezo-driven manipulator. The collected light was analyzed by a Hamamatsu PMA-12 multi-channel ultra-high sensitivity spectrometer covering the wavelength range of 200-950 nm. More detailed specifications are found elsewhere [2].

To test the present TEM-CL system, we measured site-selective light emission associated with the $^5D_0$-$^7F_2$ electric dipole transition of Eu^{3+} (616 nm) in Eu^{3+}-doped Ca_2SnO_4 [3]. We confirmed in advance that Eu^{3+} equally occupies both the Ca^{2+} and Sn^{4+} sites by X-ray diffraction (XRD)/Rietveld and EDX analyses of the sample [4]. The stronger PL is expected by the increased fraction of Eu^{3+} ions occupying the Ca^{2+} site, because the Ca^{2+} site is coordinated by seven oxygen atoms, the asymmetric configuration of which enhances the electric dipole moment, compared with the symmetric six-coordinated Sn site. We hence applied ALCHEMI-type analysis to confirm at which cation site Eu^{3+} actually more luminescent. The ICSC code [5] predicts that the Ca site is more excited when the (001) scattering angle is slightly larger than the exact Bragg condition, as shown in Fig. 3(a). The CL intensity change with the diffraction condition is shown in Fig. 3(b). The CL intensity at 616 nm is increased at the indicated diffraction condition by ~20%, compared to the symmetric condition, which actually verifies that Eu^{3+} at the asymmetric Ca site emits higher CL intensity.

References

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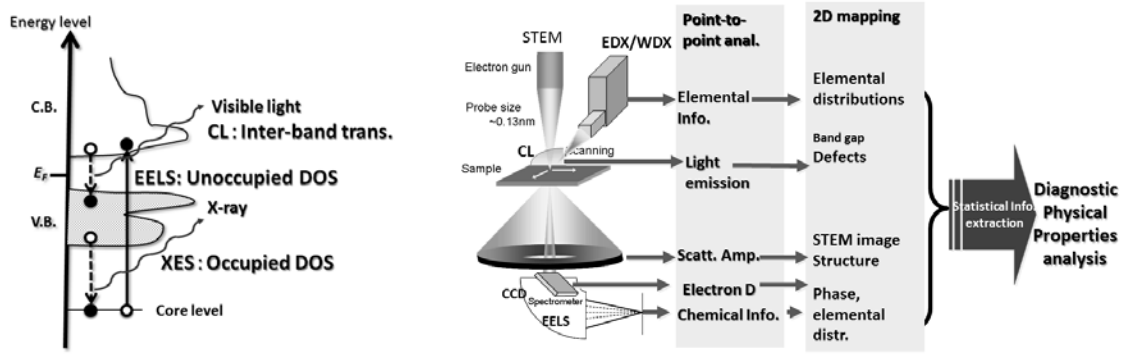
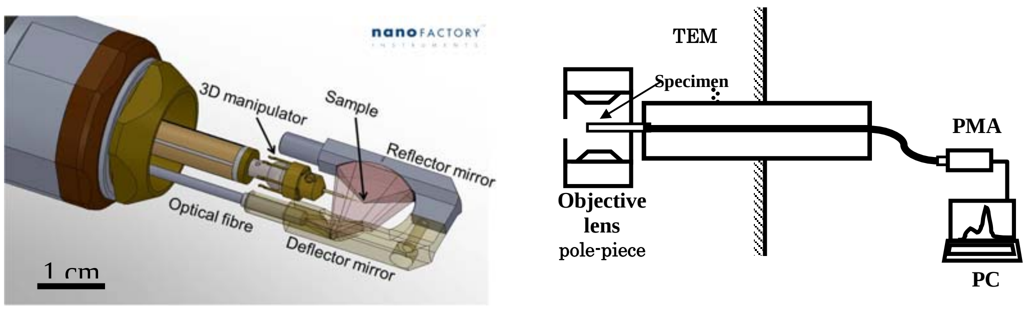


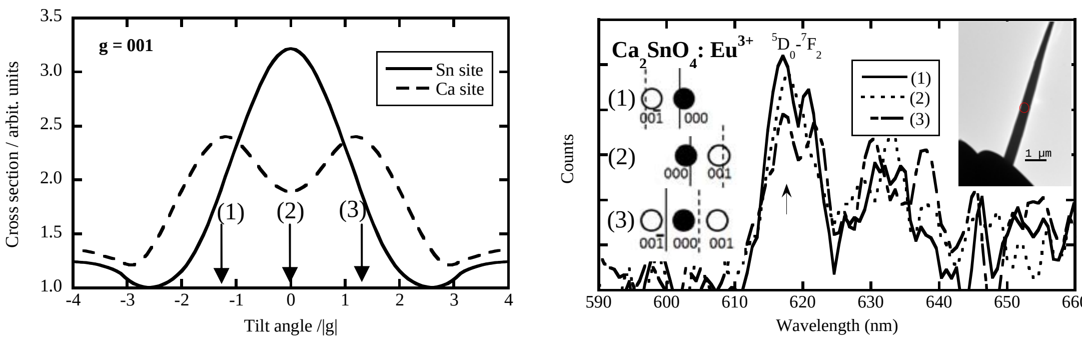
(a) (b)

FIG. 1. Conceptual diagrams of integrated electron spectroscopic S/TEM in energy space (a) and real space (b). XES (X-ray emission spectroscopy) is measured by WDX.



(a) (b)

FIG. 2. (a) Schematic design of the present sample holder for TEM-CL. (b) Block diagram of the present TEM-CL system.



(a) (b)

FIG. 3. (a) Excitation probabilities of Eu 4f state at Ca and Sn site as functions of diffraction condition at 001 systematic row excitation, calculated by ICSC code [5]. (b) Measured CL intensities by $^5D_0$-$^7F_2$ electric dipole transition (616 nm) of Eu^{3+} in Eu-doped Ca_2SnO_4 at schematically indicated diffraction conditions. A TEM image of the sample is inset.