Recent developments in soft X-ray emission spectroscopy microscopy

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Abstract. This paper discusses the path to the commercialization of a soft-X-ray emission spectrometer system for EPMA/SEM, its application, how it can be used to investigate new materials, and offers an update on improvements being investigated to further optimise the performance. The ultimate energy resolution of 0.08 eV at Al L² Fermi edge is shown with current optics using a fine pixel detector. The spectral mapping technique can show chemical shift images by using an appropriate region-of-interest energy window. L-emissions of 3d transition metal elements inform one not only of the density of states of bonding but also the number of outer shell or 3d electrons. Furthermore, progress leading to improvements in the detection efficiency has resulted in more than three times increase in the B K-emission peak. Testing and evaluation of new high energy-resolution spectrometer for EPMA, and a new calibration procedure for C K-peak on graphite has resulted in improved energy calibration procedure is presented.

1. Introduction
Observing fine structures of materials and atomic arrangements, examining the composition and the associated chemical state(s) are key issues asked in modern electron microscopy. Especially, understanding the chemical state of element and how it is related to material’s function is a core of interest for material’s scientists. Transmission electron microscope (TEM) is a powerful and widely used tool for analysing the crystalline order and orientation by electron diffraction pattern, lattice defects by Bragg contrast imaging, atomic arrangements by phase-contrast and/or high-angle dark-field contrast images, the composition by X-ray emission spectroscopy (energy-dispersive X-ray spectrometry, EDS), and chemical state analysis by electron energy-loss spectroscopy (EELS) of nm-scale specimen areas. However, these capabilities of TEM can only be applied for thin specimens. On the other hand, a chemical state analysis method for bulk specimens based on electron microscopy has not been well established in energy resolution compare with those of EELS experiments of 0.1 ~ 1 eV. In the last twenty years, soft X-ray emission spectroscopy (SXES) instruments for electron microscopes have been
developed based on TEM to examine its capability [1]. More recently, the SXES was installed on a scanning electron microscope (SEM) and subsequently commercialised as an attachment for electron probe microanalyser (EPMA) and/or SEM [2, 3].

2. X-ray emission due to electronic transition and its information

High energy electron-beam irradiation for a specimen creates a core-hole by exciting a core-electron and this process can lead to X-ray emission as a relaxation process resulting from the transition of an electron to the core-hole state. Figure 1 shows a schematic drawing of electronic transitions among conduction bands (CB), valence bands (VB), and inner-shell levels. The excitation processes, upward arrows, are used in EELS to examine a chemical state of a material. The relaxation processes, downward arrows, are used in X-ray emission spectroscopy (XES) for elemental analysis and/or phase identifications as wavelength-dispersive X-ray spectrometry (WDS) and energy-dispersive X-ray spectrometry (EDS).

Valence electron excitation EELS spectra (process a) includes information from the band-gap and interband transition energies and refractive indices. Experimental results can be compared with optical experiments by using a Kramers-Kronig analysis. Inner-shell electron excitation EELS spectra (process b) give us information of the density of states (DOS) of CB (anti-bonding states). This inner-shell excitation spectroscopy corresponds to X-ray absorption experiments. Together with the DOS of CB, the DOS of VB (bonding states) it is necessary to understand the whole electronic structure of a material. This is important because the origin of stabilising a material is the energy states of bonding electrons. This information is included in the joint DOS of CB and VB (the imaginary part of $\varepsilon$, $\varepsilon_2$). However, it is not possible to deduce the information from $\varepsilon_2$, because of a lack of information of energy dispersion of bonding states.

Electronic transitions, downward arrows in Fig. 1, from VB to inner-shell core-hole states (processes c, c’) and from a shallow core-level to a deeper-lying core-level (process d) accompanied by X-ray emission. Thus, X-ray emissions caused by the process c and c’ include information of energy distribution of bonding electrons, DOS of VB. An energy resolution better than 1 eV is necessary for
obtaining fine structures of the DOS of VB, because the energy spread of VB is typically from 5 to 10 eV. Since the transitions can happen under a dipole-selection condition ($\Delta l = \pm 1$), the intensity profile of an emission spectrum reflects a partial DOS of VB with a specific symmetry. Furthermore, X-ray emission spectra of different atoms of a compound show us the component of different atoms of the valence DOS. Those emission energies range in the soft X-ray energy region from 15 to 6,000 eV [4]. Since there are many atomic resonances in this energy region, soft X-ray emission spectroscopy (SXES) provides not only the compositional information but also chemical states of elements, which are a sensitive tool for elemental and chemical identification and can be applied to many problems. On the other hand, X-ray emissions caused by the electronic transition between inner-shell levels does not contain the information of bonding electrons.

SXES is one candidate for valence electron spectroscopy based on electron microscopy. This method does not need an ultra-high-vacuum condition, because the absorption length of soft X-rays is larger than surface thickness of a few nm [5]. It can be combined with conventional electron microscopes (SEM and TEM). One drawback of this method is the low emission efficiency. For example, the yield of X-ray emission of a carbon 1s core-hole state is $1.4 \times 10^{-3}$ [6]. A longer acquisition time is necessary compared to those of EELS experiments. This is why SXES spectrometer was commercialised for EPMA and SEM which have higher beam currents compared to the TEM and can therefore achieve acceptable signal-to-noise ratios for this technique.

3. Optics of SXES spectrometers

The SXES instrument developed for conventional EPMA/SEM does not have a motorised mechanism to move the spectrometer to satisfy the Rowland circle optics of a traditional EPMA equipped with a wavelength-dispersive X-ray spectrometer. Rather the SXES spectrometer adopts the flat-field grazing-incidence optics by using varied-line-spacing (VLS) gratings [7, 8]. Figure 2 shows a schematic figure of the optics of a spectrometer. This optics is rather compact, about 50 cm from the specimen to the detector. This compact size results in a narrow energy dispersion on the spectrum plane. Thus, a small pixel sized detector is crucial for this optics to obtain a reasonable energy resolution, typically 13 - 15 µm pixels are used. As the VLS grating forms a spectrum in a certain energy range on a flat plane, a parallel detection by using a CCD detector is employed. The measured energy resolution is typically 0.2 eV or better for Al-L Fermi edge. The grating works with a fixed grazing incidence angle, which ranges from 1.5 to 4 degrees depending on the design of the acceptance energy range of the grating. This small grazing incidence angle improves the reflection efficiency of the grating, but results in a small solid-angle for the spectrometer. To improve detection efficiency, X-ray correction mirrors have been designed and placed between the specimen position and the VLS grating. These mirrors increase the detection solid angle of the SXES instrument by a factor of 2 - 3.

![Figure 2. Schematic optics of VLS grating used.](image-url)
accommodates two VLS gratings, which limits the detection energy range compared with the original configuration. Figure 3 shows a photo of the original spectrometer with four VLS gratings attached to a conventional SEM. A fine-pitch micro-channel plate (MCP) optically coupled with a CMOS camera is used as a detector. An aluminium L-emission spectrum obtained by the MCP in photon counting mode is also shown in Fig. 3. The spectrum shows a clear separation of L3- and L2-edges. The energy width corresponds to the intensity increase from 25% to 75% of L3-edge is 90 meV. This means that the energy resolution of this spectrum is evaluated as 75 meV by taking into the thermal broadening of Fermi distribution function at room temperature.

4. SXES spectra reflecting bonding stages and its imaging

Figure 4 shows B K-emission spectra of CaB₆ and CeB₆. Those are composed of a network of B₆ octagonal clusters accommodating a metal atom at the body-centre position of the unit cell, as shown in an inset figure. A B K-emission spectrum of β-rhombohedral boron (β-r-B), which is classified to a B₁₂-cluster material, is also shown for comparison. Peak intensity at around 185 eV in each spectrum is due to intra-cluster bonding state. The tail intensity in the lower energy side is due to inter-cluster bonding states. In CaB₆, the Ca atom can transfer two valence electrons to the B₆-cluster network. Thus, VB of B₆-cluster network is fully occupied and becomes a semiconductor. The, Ce atom in CeB₆ can transfer 3 or 4 electrons to B₆-cluster network. Thus, excess electrons go into CB making it metallic B₆-material. This can be seen in the intensity profile of CeB₆. On the higher energy side of the main peak, there is an additional peak compared with that of CaB₆. This additional peak is due to electrons occupying the CB. A small onset in the right hand side end of the additional peak could correspond to the Fermi energy position of the material. In addition, the main peak position of CeB₆ is slightly shifted to the lower energy side compared with that of CaB₆. As B K-emission is due to transitions form VB to B₁s core-level, this shift is most likely a chemical shift of B₁s core-level due to a larger amount of charge transfer of Ce atom compared to the Ca atom.

CaB₆ is a n-type semiconductor. However in this case a thermo-electric device using B₆-cluster network materials [12], it is required a p-type semiconductor. Sodium was added as the Na-atom has only one valence electron, making Na-substitution to Ca-site of CaB₆ (Na-doped CaB₆) produce hole doping to B₆-cluster network, leading to the material transforming to a p-type semiconductor [13]. EDS analysis showed the Na content of the material was a few percent. However, the material may be not a uniform from a production process point of view. A piece of Na-doped CaB₆ bulk specimen was analysed by a EPMA-SXES instrument. Figure 5 shows region-of-interest intensity maps of a) Ca-Lℓ,η intensity (150 - 154 eV), b) B-K intensity (170 - 188 eV), and c) the top part of the B-K intensity (187 - 188 eV). Ca-Lℓ,η emission map shows a low intensity in the central area, due to lower Ca content in this region. B-K emission map shows little intensity change for the corresponding region.
Figure 4. B K-emission spectra of CaB$_6$, CeB$_6$ and β-rhombohedral boron (β-r-B). The spectrum of CeB$_6$ shows an additional intensity with Fermi edge in right hand side and a peak shift, chemical shift, due to a larger amount of charge transfer of Ce atom than that of Ca.

An intensity anomaly in the upper left of the image is due to a surface contamination. The composition and chemical bonding state of the central area may be different form the surrounding area. A narrow region-of-interest map for B-K (187 - 188 eV) peak, Fig. 5c, shows an apparent intensity increase for the central area. The B-K spectra from the bright region (A) and duller region (B) are shown in Fig. 5c, bottom left. The spectra show a small difference in in their distributions, suggesting some difference of bonding state of B$_6$-cluster network due to a difference in composition. The peak (arrow) position from region A shows a shift to higher energy of about 0.7 eV compared to that from region B. This shift of the whole spectrum could be due to a chemical shift originated from a larger binding energy of B1s-level of the area. The shift can be explained by a decrease of valence charge of B atoms of point A. It can be understood if the expected Na-substitution was a smaller leading to a smaller charge transfer and/or an impurity of oxygen, which removed two electrons from the B$_6$-network. Unfortunately, the Na K-peak is not in the energy range of the JS200N grating used (it is noted that the latest commercial system can detect the Na K-emission signal). The impurity oxygen atom cannot be eliminated because a small intensity at 175 eV in the spectrum from region A can be assigned to the 3rd order intensity of O-K peak. A high energy resolution SXES map can provide both an elemental map combined with a chemical bonding state map reflecting, in this case, a valence charge distribution. Chemical state mapping combined with elemental map by an EPMA/SEM-SXES system gives important information for phase identification of bulk specimens.

5. Information of L-emission of 3d transition metal elements
The bonding state and valence charge of 3d transition metal (3d-TM) elements is key for evaluating positive electrode materials used in Li-ion batteries, because a change of valence in 3d-TM elements is the origin of charge and discharge performance of the battery. Information on valence electrons of 3d-TM elements is included in L-emissions of these elements. There are four types of L-emissions of $\text{L}_\alpha$, $\text{L}_\beta$, $\text{L}_\gamma$ and $\text{L}_\eta$ as shown in Fig. 6 [14]. These are classified into two groups having close emission energies group I is $\text{L}_\alpha, \beta$ and group II is $\text{L}_\gamma, \eta$. The $\text{L}_\alpha,\beta$ emission is due to $3d_{z^2-r^2} \rightarrow 2p_{3/2,1/2}$ ($\text{L}_{2,3}$) electronic transition, its energy distribution contains an information of DOS of VB (bonding states). While the $\text{L}_\gamma,\eta$ emission energy is due to transitions from a shallow inner-shell of $\text{M}_{4,5}(3s_{1/2})$ to a deeper
Figure 5. a) Ca-Lℓ,η intensity (150 - 154 eV), b) B-K intensity (170 - 188 eV), c) the top part of the B-K intensity (187 - 188 eV), and B K-emission spectra of the areas A and B in c).

inner-shell of L_{2,3} and reflects the dielectric environment of the transition metal elements [15], which differentiates it from the Lα,β emission.

Figure 6. Schematic energy diagram of 3d transition metal elements and electronic transitions of four L-emissions [14].

Figure 7 shows raw L-emission spectra of simple metal materials of Sc (Z = 21, 3d^{1}4s^{2}), Ti (Z = 22, 3d^{2}4s^{2}), V (Z = 23, 3d^{3}4s^{2}), Cr (Z = 24, 3d^{4}4s^{1}), Mn (Z = 25, 3d^{5}4s^{2}), Fe (Z = 26, 3d^{6}4s^{2}), Co (Z = 27, 3d^{7}4s^{2}), Ni (Z = 28, 3d^{8}4s^{2}), Cu (Z = 29, 3d^{10}4s^{1}) and Zn (Z = 30, 3d^{10}4s^{2}) acquired by the SEM-SXES instrument shown in Fig. 3 at an accelerating voltage 5 kV [14]. Each spectrum intensity is normalised by the maximum intensity in each spectrum. A JS2000 grating, which covers the energy
range from 300 eV to 2,200 eV, was used. To enable a quantitative comparison of spectral intensities recorded by the MCP detector it was set to photon counting mode [14], which results in the integrated intensity of an emission peak corresponding to a number of emitted X-ray photons or related electronic transitions. It can be seen that the L-emission energy increases with an increase of Z, which is caused by an increase of the binding energy of $L_{2,3}$ level according to Z. The intensity ratio of $L_{\alpha,\beta}/L_{\ell,\eta}$ increases according to an increase of $N_{3d}$. This trend of the $L_{\alpha,\beta}/L_{\ell,\eta}$ ratio is expected as the electron number contributed for $L_{\ell,\eta}$ emission is a constant of two 3s electrons whereas that for $L_{\alpha,\beta}$ emission, the number of 3d electrons ($N_{3d}$), increases with Z. Thus, the intensity ratio of $L_{\alpha,\beta}/L_{\ell,\eta}$ can be an indicator for evaluating $N_{3d}$. Integrated intensities of $L_{\alpha,\beta}$ and $L_{\ell,\eta}$ are shown in Fig. 7. The intensity ratio of $L_{\alpha,\beta}/L_{\ell,\eta}$ increases according to $N_{3d}$, but is not linear. This is due to the two transition of $3d_{5/2,3/2} \rightarrow L_{2,3}$ and $M_{1}(3s_{1/2}) \rightarrow L_{2,3}$ competing with the L-emission process. The transition probability of $3d_{5/2,3/2} \rightarrow L_{2,3}$ should change according to a change of $N_{3d}$. The intensity of $L_{\alpha,\beta}$ compared with the whole L-emission intensity of $L_{\alpha,\beta}+L_{\ell,\eta}$, should reflect not only the number of 3d electrons but also a change of transition probability due to a change of $N_{3d}$. This is shown in Fig. 8 were the variation of $L_{\alpha,\beta}/(L_{\alpha,\beta}+L_{\ell,\eta})$ follows to $N_{3d}$, and is almost linear from Sc to Ni, except for Cr. The deviation of the Cr value from the expected linear trend line may reflect its characteristic electron configuration in 3d orbitals. The linear tendency of $L_{\alpha,\beta}/(L_{\alpha,\beta}+L_{\ell,\eta})$ was fitted by a linear equation and this was applied to some oxides. In case of 3d metal oxides, the results using the equation led to an over estimate in the number of 3d electrons. This may be due to the charge transfer from ligand oxygen atoms to 3d transition metal elements resulting in a core-hole effect in the intermediate state as reported by Grebennikov et al. [16].

Figure 7. L-emission spectra of Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu and Zn. Each spectrum intensity is normalised by its maximum intensity in each spectrum [14].

6. Improvements of SXES instrument

6.1. Improvement of detection efficiency
As mentioned in section 3, the grazing incidence optics intrinsically have a small solid angle for X-ray detection, even though the grazing incidence improves the reflectance of the grating and the optics produce parallel detection within a certain energy range through the use of a flat detector. Further improvement of detection efficiency have been investigated and new optics combined with
Figure 8. Experimentally obtained \( \frac{L\alpha,\beta}{(L\alpha,\beta + L\ell,\eta)} \) values for 3d transition metal materials.

an enhancement of diffraction efficiency of VLS grating by a coating was designed, manufactured and tested [17, 18]. One target was boron, which is important to detect with ppm sensitivity in steel compounds where it is used as a key element to improve structural and mechanical properties.

A conventional JS200N, nickel (Ni) coated VLS grating, used in a commercial SXES instrument has a grazing incidence angle of 3°. In the new optics, this angle was changed to 5.8° keeping the positions of a specimen and a detector unchanged. This improves the solid angle by a factor of two. In addition, the grating surface of Ni layer is coated by La and then carbon (JS200NLC) to improve the reflectivity. The carbon layer was added to minimise oxidation of the La layer. This coating was expected to perform with up to two times better diffraction efficiency than without coating for B K-emission based on a theoretical calculation. In total, ~4 times improvement for B-K intensity was expected compared to that of JS200N grating. A new grating was tested at synchrotron facility and performed about 5 times better [18]. The same grating was tested in a SEM-SXES instrument (Fig. 3), which was modified to accommodate the new optics. Figure 9 the result for B K-emission the observed improvement in spectral intensity was 3.4 times. This is smaller than five measured at synchrotron and is due to poorly aligned X-ray correction mirrors placed between the specimen and the VLS grating. When compared with the new grating, which has only a Ni coat, the enhancement was 2.5 times. This means that about five times enhancement is possible for this Ni/La/C grating when the X-ray collecting mirrors work as that for JS200N. Since La is an active material, a stable compound of LaF₃ was coated on a new grating and tested. For this grating, the diffraction efficiency for B-K was 2.1 times compared with that of the Ni only coated surface. Thus, an improved detection efficiency of about 4 times is produced using this configuration.

6.2. High energy-resolution spectrometer for EPMA
Improvement of the energy resolution is also important. As mentioned in section 3, the energy resolution of the commercial SXES spectrometer is limited by the pixel size of the CCD detector. There are two techniques we have investigated to improve the energy resolution. One is to use a fine pitched new detector. Secondly to construct a spectrometer with a larger energy dispersion. A larger-dispersion spectrometer was originally designed and constructed for TEM [19]. Figure 10 shows the optics of this spectrometer. The distance from the VLS grating to the detector is about twice that of a usual spectrometer. This results in a two times larger energy-dispersion being produced by these optics. However, a spectrometer with a long specimen to detector distance has a smaller solid-angle for X-ray detection and this results in it being difficult to obtain good signal-to-noise ratios when used on a TEM.
Integrating this larger spectrometer onto EPMA is a reasonable way to improve in the energy resolution with a better signal to noise ratio. Figure 11a shows a photo of the newly constructed SXES spectrometer with the optics of Fig. 10 attached to an EPMA. The EPMA is also equipped with a commercial SXES spectrometer. Two VLS gratings are accommodated in the new SXES instrument and cover the whole energy range of first order L-emissions for the 3d transition metal elements. In this case, the detector is a multichannel plate optically coupled to a CCD camera. The energy resolution at the Fermi energy for B K-peak measured on LaB₆ was 0.3 eV (E/ΔE ≒ 630) as shown in Fig. 11b. A further improvement can be expected when a finer pixel detection system is utilised. The fine pitched MCP detector already used in SEM-SXES of Fig. 3, resulted in an energy resolution more than three times better than the commercial spectrometer. This performance will be useful for investigating chemical states of 3d transition metal elements together with imaging.

6.3. Energy determination for improving energy calibration
As K-emissions of light elements of B, C, N are due to electronic transitions of bonding electrons to K-shell core-hole state, those intensity distributions reflect the chemical bonding state of the material examined. This means that the peak energy position depends on the chemical bonding state of the atom in the material. It is difficult to perform an energy calibration on the SXES since there are not a set of suitable metals with known peak positions. Thus, we normally use the sharp peak structure of K-emission from amorphous graphite, which has a peak structure due to sp²-σ bonding state; however, an alternative calibration can be obtained by using the Al L-Fermi edge and higher-order reflections from Sc. The second and third order sp²-σ peak energies were consistently explained by the first order energy of 277.0 eV. The peak energy from B K-peak measured on crystalline β-rhombohedral boron was measured to be 185.3 eV. This value is 2 eV higher than the usually reported value of 183.3 eV for B-Kα. This value is close to the peak energy of B K measured on hexagonal BN.
7. Summary
Following the developments of SXES spectrometers for TEM, the SXES spectrometer was commercialised as an attachment for EPMA and SEM. This system has a much better energy resolution owing to a high quality VLS gratings combined with a CCD detector and a high detection efficiency owing to a parallel detection. This has enabled compositional analysis and chemical state analysis to be performed in parallel together in either a point analysis mode or an imaging mode. With higher detection efficiencies, new optics and improved grating coatings specifically tuned for a target energy range, we have shown up to five times improvement is possible for B K-emission. A higher energy resolution targeting a chemical state of 3d transition metal elements has just constructed and evaluated.

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