Characterization of Mn oxides using “flank” method in SEM-SXES system

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A soft X-ray emission spectrometer (SXES) is a recently developed spectrometer with high energy resolution and high sensitivity that can be installed in SEM and EPMA (Electron Probe Micro Analyzer) [1]. FE-SEM equipped with SXES enables analysis of the chemical state of micro- or even nano-textures. This paper presents analysis of valence state in Mn oxides using the SEM-SXES system. Mn-containing oxides are widely used in battery cathode materials and perovskite-type magnetic materials. The changes in the valence of Mn affect their physical properties and performance. Therefore, characterization of Mn valence state in Mn-containing oxides is very important. The SXES examination was performed by using a Schottky type FE-SEM (JEOL JSM-IT800 (SHL)) equipped with a SXES (JEOL SS-9404SXER). The energy range of this spectrometer with a JS2000 diffraction grating is from 350 to 2300 eV, and the energy resolution is defined to be 5.0 eV by the FWHM of Fe-Lα line. MnO, Mn2O3 and MnO2 purchased from Hori Mineralogy were used for samples. Figure 1 shows the Mn-L emission spectra of MnO, Mn2O3 and MnO2 collected by SXES at accelerating voltages of 2, 5 and 10 kV and self-absorption spectra calculated from the SXES spectra. The peak position of the Mn-Lα line shifts to the lower energy with increasing accelerating voltage and the intensity ratios of Mn Lβ/Lα do not exhibit any tendency. This indicates that the conventional peak-top intensity ratio and peak-area intensity ratio methods cannot be applied. This is due to self-absorption effect of characteristic X-rays. Characteristic X-rays generated by electron beam irradiation are affected by self-absorption in which energy is absorbed by the sample itself before the X-rays escape from the sample surface. Generally, the self-absorption effect becomes more prominent with increasing accelerating voltage. Therefore, the self-absorption spectra can be expressed by dividing the SXES spectrum at a low accelerating voltage by the one at a high accelerating voltage (Fig. 1) [2]. The energy position of the strongest self-absorption is constant regardless of the accelerating voltage (Fig. 1), and such phenomenon can be also observed in the case of Fe-L emission [2]. Hofér et al. has developed a method called the “flank” method which takes advantage of the difference in chemical bonding and the self-absorption effect due to the difference in the Fe valence [2]. This method follows the steps below: 1) Measure the spectra of the end-member of the material and calculate the difference spectrum from them. 2) Calculate the intensity ratio of Lβ and Lα at the flank positions which are determined by the maximum or minimum energy position in the Lα and Lβ regions of the difference spectrum. 3) Plot the obtained Lβ/Lα intensity ratio related to the valence obtaining a calibration curve. They reported that the “flank” method has a higher sensitivity to Fe valence than the peak-top intensity ratio and peak-area intensity ratio methods in Fe oxides and garnet system [2, 3]. In this study, we clarified whether this method can be applied to the analysis of Mn valence change. Figure 2a shows the SXES spectra of MnO, Mn2O3 and MnO2 taken at an accelerating voltage of 10 kV and the difference spectra with respect to MnO2. The flank positions in Lα and Lβ regions are respectively determined to be 639 and 647 eV by the difference spectra. The intensity ratio of Mn Lβ/Lα are calculated at the flank positions. The intensity ratios obtained by the “flank” method and two conventional methods are plotted as a function of Mn valence in Fig. 2b. The “flank” method has a higher resolution and its calibration curve tends to be more linear compared to the two conventional methods. This trend is observed at an accelerating voltage of 5 kV. The results in this study indicate that the “flank” method is applicable to Mn oxides as well as Fe oxides. In the “flank” method, a calibration curve should be obtained for each system because the self-absorption effect changes when the system becomes multi-component. Since Mn-containing oxides, which are widely used for industrial applications such as a cathode of LIBs, are multi-component, we would like to establish this method and apply it to such materials in the future.
Figure 1. SXES (upper graphs) and self-absorption spectra (lower graphs) of (a) MnO₂, (b) Mn₂O₃ and (c) MnO.

Figure 2. (a) SXES spectra (upper graph) of MnO, Mn₂O₃ and MnO₂, and difference spectra (lower graph) with respect to MnO₂ at acceleration voltage of 10 kV, (b) the intensity ratio plotted as a function of Mn valence by each method.

References