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NEW DEVELOPMENTS IN DETECTING LOW-ENERGY X-RAYS USING SXES

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1. *ABSTRACT*

An X-ray emission spectrum obtained with the soft X-ray emission spectrometer (SXES) (Fig. 1) is a low energy emission spectrum associated with the transition from the valence band to the inner shell, and includes the information on chemical bonding states. Therefore, the SXES can be said to be an advantageous instrument for measuring the chemical bonding state of the specimen [1]. On the other hand, there are high demands for quantitatively analysing small regions at depths from several tens of nm to hundreds of nm in bulk samples using an electron probe microanalyser (EPMA) or scanning electron microscope with an energy- dispersive X-ray spectrometer system (SEM-EDS). The SXES is a powerful instrument that can measure soft X-ray spectra of materials with high energy resolution at lower accelerating voltages (≤ 5 kV). The L-emission of fourth-period transition metals below 1 keV is due to the transition between the valence band and the inner shell, and this spectrum shape is very different depending on the chemical bonding states of the metal or oxide. If a single element specimen is analysed as a standard sample with existing ZAF or $\varphi(\rho Z)$ quantitative calculation, it seems that sufficient quantitative analysis accuracy cannot be obtained. In this paper, we will report an attempt to quantitively analyse transition metal oxides using the SXES.

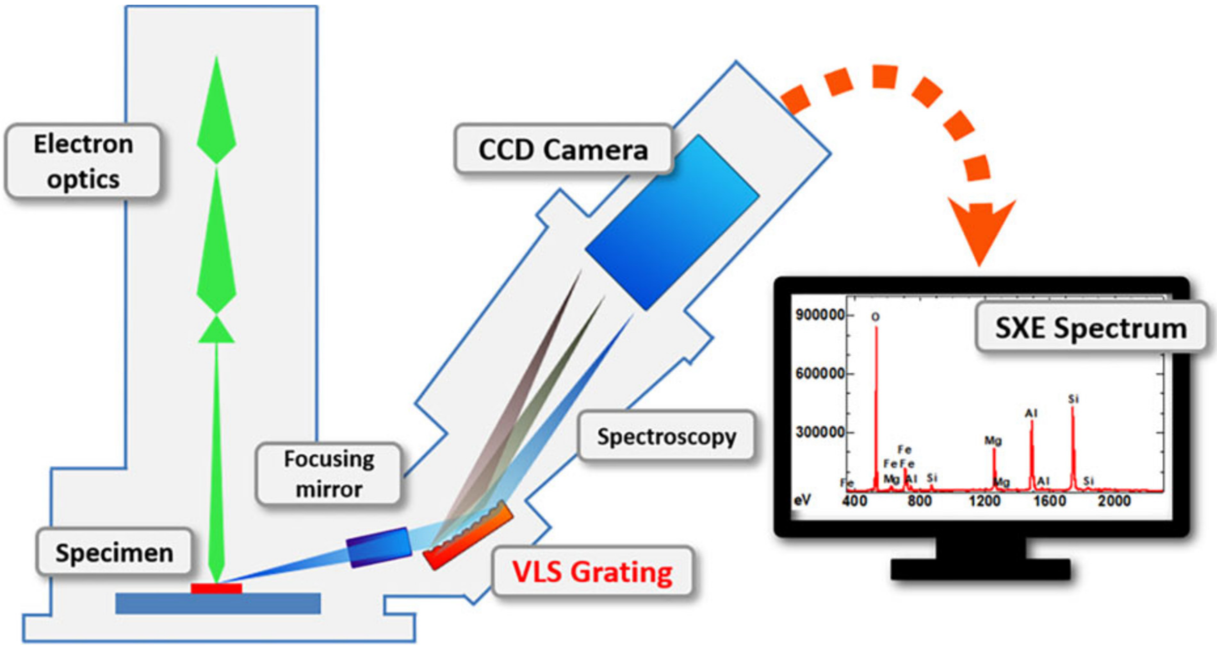

Figure 1. Schematic view of SXES system.

In materials containing transition metals, some signals such as the Lλ emission line, are due to the transitions between the inner shells, and may be quantitatively analysed. Gopon *et al.* [2] reported good results using Fe-Lλ emission spectrum in Fe silicide with an EPMA. Transition metals can have different valence numbers in each oxide or mineral. In the Lα (Lα: L_3-$M_{4,5}$)

emission, the spectral shape reflects the so-called chemical bonding state (see Fig. 2), and chemical state analysis research is progressing. Also, this peak is very close to the L3 absorption edge. According to Höfer *et al.* [3], the L3 absorption edge of iron oxides shifts differently depending on the oxide, and it was claimed that the Fe-Lα peak shape changes due to this effect. Therefore, it seems that the accuracy of quantitative analysis using Fe-Lα emission cannot be expected. Fe-Lλ (Lλ: L_3-M_1 615.3 eV) emission is based on the core level transition, and this peak is farther from the L3 absorption edge (710 eV) than Fe-Lα (704.8 eV), so physical parameters such as mass absorption coefficient (MAC) can be obtained with high accuracy. In this study, we extracted MACs of the Lλ emission from ^{16}S (148.7 eV) to ^{44}Ru (2,252.8 eV) from the NIST FFAST table [4], and performed quantitative calculations using the Lλ emission spectrum. In order to quantify multiple Fe oxides with different compositions, oxygen is also directly analysed using the area intensity of O-K emission (525 eV) spectrum instead of the stoichiometry ratio. Al_2O_3 was used as the standard sample for O. As for Fe, metallic Fe and Fe_2O_3 were evaluated. An accelerating voltage of 5 kV, a probe current of 50 nA, and an exposure time is 1 min x 5 times were used.

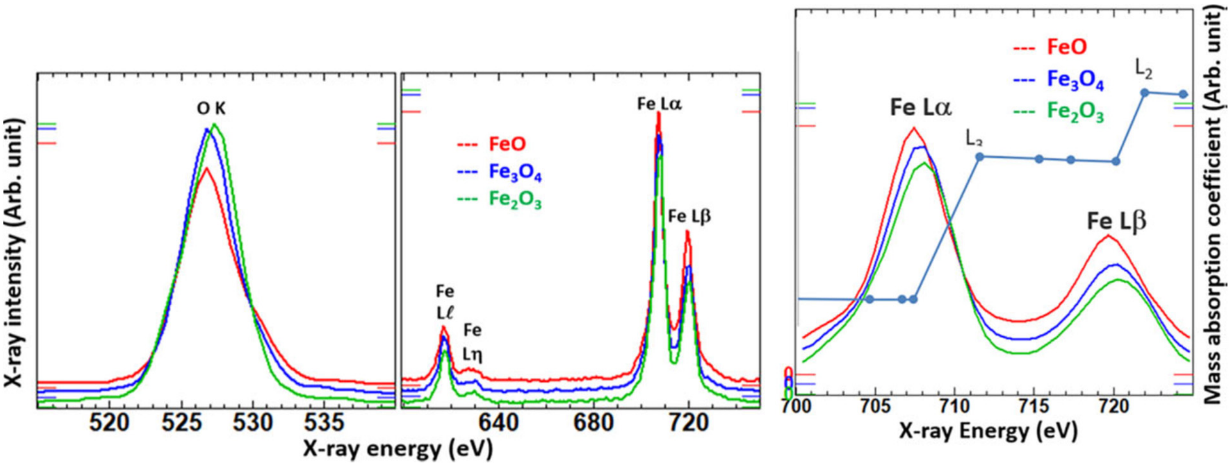

Figure 2. SXE spectra of iron oxide.

Table 1 shows the quantitative analysis results for a) metallic Fe as the iron standard, and b) Fe_2O_3 as the standard sample for FeO and Fe_3O_4 quantification. In the case of metallic Fe as the standard, Fe concentration is insufficient regardless of which line is used. The Fe concentration is slightly higher in the case of Fe-Lλ emission, but the analytical results are not enough. When the Fe standard is Fe_2O_3, Fe concentration in the FeO sample is slightly lower in the case of Fe-Lα, but in the case of Fe-Lλ, this result is close to the stoichiometric ratio of FeO. As for Fe_3O_4, both standard Fe-Lα and Fe-Lλ emission is close to the stoichiometric ratio, and the results are sufficient for quantitative analysis at a lower accelerating voltage, which is a severe analytical condition. As shown in Fig. 2, the O-K emission spectrum shapes of each iron oxides are different. Also, these spectra shape are different from that of Al_2O_3 used as a standard sample. However, fairly good results were obtained as a direct quantitative evaluation of oxygen. This is because the O-K absorption edge (532 eV) is slightly away from the O-K peak position on the high energy side, which did not cause a large error when calculating the area intensity.

Table 1. Quantitative analysis result of iron oxide using SXE spectra. a) Standard Fe: metallic Fe, O: Al_2O_3. b) Standard Fe: Fe_2O_3, O: Al_2O_3.

a)

Sample	Signal	Std.	mass %	[ZA]	k-ratio
FeO	Fe Lα	metal Fe	59.3	1.079	54.97
	O K	Al_2O_3	22.7	0.910	24.96
		total	82.0		

Sample	Signal	Std.	mass %	[ZA]	k-ratio
FeO	Fe Lℓ	metal Fe	64.5	1.066	60.49
	O K	Al_2O_3	22.6	0.905	24.96
		total	87.1		

Sample	Signal	Std.	mass %	[ZA]	k-ratio
Fe_3O_4	Fe Lα	metal Fe	59.1	1.087	54.38
	O K	Al_2O_3	27.0	0.920	29.34
		total	86.1		

Sample	Signal	Std.	mass %	[ZA]	k-ratio
Fe_3O_4	Fe Lℓ	metal Fe	60.5	1.076	56.22
	O K	Al_2O_3	27.0	0.919	29.34
		total	87.5		

b)

Sample	Signal	Std.	mass %	[ZA]	k-ratio
FeO	Fe Lα	Fe_2O_3	71.8	1.004	71.55
	O K	Al_2O_3	22.4	0.899	24.96
		total	94.2		

Sample	Signal	Std.	mass %	[ZA]	k-ratio
FeO	Fe Lℓ	Fe_2O_3	78.2	1.001	78.08
	O K	Al_2O_3	22.3	0.894	24.96
		total	100.5		

Sample	Signal	Std.	mass %	[ZA]	k-ratio
Fe_3O_4	Fe Lα	Fe_2O_3	71.6	1.011	70.78
	O K	Al_2O_3	26.7	0.908	29.34
		total	98.3		

Sample	Signal	Std.	mass %	[ZA]	k-ratio
Fe_3O_4	Fe Lℓ	Fe_2O_3	73.3	1.010	72.56
	O K	Al_2O_3	26.6	0.907	29.34
		total	99.9		

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