X-ray emission spectroscopy optimization for chemical speciation in laboratory

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A B S T R A C T

K X-ray emission spectra emitted from carbon, aluminum, silicon, phosphorus, titanium, chromium, and manganese compounds were measured, using a compact lab-scale flat crystal X-ray fluorescence spectrometer. The sensitivity of K X-ray transitions line-shape, relative to the atom's chemical speciation, is considered. Spectrometer's optimization concerning high energy resolution takes place for each measured fluorescence transition. The detected changes on the measured X-ray line-shapes allow extracting the chemical speciation of the emitting atom. In-lab high-resolution X-ray emission spectroscopy is shown to be a highly versatile technique for materials chemical characterization.

1. Introduction

High-resolution X-ray emission spectroscopy (XES) provides information on materials chemical speciation, based on the measured transition line-shape [1–3]. It is complementary to the chemical information obtained with more demanding X-ray spectroscopic techniques, like X-ray absorption near edge structure (XANES) [1, 4, 5] or X-ray photoelectron spectroscopy (XPS) [6]. X-ray emission spectroscopy, as a spectroscopic method involving two atomic states, is inferior to XANES or XPS, concerning inherent energy resolution. But, XES offers excellent features as there is no requirement for special specimen treatment, the target could be either bulk or film, in solid, liquid or gas state, could be measured in vacuum or atmosphere, while it provides non-destructively in-depth information relative to other analytical techniques. Moreover, a significant feature of XES is that the white X-ray spectrum emitted by conventional X-ray tubes is, in most cases, directly suitable for ionization compared with techniques requiring monochromatic ionization beam.

The emitted X-ray emission spectrum conveys information related to the atom's chemical speciation, as the cluster's charge distribution influences the electrons involved in the relaxation process. The information is encoded as variations of the line width, peak energy, energy splitting, or intensity ratios. Especially designed wavelength dispersive crystal spectrometers offer ultimate energy resolution, which allows the measurement of the transition's natural line-shape. High-resolution specifications require intense primary beams (e.g. synchrotron radiation) and specifically designed geometries, allowing spectra acquisition almost free from geometrical aberrations. Such spectrometers are realized as single or double flat crystal arrangements, as well as in focussing geometry [7–12]. It is of primary analytical importance to extract comparable information with conventional lab-scale instruments, allowing easy access for chemical characterization, on a daily basis [13–15].

In the present work, the Kα and Kβ fluorescence spectra emitted from carbon, aluminum, silicon, phosphorus, titanium, chromium, and manganese atoms measured in a variety of chemical environments. A commercial flat crystal spectrometer, designed for qualitatively/quantitatively X-ray fluorescence (XRF) elemental analysis, was used for the measurements. The energy range of the measured transitions extends from 0.27 up to 7.5 keV. Enhanced energy resolution, obtained by adjusting the spectrometer's beam optics and crystal analyzer for each particular transition, fulfils the requirements to ensure chemical speciation information.

The K X-ray spectrum originates from radiative electron transitions either from a core or from a valence state to the K hole. The main K transitions are the electric dipole $K\alpha_{1,2}$ and the $K\beta_{1,3}$ transitions, which correspond to the 2p and 3p shell electron transition to the 1 s shell core hole, respectively. The energies of Kα and Kβ transitions are given in Fig. 1. These diagram transitions are accompanied by satellite transitions, which may overlap or may appear as discrete structures on the low and high energy side [16]. The satellite transitions originate from the presence of spectator holes, incomplete occupied shells and chemical bonding, and they are influenced by the atom's chemical environment. As example, the $K\beta'$ satellite structure of elements with atomic number Z in the range $12 \leq Z \leq 17$ is shifted in energy, relative to the $K\beta_{1,3}$, as function of the atomic number of the ligand atoms
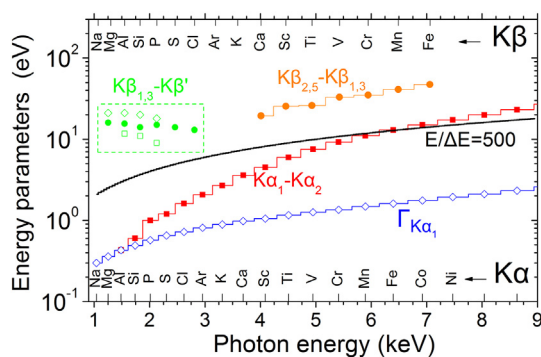
Fig. 1. Energy parameters associated with the K X-ray transition energies. The energies of the $K\alpha_{1,2}$ and $K\beta_{1,3}$ transitions are marked on the bottom and top horizontal axis, respectively. $\Gamma_{K\alpha_1}$ is the natural width of the $K\alpha_1$ transition (in blue) [17]. $K\alpha_1$ -$K\alpha_2$ is the fine structure splitting of the $K\alpha$ transition (in red) [18]. $K\beta_{1,3}$-$K\beta'$ is the energy difference value between the corresponding transitions for nitrides (green open squares), oxides(green solid circles) and fluorides (green open rhombus) for the elements $12 \le Z \le 17$ [19]. $K\beta_{2,5}$-$K\beta_{1,3}$ denotes the smaller energy difference value between the corresponding transitions of the elements $20 \le Z \le 26$ according to [20] (in orange). The locus of points with energy resolution equal to 500 offers a hint about the order of the required resolution to resolve energy structures (black continuous line). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

(Fig. 1). Measurement of the energy difference $K\beta_{1,3}$-$K\beta'$ allows the determination of the atomic number of the ligand atom(s). The $K\beta_{2,5}$ satellite structure is well separated from the $K\beta_{1,3}$ transition for elements $20 \le Z \le 26$ (Fig. 1). Experimental determination of their intensity ratio allows extracting the valence of the emitting atom. A more detailed description of the origin and interpretation of the satellite transitions are given in Paragraph 3.2, in connection with each specific element.

2. Experimental set-up

The measurements were performed using the flat crystal X-ray spectrometer S4-Explorer from Bruker. The spectrometer's X-ray tube is equipped with a rhodium anode operated at maximum high voltage of 50 kV and maximum power of 1 kW. A mask between the target and the crystal-analyzer determines the target size (Fig. 2). Five variable masks define different circular effective target areas with diameters 5, 8, 18, 28 or 34 mm. The angular spread of the fluorescence X-rays, impinging on the crystal-analyzer, is adjusted by a Soller collimator. Three exchangeable Soller collimators, with a nominal opening angle of 0.46°, 0.23° and 0.12°, respectively, were installed on a collimator changer. The crystal-analyzer diffracts the photons according to the Bragg law. The crystal planes distance of the crystal analyzers available in the present study is given in Table 1. A comprehensive list of existing analyzer crystals may be found in [23]. All five crystals were mounted on a crystal changer, which is rotated remotely (the changer accepts up to eight monocrystals). The diffracted X-rays are detected in scattering angle corresponding to twice the Bragg angle by a gas flow proportional counter equipped with a thin Mylar window. A Soller collimator in front of the detector suppresses directly scattered radiation. Crystal-analyzer and detector are moving sequential in θ-2θ mode. The set-up allows measurements of scattering angles 2θ in the range 14.0° and 149.0°, with minimum angular step 0.001°. The spectrometer is pumped to a pressure better than 0.2 mbar, allowing measurements of low energy photons.

3. Results and discussion

The application of the X-ray fluorescence spectroscopy for the
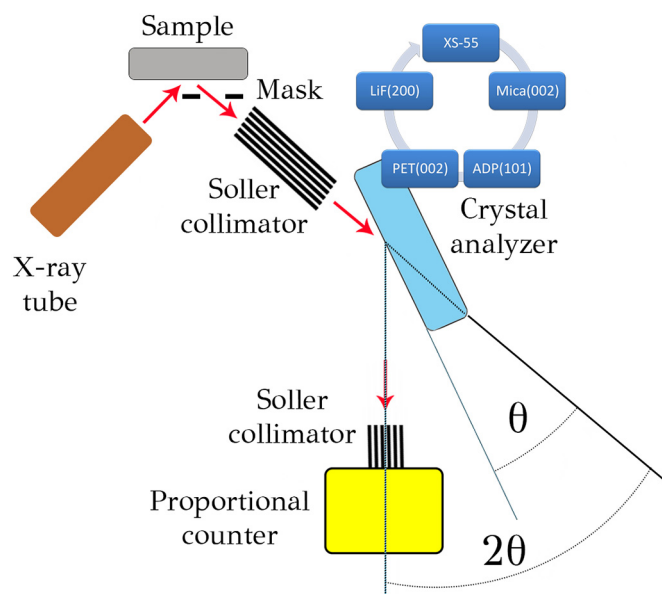

Fig. 2. Flat crystal spectrometer set-up. The X-ray tube is used for the sample ionization. The sample's effective size is determined by the size of the mask. The fluorescence spectrum, emitted from the sample, passes through the Soller collimator, defining a narrow angular interval, and impinges on the crystal-analyzer. Photons with wave lengths fulfilling the Bragg condition (Eq. (2)) are diffracted by the scattering angle 2θ. The proportional counter placed in the trajectory of the scattered beam records the photon intensity. The fluorescence spectrum is recorded by rotating the crystal-analyzer and the detector sequentially in θ-2θ mode. A crystal changer allows remote change of the crystal analyzer.

Table 1
Crystal analyzers used with corresponding crystal planes distance [23]. Measured transitions and corresponding transition energies. The order of reflection and the corresponding Bragg angle are given in the two last columns.

Crystal	2d (Å)	Transition	Energy (keV)	n	θ_B
XS-55	55.0	C Kα	0.274	1	55.4°
Mica(002)	19.84	P Kβ	2.136	3	61.2°
ADP(101)	10.640	Ti Kβ	4.931	4	71.0°
		Cr Kβ	5.946	4	51.6°
PET(002)	8.752	Al Kα	1.487	1	72.3°
		Si Kβ	1.836	1	50.6°
		Ti Kα	4.510	3	70.3°
		Cr Kβ	5.946	4	72.5°
LiF(200)	4.027	Ti Kα	4.510	1	43.0°
		MnKβ	6.490	2	71.7°

qualitative and quantitative elemental analysis is performed using either wavelength dispersive (WD) crystal spectrometers or energy dispersive (ED) spectrometers. Crystal spectrometers in Bragg geometry offer superior energy resolution relative to energy dispersive devices at least for transition energies up to 10 keV, allowing the separation of close laying transitions, while the energy dispersive spectrometers allow significantly shorter measuring time. As an example, part of the fluorescence spectra from a glass sample, as they measured with the present WD spectrometer and the ED handheld spectrometer Tracer IV-SD (Bruker), are compared in Fig. 3. The WD spectrometer was equipped with a LiF(200) crystal-analyzer, while the ED was equipped with a silicon drift detector (SDD). The superiority of the crystal spectrometer concerning energy resolution is apparent. The WD spectrometer disentangles the close lying Ti K transitions from the Ba L transitions. Specifically, the energy difference between Ti Kα and Ba Lα is 43 eV, while the one between Ti Kβ and Ba Lβ is 103 eV [24]. Nevertheless, even using the crystal spectrometer the Ti $K\alpha_{1,2}$ fine structure is