

X-ray spectroscopy of lithium

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Lithium is a light metal which is nowadays very important for applications, in particular in the energy domain. Thus, characterization and quantification of lithium, that is to say determination of the chemical state, location and number of Li atoms in a sample, is of high interest. If x-ray spectroscopy of lithium could be implemented efficiently in scanning electron microscopes (SEM) or electron microprobe analyzers (EPMA), then one could expect to use the standard processes and quantification tools to study the electronic structure and determine the weight fraction of lithium in solid samples. Thus, SEM and EPMA could be used at all the stages of the production and use of lithium, from the characterization of geologic samples to battery devices.

Owing the atomic number of lithium equal to three, its electronic structure is very simple: two $1s$ core electrons and one valence electron with $n=2$ principal quantum number. In consequence the Li x-ray emission spectrum is also quite simple: it consists in the $K\alpha$ emission band corresponding to the $2p - 1s$ electron transition. Following the low binding energy of the Li $1s$ core level, the Li $K\alpha$ emission band lies in the ultra-soft x-ray or extreme ultraviolet spectral range, at photon energies around 50 eV (25 nm).

However, despite the development of new dispersive elements, optimized periodic multilayers and variable line spacing gratings, the spectroscopy of lithium is still, for both emission and detection reasons, a difficult to obtain on both SEM and EPMA.

- First, in the ultra-soft x-range there is no transparent materials. The strong attenuation of the radiation makes the analyzed thickness quite shallow, from a few tens of nanometers to a maximum of hundred of nanometers, so that few lithium atoms contribute to the emission. In addition, the Li $1s$ fluorescence yield is extremely low, leading to a quite low emitted intensity. Regarding the possible quantification, attenuation coefficients are not well known in this spectral range. Moreover, Li $K\alpha$ being an emission band the position of its maximum and its shape depend on the chemical state of the emitting lithium atom. So, standard process relying on the determination of the intensities from the height of the considered emission cannot be used.
- Second, from the experimental point of view, any window in the spectrometer will lead to a strong loss of photons. Owing to the long wavelength, crystals cannot be used to disperse the radiation. Thus, periodic multilayers or gratings must be used, both having limited reflectance. In both cases, the used spectrometers have small solid angles of collection, making necessary to use large incident electron currents, of the order of a few hundreds of nA, in the SEM and EPMA. This is not harmless, since these currents, focused in spots of micrometer size, can lead to the damaging of the sample or to the migration of the lithium atoms.

We shall review the different points mentioned above.

Quantitative electron probe microanalysis of lithium in different materials including battery compounds

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Electron probe microanalysis (EPMA) is a reliable and widely used technique to do non-destructive, accurate material characterisation for scientific and industrial applications. Nevertheless, despite of the great interest in lithium (Li) and the urgent need to do accurate non-destructive analysis at a micron scale, quantification of Li using EPMA has not been performed successfully yet. Recently developed periodic multilayers allow spectroscopy in the energy range around the characteristic Li K emission ~ 50 eV [1] but the detection and quantification of Li by a microprobe equipped with a bent crystal spectrometer and standard commercialised multilayers without diffraction gratings still is challenging.

The difficulties of Li detection are caused by different factors: the fluorescence yield of Li is extremely low, few characteristic photons are produced by the decays of the Li 1s core hole, favoring the emission of Auger electrons. Because of their low energy, the photons are strongly absorbed before even leaving the sample and its eventual coating. The signal therefore is principally coming from a thin surface layer that can be subject to contamination and that may be sensitive to electron bombardment. Further photon absorption by the microprobe components, especially by separation windows, will additionally decrease the measured intensity. As the Li K emission (2p – 1s transition) involves valence electrons, the shape of the Li emission band is highly dependent on the density of states (DOS) of the valence band and so highly dependent on the chemical state of the sample. Chemical shifts of some eV and strong peak shape alterations can occur and should be expected for EPMA of light elements [2], complicating quantitative analysis.

This work shows, to our knowledge for the first time, quantitative EPMA of Li in different materials including battery compounds and metal alloys with Li concentrations down to 2 %. This was made possible after the integration of a new detection system. Further work on the quantification procedure using real standards and correction programs suited for low voltage EPMA has also been accomplished. We show that EPMA is a powerful tool to do quantitative analysis of Li even if it is contained in heavy matrices with elements showing characteristic emission bands in the same spectral range as Li. This novel Li quantification method is more accessible than other techniques using synchrotron radiation and less expensive than detection using a SEM equipped with multilayer gratings.

References

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Detection of Li K Emission in Different Lithium Compounds

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Soft x-ray emission spectroscopy (XES) is a technique used to study the electronic structure of materials. It measures the energy spectrum of emitted x-rays from a sample. It is performed by irradiating the sample with ionizing particles (electrons in our case) and measuring the energy distribution of the x-rays that are subsequently emitted. The emitted x-rays are characteristic of the electronic states of the sample, thus, the presence of an element can be detected, and could be also used to perform quantitative analysis.

Reflection zone plates (RZP) can be used in XES as a wavelength-dispersive element [1]. They consist of a series of concentric zones, each with a slightly different thickness. When x-rays are incident on the zone plate, the different zones act as diffraction gratings, causing the x-rays to diffract and interfere with one another while focusing them at the same time. They have higher spectral resolution and cover wider energy ranges compared to other optical elements such as periodic multilayers. RZPs allow to reach energy resolutions as low as 0.49 eV at the Al L_{2,3} line (around 72 eV) [2]. With parallel detection of x-rays in contrast to conventional wavelength dispersive spectroscopy (WDS) spectrometers with a dispersive crystal (or multilayer) based on Rowland mounting they do not have a scanning mechanism.

In this work, we demonstrate the use of a Fresnel (RZP) implemented in an electron microprobe for the detection of Li K (around 50-55 eV) emission in different lithium compounds. Li K emission is a characteristic emission band produced when Li 1s levels are ionized inside the material. However, it can be challenging to detect this emission due to its low fluorescence yield, re-absorption effects, and the presence of other spectral lines in the same energy range. We report on our measurements of the Li K emission bands in several lithium compounds with an RZP spectrometer. Our results demonstrate this approach's potential for various applications in the field of x-ray spectroscopy.

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References

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