

A Multi-Technique Database for Spectrum Identification in Luminescence and X-Ray Maps

A. Torpy¹, S. McMahon², J. Anticev³, C. M. MacRae¹, N. C. Wilson¹ and M. I. Pownceby¹

¹ CSIRO Mineral Resources, Clayton, Victoria, Australia

² CSIRO IM&T, Black Mountain, ACT, Australia

³ CSIRO IM&T, Clayton, Victoria, Australia

Databases of measured lines or spectra are vital resources when interpreting spectroscopic measurements of unknown specimens. For some techniques, this database may be only a table of line positions and intensities, such as the KLM tables used in x-ray spectrometry. However, for techniques such as luminescence spectroscopy, the position, intensity and width of emission lines from an emitter may vary significantly between materials, depending on diverse factors such as the composition and crystallographic structure of the host matrix, trace concentrations and site occupancies of dopants and defects, and the experimental conditions of the measurements. The spectroscopic databases for such techniques are necessarily large and complex, requiring purpose-built software to allow convenient searching and presentation of results.

The authors had previously compiled a database of luminescence emission lines from published literature [1], which initially included ~1100 lines from 70 minerals and materials. This database was subsequently made freely available to search on-line [2], and was integrated with the off-line *OpticalFit* analysis software [3]. The database continues to grow, and now contains ~3750 luminescence emission lines and ~220 luminescence spectra, measured from ~400 materials, collected from ~270 references. Approximately half of the luminescence spectra currently in the database were collected in-house using a grating CCD spectrometer attached to an electron probe microanalyser (EPMA), and were measured from a range of synthetic standards and naturally occurring mineral specimens. The database has also recently expanded with the addition of published photoluminescence (PL) and cathodoluminescence (CL) spectra provided by M. Gaft [4], J. Götze [5], and C. Lenz [6], as well as PL images of minerals provided by J. O. Hamblen [7], and photographs of mineral specimens provided by J. Post and E. Vicenzi of the Smithsonian Institution [8], whose contributions are all most gratefully acknowledged. The database displays the published reference for all lines, spectra and images, along with DOI/publisher links, to ensure appropriate attribution of contributors, and to allow users to conveniently access the original publication for further details.

A recent upgrade of the CSIRO spectroscopy database added an interactive spectrum display that allows the comparison of multiple spectra, including measurements of different materials or from different references (Figure 1a), with the option to overlay labelled peak markers showing the positions, widths and relative heights of emission lines. Significantly, this upgrade also generalised the database structure and interface to support other experimental techniques, in addition to luminescence. The on-line database now includes measurements made by soft x-ray emission spectroscopy (SXES), which show

changes in x-ray peak energy, relative height, and line width due to chemical bonding and matrix effects. Users may compare SXES spectra from 72 elements in 144 spectra, measured from a range of metals, sulphides, oxides, silicates, phosphates, carbonates, and other available reference materials. When displaying SXES spectra, KLM line markers are shown to assist with peak identification, including those for higher-order Bragg reflections (Figure 1b).

This multi-technique spectrum database was also integrated in off-line analysis software packages (*OpticalFit* and *Chimage*) to assist the interpretation of measured spectra and hyperspectral maps. An example application of the off-line spectroscopy database in identifying mineral phases is provided in Figure 2b, which shows a clustered phase map of a combined WDS and hyperspectral EDS and CL map (CL shown in Figure 2a, methods described in [9]) that was measured from a specimen of sintered lunar mare regolith simulant (LMS-1, Exolith Lab). The phase identifications were performed automatically using a spectrum matching algorithm that compared the EDS and CL spectra of the map clusters with a database of spectra collected from previous studies of mineral specimens (e.g., [9]). Although several mineral species were weakly luminescent (Figure 2a) and were thus identified by EDS alone, the analysis of the CL spectra provided an independent confirmation of the phase identification of the many luminescent species (e.g., feldspars, quartz, rutile, etc.). The identity of the major phases and the modal abundances thereof were also in agreement with measurements made by quantitative powder x-ray diffraction (QPXRD). The spectral phase identification process successfully identified both nominally pure end-members phase such as zoisite, forsterite, enstatite and albite, as well as phases containing solid solutions with other related species, which were automatically identified by their appropriate group name (e.g., epidote, olivine, pyroxene, plagioclase, etc).

The only phase in the lunar mare regolith map that was not identified automatically by spectrum matching was a glass phase, as the spectrum database did not contain a measurement near this melt composition. This failure of identification highlights that the ability of spectrum matching methods to identify unknown spectra is constrained by the range of spectra in the database. Consequently, the off-line analysis software (e.g., *OpticalFit*) allows users to easily add spectra to their own off-line database for later comparison, including storing all experimental parameters, material compositions, publication details, and related images or other files. The off-line database software includes import/export tools to allow users to privately share databases (or subsets thereof) with other users, or submit measurements for public release in the on-line database. Submissions of luminescence or SXES spectra to the on-line database will be most gratefully received. It is hoped that such spectrum database and identification tools may be of use to the microanalysis community.

References

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