Advanced Materials Characterization with Full-Spectrum Phase Mapping

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Introduction

X-ray mapping in electron microscopes with energy dispersive spectrometry (EDS) builds on the basics of qualitative X-ray microanalysis by providing a visual representation of the elements present. Mapping routines have long identified elements within a sample and displayed the elemental distribution in an image map of the sample area [1]. Often, visual comparisons of different element maps, side-by-side or overlaid, show where combinations of elements occur. These combinations of elements together in a map give a deeper understanding of the chemical nature of the material. However, image map comparison is only a starting point and does not make use of subtle differences in the full spectrum of elements. Therefore, more sophisticated routines that directly evaluate the total spectrum chemistry from a map dataset have been designed and incorporated into advanced systems to create a stronger foundation for advanced materials characterization.

Traditional Mapping Approaches

The starting point for X-ray mapping is the division of a field of view into a matrix of pixels. Each pixel in a map represents the intensity of the X-ray signal from an element at that location in the sample. The map of a single element shows where that element is present and where it is absent, as well as intensity variations of the element in that field. Traditionally, elements of interest were selected prior to map acquisition, but more modern approaches allow the addition and removal of elements as part of post-processing routines because the full spectrum is available at each pixel [2]. Many different element maps can be produced from a single pixel-by-pixel scan of a region of the specimen. The maximum useful magnification of the X-ray map can be determined by setting the pixel size to the size of the X-ray emission region [3].

Element distributions. One of the clearest benefits of mapping is that it gives the analyst the ability to see what elements are present, where they are located in the sampling area, and how concentration variations occur between elements. This method is also useful for identifying unexpected elements present, or elements located in unexpected areas, such as in failure analysis [4]. For example, maps can show whether there is a contaminating substance present near a failure, whether elemental variation contributed to a fracture, or whether oxidation occurred in an area of interest. Maps are also useful for understanding the volume fractions of compounds and phases containing certain elements.

Element associations. A significant benefit of mapping is the ability to see how the elements in a sample occur in combination with each other. The example shown in Figure 1 shows an area of an automotive brake pad. Two of the many components are barium sulfate (barite) and iron sulfide (pyrite); element maps show the barium, sulfur, and iron contributions. A map overlay of all three elements shows where the sulfur occurs with barium and where it occurs with iron. It is also apparent that there are some areas where those elements are not in combination with any of the others. For example, if metallic iron were present that was not associated with sulfur, this would be apparent in a comparative overlay.

X-ray Map Overlay Displays

To help show the distribution of multiple elements in a map area, X-ray map image overlays are routinely available to characterize which element or element combinations are present in an area. Several basic approaches are described here.

Maximum intensity overlay. In this routine, the user selects the element maps of interest for comparison and then the software overlays these maps. The overlay creates one image of multiple elements, where only the element with the highest intensity at each pixel is displayed.

Blended primary color diagrams. Using this routine, the user selects three elements of interest for comparison and then assigns a primary color (red, blue, or green) to each element. The software creates one image with a display of either a primary color (if an element is the only one of the three in an area) or a blended color (if more than one of the selected elements is present). For example, if blue is assigned to Si and red is assigned to Al, pure Si areas will appear blue in the map whereas Si-Al areas will be magenta (a blend of blue and red). Figure 2 shows an example of this map type, using the same brake pad example.

Layered phase image correlation. With this routine, spectra from a map can be processed first to perform background removal and peak deconvolution before the processed maps are displayed. The software then automatically chooses the element maps to mix together to create an overlay from the processed images. As with any map, extraction of spectra from uniform regions within the images is useful for identification of phases.

Each of these routines is highly dependent upon the amount of signal represented in the individual elemental map images. It may take several minutes of collection time for an element map to have enough intensity at each pixel before it can provide usable information. The success of the element correlation is dependent on the amount of signal available in the pixels of the X-ray map.

Phase Mapping Approach

Phases in EDS are defined as areas in a sample that are chemically distinct and physically separate. Phases also have different crystal structures, but to determine such structures, a diffraction technique, such as electron backscatter diffraction (EBSD), is required. Thus, for the purposes of this article, a phase means a certain combination of elements.
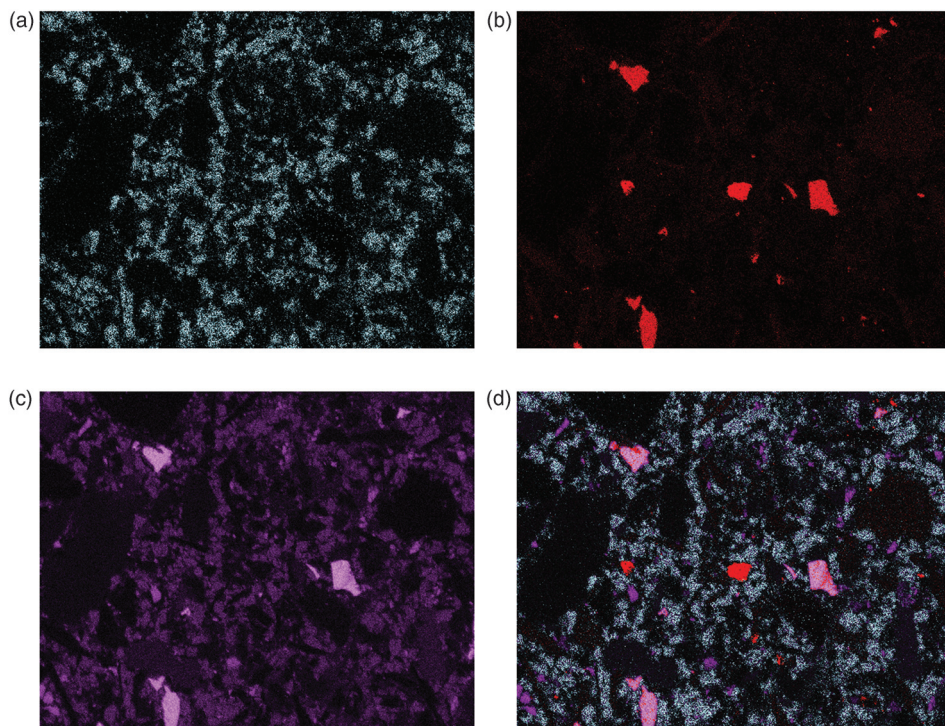
Figure 1: Traditional X-ray mapping showing Ba L in blue, Fe K in red, S K in purple, and a substitution overlay of all three elements. Even if it is known that Ba and S occur in combination, it is difficult to see where each element is combined with another element, even in a blended overlay of Ba L, Fe K, and S K maps (**Figure 1b**). Operating conditions: 200× magnification, 100K input CPS, 90K output CPS (10% dead time), energy resolution 126 eV, and 10-minute collection time. These maps include background removal and peak deconvolution, which allowed the barium to be separated from titanium. Full width = 630 μm.
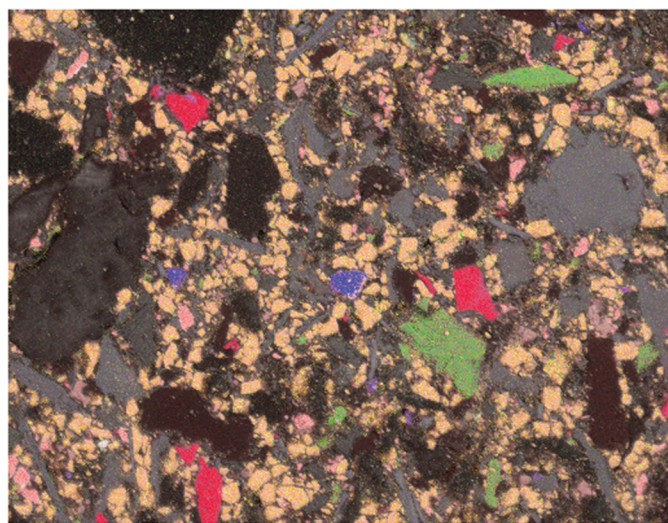

Figure 2: A color blended map highlights where elements occur in combination with each other. Here the primary colors green (Ba K) and red (S K) (green) create a blended color of orange, showing where Ba and S occur together. Fe K maintains its original blue color when not combined with Ba or S. Full width = 630 μm.

Full-spectrum phase mapping is a data evaluation tool that automatically evaluates and processes each spectrum directly and then displays a map image representing the phases present. The element peaks within the spectrum, and not the maps of these elements, are the basis for phase image generation. In this approach software evaluates the elements present from the spectrum peaks, generates peak intensity data, and then uses the intensity values to designate phases made from different elemental associations. The various combinations of elements are then displayed in a phase image. Because the basis for this map type is the spectrum, and not any images, a true phase map is independent of the amount of signal available in the pixels of an X-ray map, unlike the previous maps described.

In this automated data-driven approach, a spectrum is gathered at each pixel and real-time evaluation equations determine which areas contain the same specimen chemistry. These regions of similar chemistry are grouped together by common colors. Other routines assess the elements present, the intensity for each element in terms of the collected counts per second (CPS), and the ratios or relationships among all elements present. The basis for phase assignment at each pixel is therefore the presence or absence of elements, the intensity of the signal from each element, and the comparison of all elements to each other. Spectra are collected in real time, and the comparison of spectral data automatically occurs during this process, even before the creation of any elemental maps. This procedure results in an immediate phase map, which will be refined in subsequent frames. As an example, a sample might contain silicon and oxygen in an area for one phase, but silicon, oxygen, and low iron in an area for a second phase. A third phase may have silicon, oxygen, and high iron. Increasingly complex elemental associations are possible, based on the numerical intensity values and not just the "high" and "low" values used here for simplicity. Figure 3 graphically illustrates element ratios in various phases and their spectra in increasing complexity. This approach offers several advantages as described below.

Deconvolution of overlapping peaks. With spectrum phase evaluation, entire spectra are used to determine element associations in phases. In an overall map set and sum spectrum, there may be overlapping element peaks, such as Na K and Zn L. However, in individual site-specific sample areas, the spectrum from the material contains Na associated with Si or other areas of the sample Zn associated with S, but not both overlapping elements together in the same area. In a traditional approach, image correlation routines must first perform a deconvolution of the Na-Zn overlap peak and then display the potentially deconvoluted map. Spectrum phase routines determine the difference in these cases by referencing the entire set of elements in the full spectrum, using the Si or S non-overlapped peaks to determine whether a pixel is either the Na-Si phase or the Zn-S phase. The result provides the analyst with a reliable phase solution.
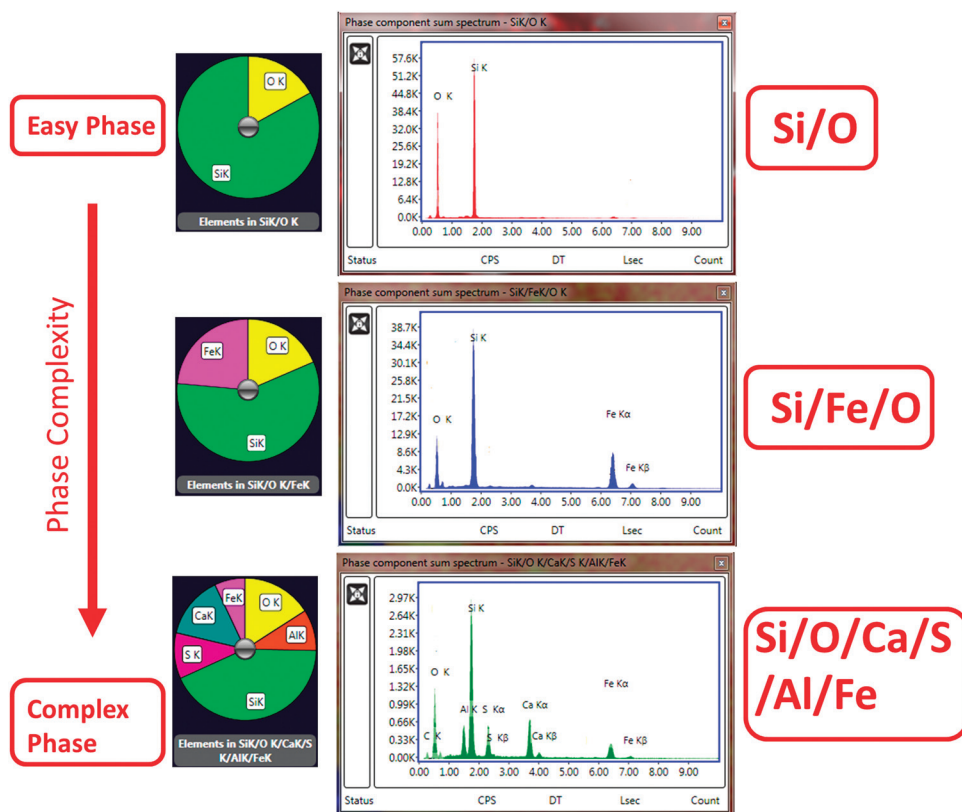
Figure 3: Rapid generation of phase map data. The geological specimen shows the progression from simple two-component quartz phase to the more complex multi-element phase in a pyroxene. The elemental pie charts show the relative intensities of the elements within the phase.

Generation of a phase library. Spectrum phase mapping uses spectra to determine phases, and these spectra can be saved together as a library of phase spectra. Once a representative library of phases is created and stored, it can be reapplied to subsequent analyses. Libraries can be activated for post-processing refinement of the same sample area map, for application to subsequent map sets in a different area, or for an altogether different sample. This provides reproducibility in phase mapping among many sample analyses and standardizes the approach among users.

Multifield phase mapping. With spectrum phase libraries, phase designations generated from the first field may then be applied throughout an entire sampling area, regardless of the number of fields or their size. The software will add new phases if they are found in subsequent fields. An entire multifield map will have the same phases visibly displayed with the same assigned color, regardless of where they are located.

CPS mapping. In a CPS map, a corollary to the phase map, image intensity is a representation of the X-ray intensity at each pixel in the map. There are certain benefits to this type of information. For example, it may reveal areas that are shadowed from the EDS detector, generally due to specimen topography, and these areas will appear as darker or "shadowed." This can explain why expected elements are "missing" from an element or phase map.

The revelation of differences in ionization potential for different elements is a less obvious benefit of CPS mapping.

For example, in a copper/aluminum sample, the copper has a higher atomic number than aluminum and will appear brighter in a backscattered electron (BSE) image, but aluminum produces a higher X-ray intensity relative to copper under most normal conditions, therefore aluminum will appear brighter in a CPS map. Conversely, materials that suffer absorption effects within the sample will appear darker in a CPS map, which explains why that element's map appears relatively less intense compared to lesser-absorbed elements. The CPS deviation routine takes this analysis further by calculating an average CPS value and then displaying the deviation from the average for each pixel. This allows normalization for elemental map sets, which corrects for over- or under-represented pixels due to ionization or absorption effects.

Phase Map Example

A phase map of an alumina sample was collected with an EDAX TEAM™ EDS system, and various phases were automatically identified by the phase routine (Figure 4a). Major phases present included pure Al (blue), alumina (orange), alumina with Mg (magenta), and alumina with Si (yellow). With this approach, one image describes the total phase chemistry, without having to overlay four or more different element maps to be able to visualize the relationship of the elements to each other. The map was further processed (Figure 4b), reassigning different phase colors from the phase library, which customizes phase views for user preference or keeps consistency between samples. Using the phase library created from the dataset, the phase colors were reassigned, and the major alumina phase was redefined as red instead of the original orange color. Figure 4c shows the phase library that was created and modified. These phase library data and color combinations can be applied to any subsequent sample or sample area, allowing the analyst to consistently determine where these phases occur in different samples.

Figure 5 is a phase map display of the brake pad specimen shown in Figure 1. With this phase map, the complete phase chemistry is described in one image. For example, the barium- and sulfur-containing areas are shown in orange, whereas in Figure 1, it was difficult to see where those two elements occurred together in an overlay map. The phase map also allows many elements to be combined together to understand compounds and alloys. Although Figure 2 showed the blending of elements together, it was limited to three elements at a time related to the blending of the three primary colors.
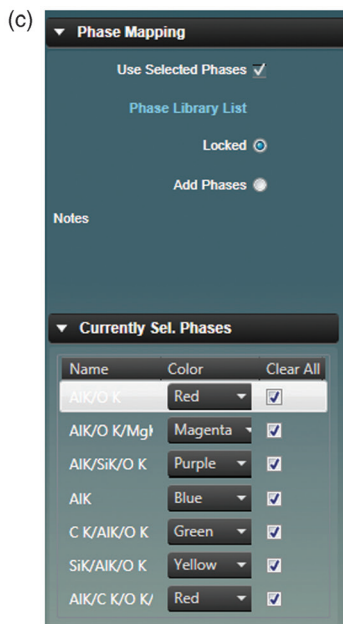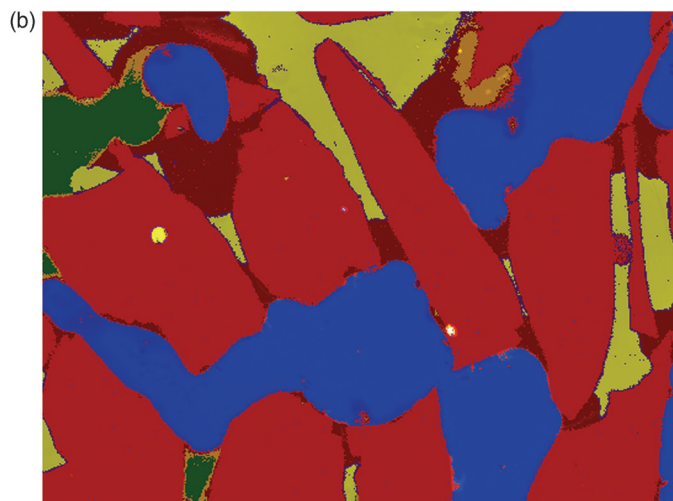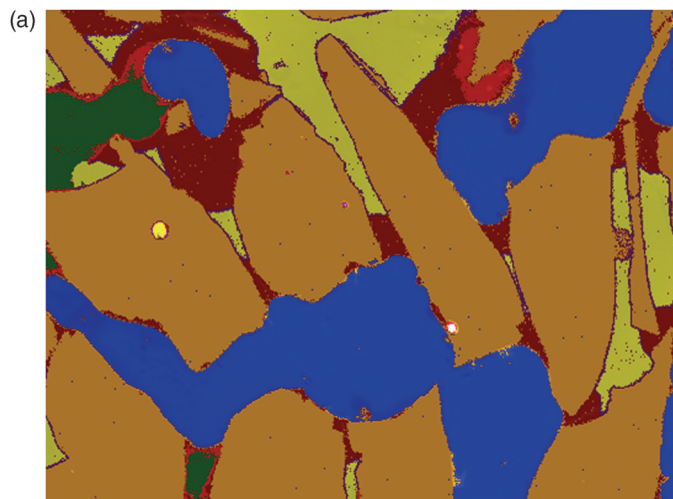
(a)

(b)

(c)

Figure 4: An alumina sample containing grains of varying composition. (a) The original major phase of alumina was coded in orange. (b) Phase image modified so that the major phase is red. (c) Phase library used to coordinate color scheme with that stored in the library from previous work. Image full width = 550 μm.

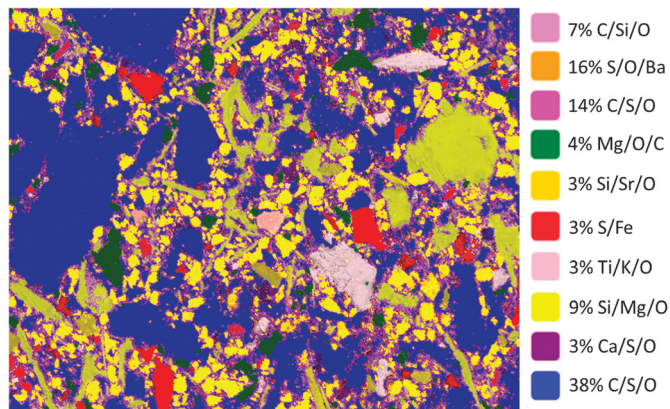|	
	7% C/Si/O
	16% S/O/Ba
	14% C/S/O
	4% Mg/O/C
	3% Si/Sr/O
	3% S/Fe
	3% Ti/K/O
	9% Si/Mg/O
	3% Ca/S/O
	38% C/S/O

Figure 5: Phase map of the same sample area as Figure 1. With this phase map, the complete phase chemistry may be described in one image by consulting the phase map color legend at the right. Full width = 630 μm.

As a phase map, the fine-grained barite (orange) and larger-grained iron pyrite (red) can be observed, and an area or volume fraction can be found for each compound, 16% and 3%, respectively. A calcium sulfate phase (purple) is also identified to be a minor component at 3% area fraction, showing yet another sulfur-containing compound that was not readily apparent in the sulfur map or in any of the overlays. Also, the titanium phase (lavender) is deconvoluted and makes up 3% by area fraction. This phase is confidently separated from an overlapping barium phase because of the presence of other elements not found in the barium-containing phase.

Conclusion

Basic elemental X-ray mapping performs an important function that allows a visible understanding of element distributions within a sampling area. Image processing routines are a first step in providing a map display of where elements occur in combination. Advanced phase algorithms based on full spectrum data use X-ray peak information to uncover complex aspects of element combinations and provide standardized results among different samples and different users. These associations of elements are displayed in a single phase image, in which complex phase relationships can be understood.

References

[1] JI Goldstein et al., *Scanning Electron Microscopy and X-ray Microanalysis*, 3rd edition, Kluwer Academic Plenum Press, New York, 2003, p. 689.

[2] RB Mott et al., "Position-Tagged Spectrometry: A New Approach for EDS Spectrum Imaging" in *Proccedings of Microscopy and Microanalysis*, eds. GW Ellisman, MH Ellisman, RA Hennigar, and NJ Zaluzec, Jones and Begell, New York, 1995, p. 592–93.

[3] JJ Friel and CE Lyman, *Microsc Microanal* 12 (2006) 2–25.

[4] EDFAS Desk Reference Committee, *Microelectronics Failure Analysis: Desk Reference*, RJ Ross, ed., ASM International, Materials Park, OH, 2011, p. 555.

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