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Multivariate Analysis of X-ray, Ion and Electron Spectral Images: From Surface to 3D Materials Characterization

P.G. Kotula and M.R. Keenan

Sandia National Laboratories, PO Box 5800, Albuquerque, NM 87185-0886

Spectral imaging where a complete spectrum is collected from each of a series of spatial locations (1D lines, 2D images or 3D volumes) is now available on a wide range of analytical tools—from electron and x-ray to ion beam instruments. With this capability to collect extremely large spectral images comes the need for automated data analysis tools that can rapidly and without bias reduce a large number of raw spectra to a compact, chemically relevant, and easily interpreted representation. It is clear that manual interrogation of individual spectra is impractical even for very small spectral images (<5000 spectra). More typical spectral images can contain tens of thousands to millions of spectra, which given the constraint of acquisition time may contain between 5 and 300 counts per 1000-channel spectrum. Conventional manual approaches to spectral image analysis such as summing spectra from regions or constructing x-ray maps are prone to bias and possibly error. One way to comprehensively analyze spectral image data, which has been automated, is to utilize an unsupervised self-modeling multivariate statistical analysis method such as multivariate curve resolution (MCR) [1]. This approach has proven capable of solving a wide range of analytical problems based upon the counting of x-rays (SEM/STEM-EDX [1,2], XRF, PIXE [3]), electrons (EELS [4], XPS [5]) and ions (TOF-SIMS [6]).

As an example of the MCR approach, a STEM x-ray spectral image from a ZrB_2-SiC composite was acquired and analyzed. The data were generated in a FEI Tecnai F30-ST TEM/STEM operated at 300kV, equipped with an EDAX SUTW x-ray detector. The spectral image was acquired with the TIA software on the STEM at 128 by 128 pixels (12nm/pixel) for 100msec dwell per pixel (total acquisition time was 30 minutes) with a probe of approximately the same size as each pixel. Each spectrum in the image had, on average, 500 counts. The calculation took 5 seconds on a PC workstation with dual 2.4GHz PentiumIV Xeon processors and 2Gbytes of RAM and resulted in four chemically relevant components, which are shown in Figure 1. The analysis region was at a triple junction of three ZrB_2 grains that contained zirconium oxide, aluminum oxide and a glass phase. The power of unbiased statistical methods, such as MCR as applied here, is that no *a priori* knowledge of the material's chemistry is required. The algorithms, in this case, effectively reduced over 16,000 2000-channel spectra (64Mbytes) to four images and four spectral shapes (72kbytes), which in this case represent chemical phases. This three order of magnitude compression is achieved rapidly with no loss of chemical information. There is also the potential to correlate multiple analytical techniques like, for example, EELS and EDS in the STEM adding sensitivity to light elements as well as bonding information for EELS to the more comprehensive spectral coverage of EDS [7].

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[7] Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United Stated Department of Energy (DOE) under contract DE-AC04 94AL85000.

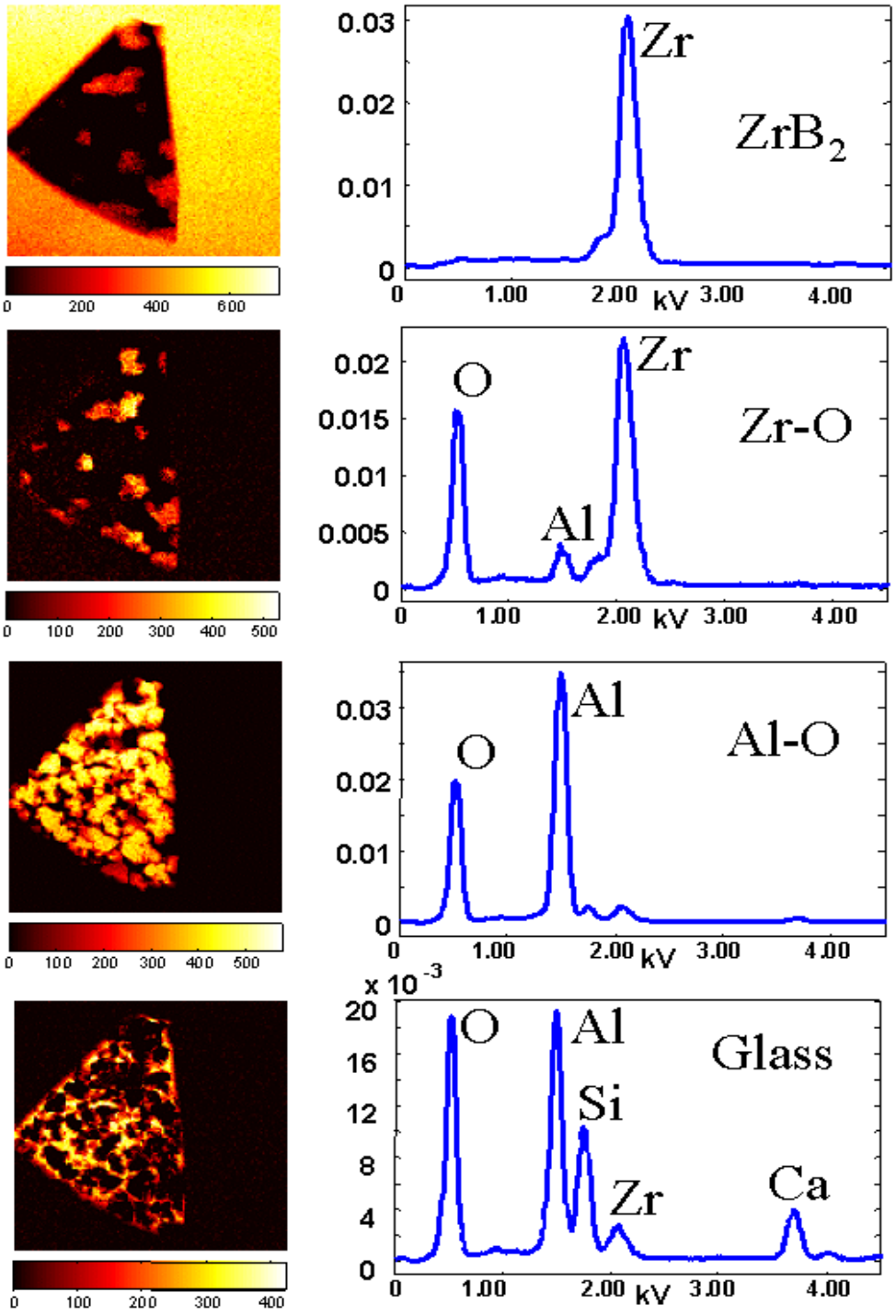

FIG. 1. Respective component image/spectrum pairs from the automated MCR analysis of a STEM x-ray spectral image of a ZrB_2-SiC composite. The pocket at the junction of three grains if ZrB_2 contained Zr-oxide, Al-oxide and a glassy phase.

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