

Fast Atomic Level EELS Mapping Analysis using High-Energy Edges in DualEELS™ mode

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Introduction

With advancements in aberration-correction, the spatial resolution of scanning transmission electron microscopy has been enormously improved [1]. In addition to the reduction of the STEM probe size, a dramatic increase in the STEM probe current has been realised leading to the routine acquisition of high-resolution elemental and chemical maps using electron energy loss spectroscopy (EELS) [2]. Atomic level EELS maps can now be obtained with the acquisition time largely limited only by the speed of the EELS spectrometer and not by the signal measured. However the introduction of fast EELS spectrometers such as the GIF Quantum® and the Enfinium™ with large collection efficiency [3,4] has closed the gap between the rate of signal generation in the specimen and the speed at which the signal can be detected. EELS data can now be acquired at well over 1000 spectra per second with high duty cycle. Fifth-order spectral aberration correction in this generation of spectrometers allows the use of the large collection angles needed to match the increased convergence angle which Cs-probe – corrected systems present while maintaining the energy resolution. These advances result in a well matched source/detector system capable of recording high-energy EELS edges at a rate fast enough to limit electron beam damage to the sample.

Methods and Materials

Data were acquired at Arizona State University using a probe corrected JEOL ARM 200 STEM equipped with a Schottky FEG source. The EELS data were acquired using a Gatan Enfinium™ ER spectrometer that included: (a) DualEELS™ capability which allows two different regions of the EELS signal to be recorded simultaneously under the same experimental conditions [3,4]; (b) a 2-K CCD camera with low dispersion mode which allows to record EELS data with a field of view extending for 2000eV (4000eV in DualEELS™ mode); (c) fast acquisition mode which allows the acquisition of over 1000 spectra per second; (d) dodecapole lens system capable of correcting spectral aberrations up to the 5th order. Two different samples were analyzed: a conventional SrTiO₃ (STO) single crystal and SrTiO₃/LaMnO₃ (STO/LMO) interface. For the both samples, EELS data were acquired using 0.13nm STEM probe with a convergence angle of 25mrad and the EELS collection angle estimated to be greater than 100mrad. The EELS SI acquisition was carried out in DualEELS™ mode; the regions of the EELS spectrum from 350eV to 2350eV and 1000eV to 3000eV were nearly simultaneously acquired using acquisition times of 4ms and 11ms respectively.

Mapping High-Energy edges

Most work on atomic level EELS mapping of SrTiO₃ has been carried out using the Sr M_{4,5}-edges at 133eV and the Ti L_{2,3}-edges at 456eV. While the low-energy Sr M_{4,5}-edges have a high signal-to-noise ratio, they also show a poor signal-to-background ratio. As Reported in [5], the contrast of the Sr M_{4,5}-edges elemental map increases progressively as the integration window is shifted away from the actual edge threshold. The best contrast was achieved by placing the integration window from 360eV to 410eV beyond the Sr M_{4,5}-edges onset. The contrast is improved as a result of the increased signal-to-background at higher energies. However, the delayed window placement may lead to misinterpretations because of C contamination with its K-edge at 284eV and other possible elements present in that region. This problem can be overcome by recording the Sr L_{2,3}-edges at 1940eV, but the absolute signal is significantly reduced compared to the Sr M_{4,5}-edges at 130eV. However, the signal-to-background ratio is dramatically improved and the background is a nearly constant power law at these energies leading to a more reliable background removal. Simultaneous mapping of high-energy edges such as the Sr L_{2,3} and lower ones such as the Ti L_{2,3} is now possible using the DualEELS™ capability [3,4] available in the GIF Quantum® and Enfinium™ spectrometers. In DualEELS™ every edge can be collected and the acquisition time adjusted accordingly. Figure 1 shows the EELS spectrum extracted after splicing the DualEELS™ data into a single continuous dataset.

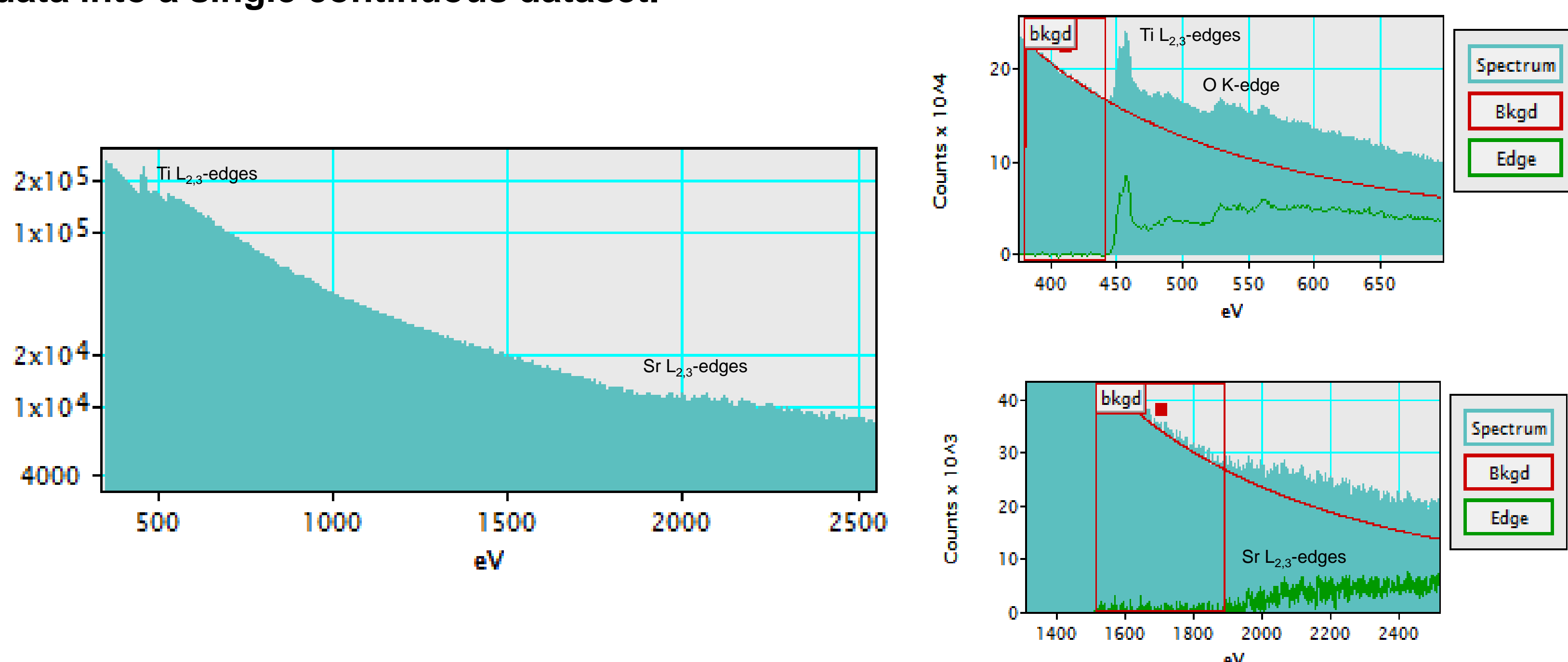


Figure 1a: Extracted EELS spectrum from the spliced SI of the lower core loss region at 350eV and the higher core loss region at 1000eV. Both the Ti L_{2,3}-edges and the Sr L_{2,3}-edges are in the same spectrum. The dynamic range of the EELS spectrum is increased as a result of the splicing of the two datasets. Figures 2b,c are the enlarged regions of the EELS spectrum for the Ti L_{2,3}-edges at 456eV and the Sr L_{2,3}-edges at 1940eV respectively.

References

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Background Removal

Another problem that can be encountered when analysing atomic level EELS maps is the background removal. In general, the most common way of removing the background is a power law fitting. Removing the background in such a way can lead to extrapolation errors. However, as reported in [6,7], the background can be significantly improved using the multiple linear square fitting approach for the background and the edge signal. In this way, the background is forced to retain a constant shape across the whole region. The signal-to-ratio of the background-subtracted elemental maps is significantly improved as shown in Figures 2b and 3b. The contrast of these elemental maps appears to improve in the case of the MLLS fitting approach. The improvement is clearly more evident in the case of the Ti L_{2,3}-edges elemental map Figures 2a,b where the background fitting is more problematic. As mentioned previously, the background fitting at high-energy edges is more robust and not significantly improved by standard MLLS fitting.

Figure 4 shows a colored EELS elemental map of the Sr L_{2,3}-edges at 1940eV and the Ti L_{2,3}-edges at 456eV. The contrast between the Sr and the Ti atomic columns is high and this confirms the advantage of mapping high-energy edges when the system is capable of delivering high-current.

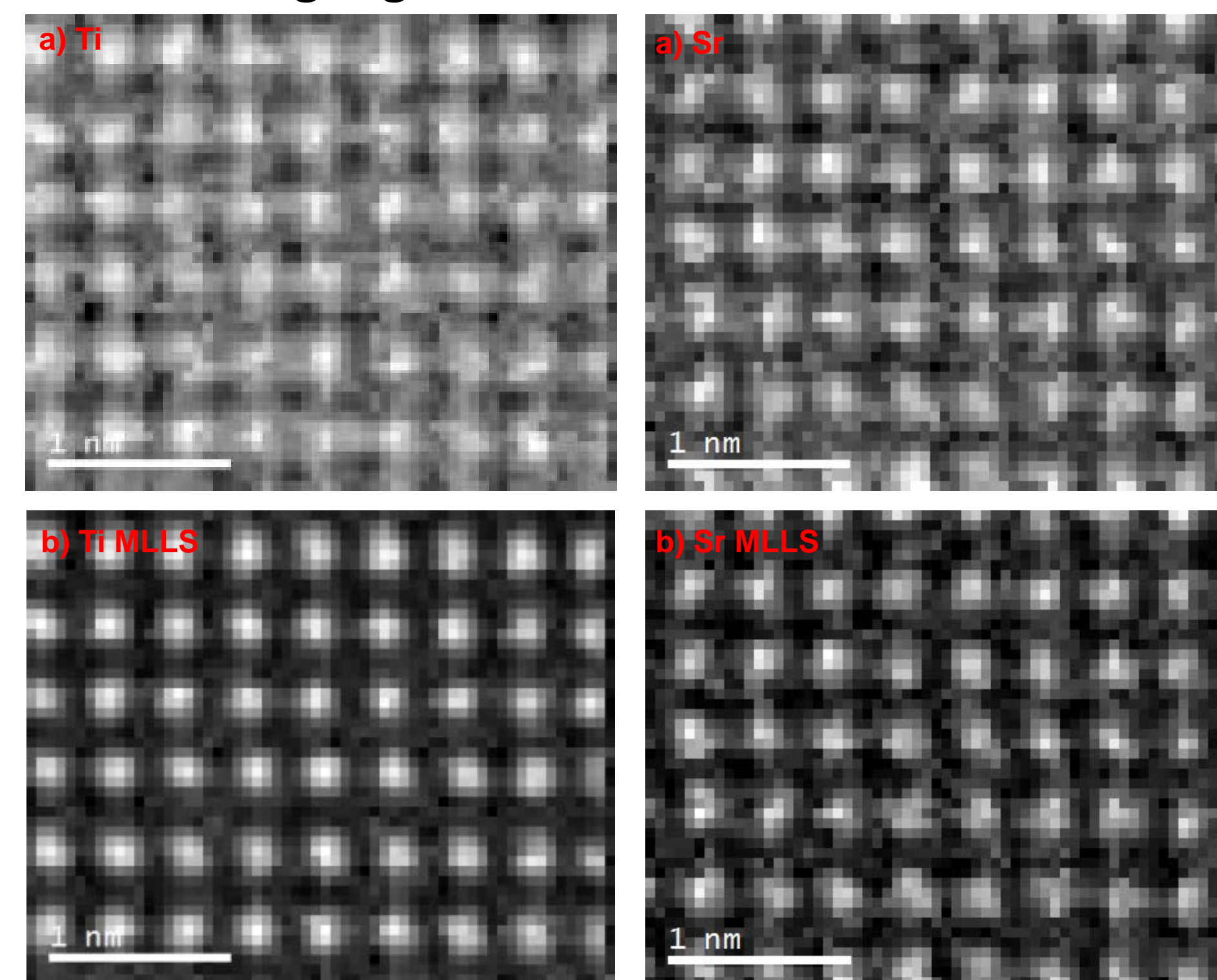


Figure 2. a) Extracted Ti L_{2,3}-edges elemental map by simple background removal using power law; b) elemental map extracted using MLLS fitting procedure.

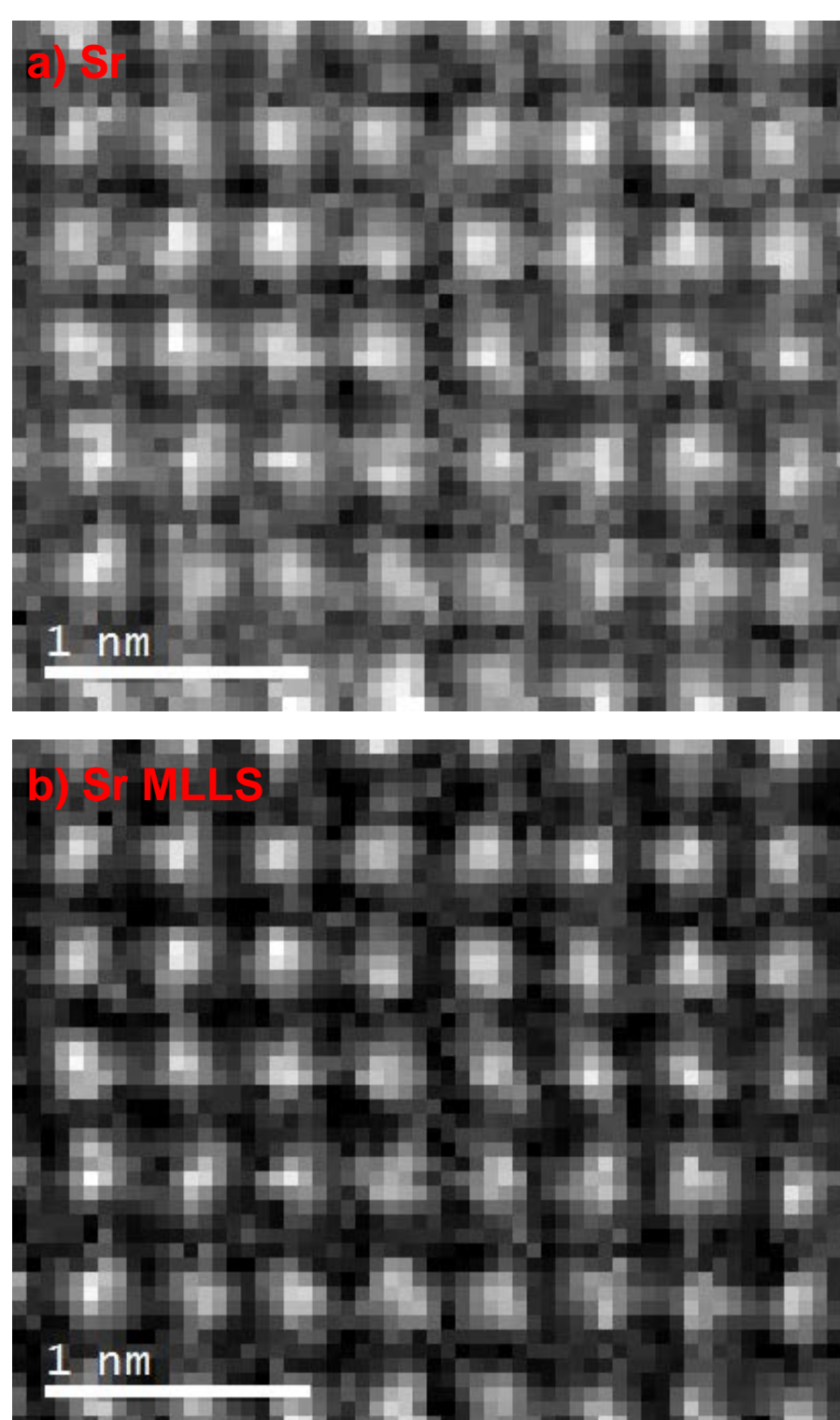


Figure 3. a) Extracted Sr L_{2,3}-edges elemental map by simple background removal using power law; b) elemental map extracted using MLLS fitting procedure.

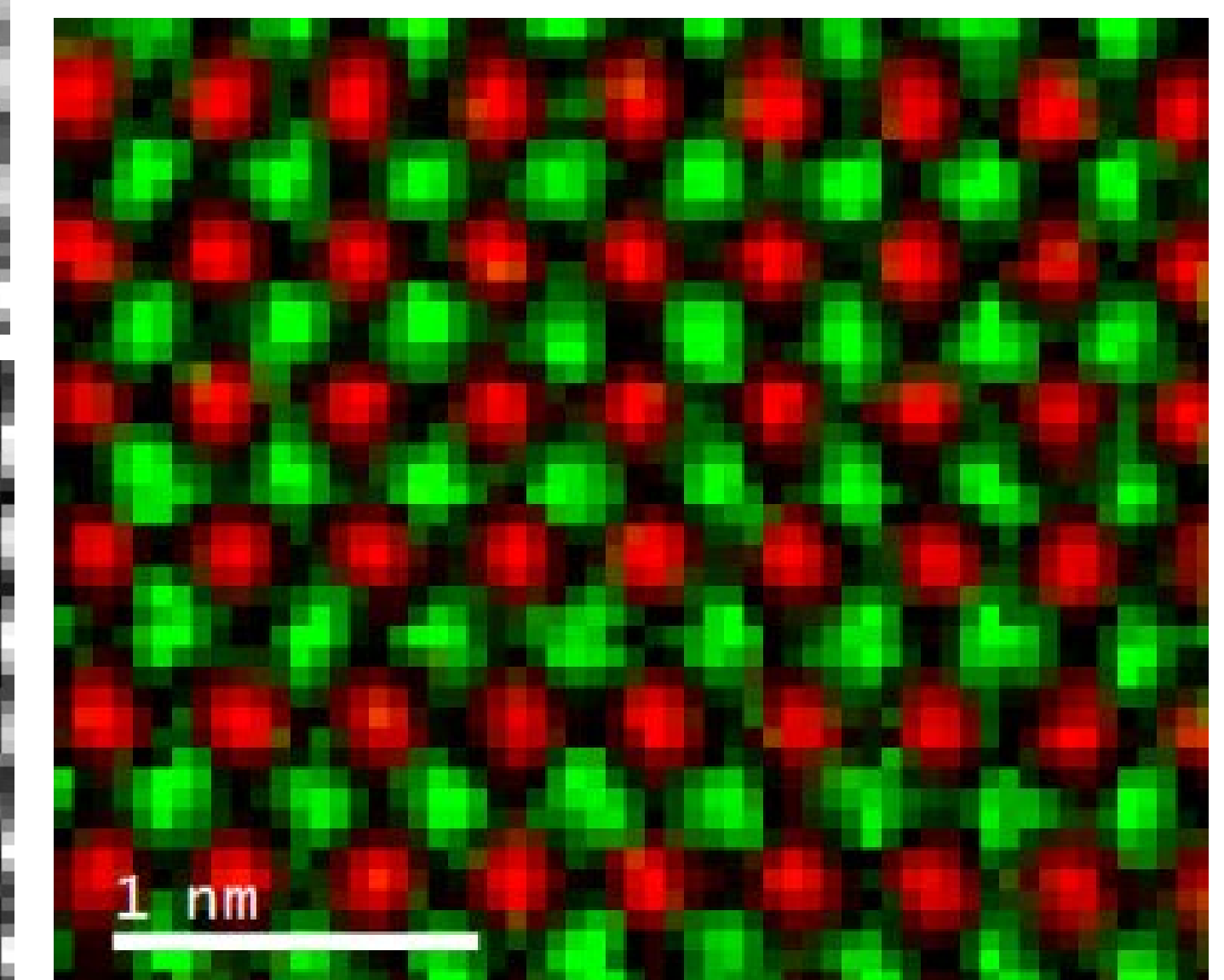


Figure 4: High-quality colored EELS map with enhanced contrast of the Ti and Sr elemental. Ti is red and Sr is green.

Revealing the Interface.

The same approach was used to characterize the SrTiO₃/LaMnO₃ GIF Quantum® and Enfinium™ crystalline sample. EELS can give a deep insight into the chemistry and elemental distribution across this interface. Figure 5 shows a colored elemental maps obtained from the La M_{4,5}-edges at 832eV in yellow, the Mn L_{2,3}-edges at 640eV in blue, the Ti L_{2,3}-edges at 456eV in red and the Sr L_{2,3}-edges at 1940eV in green. Note that, there appears to be an intermixing between the Ti and Mn that extends for a few monolayers across the interface. This is evidenced in the colored map by the presence of atomic columns showing both red and blue colours which can be explained by the presence of both Ti and Mn in the same atomic columns. Quantitative analysis carried out across the same region shows the presence of 12% Ti and 10% Mn.

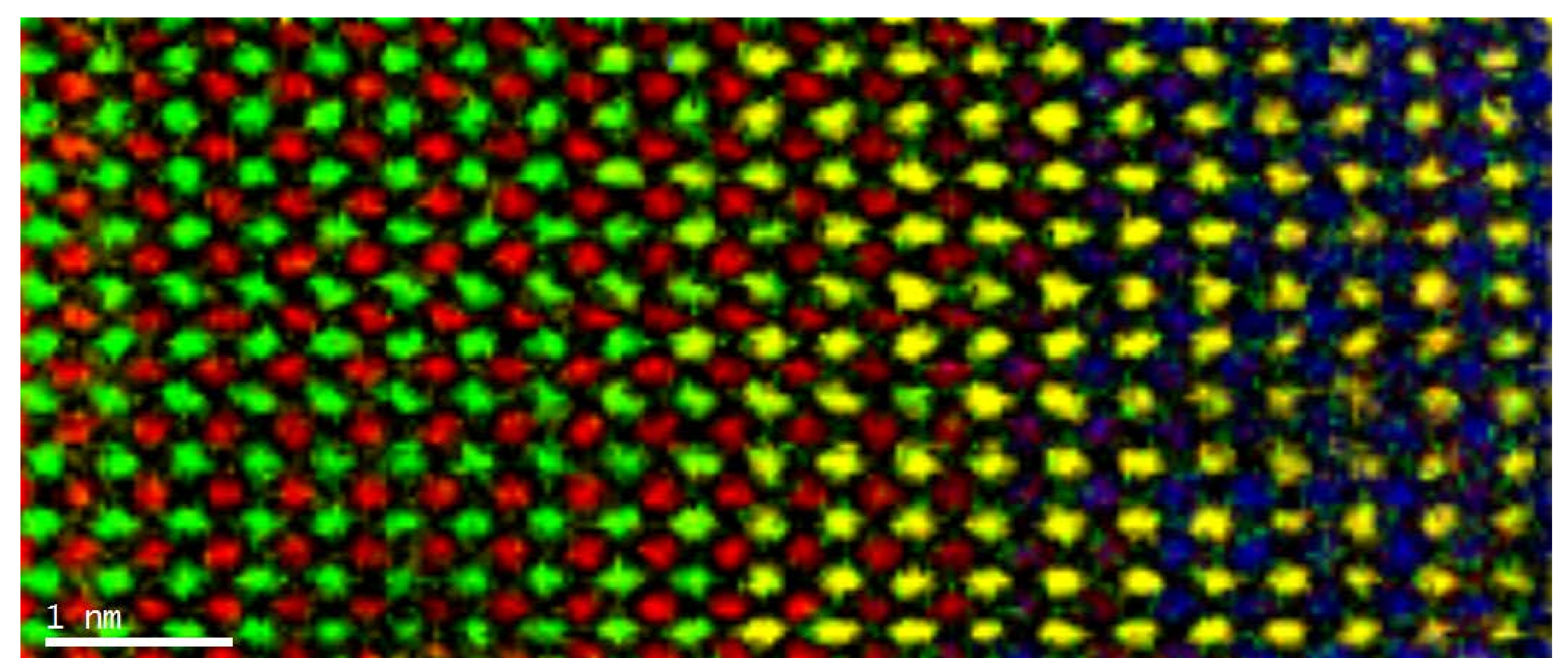


Figure 5: High-quality colored EELS map with enhanced contrast of the STO/LMO interface region. Ti L_{2,3}-edges at 456 eV in red; Sr L_{2,3}-edges at 1940eV in green; La M_{4,5}-edges at 832eV in yellow; Mn L_{2,3}-edges at 640eV in blue.

Conclusions

We have shown that atomic EELS mapping using high-energy edges is very effective. The signal-to-background ratio is much higher leading to a more reliable edge extraction. In addition the background removal can be greatly improved using the MLLS fitting procedure. High and low energy edges in the EELS spectrum can be simultaneously acquired using DualEELS™ capability available in the GIF Quantum® and Enfinium™ spectrometers. In addition, the energy range of the acquired EELS data extends up to 4000eV. More importantly by combining the increased probe current present in a aberration corrected microscope with the fast EELS spectra acquisition capability available in the GIF Quantum® and Enfinium™ spectrometers, mapping high energy edges at the atomic level with good signal-to-noise ratio and in a short amount of time is now possible. The quality of these maps in terms of contrast is very high and this is due to high signal-to-noise background which these edges show.

