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Quantitative atomic-site-analysis of functional dopants/point defects in crystalline materials by electron-channeling-enhanced microanalysis
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1 **TITLE:**
2 Quantitative atomic-site analysis of functional dopants/point defects in crystalline materials by
3 electron-channeling-enhanced microanalysis
4
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16 **KEYWORDS:**
17 Transmission electron microscopy; Electron channeling; Energy-dispersive X-ray spectroscopy;
18 Electron energy-loss spectroscopy; Dopant occupancy; Point defect geometry; Statistical
19 analysis; Quantitative analysis; Electron beam-rocking
20

21 **SUMMARY:**
22 We provide a general outline of quantitative microanalysis methods for estimating the site
23 occupancies of impurities and their chemical states by taking advantage of electron-channeling
24 phenomena under incident electron beam-rocking conditions, which reliably extract information
25 from minority species, light elements, oxygen vacancies, and other point/line/planar defects.
26

27 **ABSTRACT:**
28 A novel elemental and chemical analysis scheme based on electron-channeling phenomena in
29 crystalline materials is introduced, where the incident high-energy electron beam is rocked with
30 the submicrometric pivot point fixed on a specimen. This method enables us to quantitatively
31 derive the site occupancies and site-dependent chemical information of impurities or
32 intentionally doped functional elements in a specimen, using energy-dispersive X-ray
33 spectroscopy and electron energy-loss spectroscopy attached to a scanning transmission
34 electron microscope, which is of significant interest to current materials science, particularly
35 related to nanotechnologies. This scheme is applicable to any combination of elements even
36 when the conventional Rietveld analysis by X-ray or neutron diffraction occasionally fails to
37 provide the desired results because of limited sample sizes and close scattering factors of
38 neighboring elements in the periodic table. In this methodological article, we demonstrate the
39 basic experimental procedure and analysis method of the present beam-rocking microanalysis.
40

INTRODUCTION:
42 With the demand of downsizing most current industrial products, it is getting more and more
43 important to understand the physical/chemical properties of materials from the microscopic
44 perspective, sometimes in terms of atomic-scale spatial/electronic structures. Novel properties

45 are often discovered unexpectedly when synthesizing materials by trial and error, selecting
46 different numbers or kinds of elements, although current measurement techniques and ab initio
47 theoretical calculations based on density functional theory have enabled design of novel
48 materials with improved properties without time-consuming trial and error experiments. For
49 example, some of the host atoms are substituted with other elements that can possibly improve
50 the target property as results of either experimental or theoretical considerations. In this context,
51 an important component of experimental information is brought about from detailed knowledge
52 of the position of each constituent in the atomic structure of the material.
53
54 X-ray and/or neutron diffraction methods are conventionally and widely used not only because
55 the structural analysis based on Rietveld analysis[1,2] techniques has been well established and
56 open to the public, but also owing to the development of high-flux X-ray sources (e.g.,
57 synchrotron radiation facilities) and modern neutron sources, which are easily accessible to
58 general researchers. However, these techniques require samples with homogeneous structures,
59 and they also require the Rietveld fit between the experimental and theoretical sets of diffracted
60 peak intensities using structural factors. It can thus be difficult to distinguish between different
61 elements if their structural factors are close to each other, such as in X-ray diffraction of
62 neighboring elements in the periodic table.
63
64 In most current advanced materials, the compositions, precipitates, grain size, and impurities are
65 adjusted and optimized to maximize the desired role at the nanometer scale. This means that
66 these materials require characterization at the nanometer scale or even sub-nanometer scale to
67 investigate whether they are synthesized as designed. In this context, it could be best achieved
68 using transmission electron microscopy (TEM) and related analytical techniques.
69
70 The recent dramatic development of scanning TEM (STEM) in these decades, particularly based
71 on aberration correction technologies, has accelerated a state-of-the-art technique to reveal the
72 structure of a material and its elemental distribution at an atomic scale[3,4]. This method, however,
73 requires precisely setting the crystalline material parallel to a low-order zone axis and to the
74 extreme stability of the instrument during the measurement, which is a drawback. Hence, we
75 demonstrate an alternative method that requires no such limitations, aberration, correction, or
76 even field emission electron gun.
77
78 Electron channeling in a crystalline material occurs if an incident electron beam propagates along
79 particular atomic planes or columns, which depends on the direction of the incident high-energy
80 electron beam with respect to the crystal axes, where an appropriate set of Bragg reflections and
81 the excitation error of each reflection in a TEM are selected. The site-specific energy-dispersive
82 X-ray (EDX) analysis technique that uses electron channeling is called the atom location by
83 channeled electron microanalysis (ALCHEMI) method to evaluate the occupancies of host atomic
84 sites by impurities[5,6]. This method has been extended to a more complex and quantitatively
85 reliable approach, called high-angular-resolution electron-channeling X-ray spectroscopy
86 (HARECXS), to determine impurity/dopant occupancies. This is realized by comparing the
87 experimental beam-rocking curves with theoretical simulations[7]. This technique is further
88 extended to high-angular-resolution electron-channeling electron spectroscopy (HARECES),

89 which records electron energy loss spectra (EELS) instead of EDX[8]. This provides information on
90 the site-specific local chemical states of a given element in different atomic environments[9-11]. In
91 cases where each host element occupies a single crystallographic site, a simple linear regression
92 and application of several formulae to the experimental dataset quantitatively determines the
93 site occupancies of doped impurities without any theoretical simulations.
94
95 In the following sections, we provide detailed procedures of the method specific to the Jeol
96 JEM2100 STEM system because it is explicitly equipped with the beam-rocking mode in the STEM
97 operation menu. For users of other microscopes, please refer to the descriptions in the final
98 paragraph of the Discussion section of this article.
99
100 **PROTOCOL:**
101
102 **1.   Sample preprocess**
103
104 1.1.   Thin film preparation for TEM
105
106 1.1.1.   Prepare a sample for the present analysis method using standard transmission electron
107 microscopy (TEM) sample preparation techniques, such as electropolishing for metal materials,
108 ion milling for semiconductors or ceramics, typically less than 100–200 nm for HARECXS,
109 uniformly flat over the area of ~1 μm. Prepare thinner (50–100 nm) samples for HARECES in
110 general.
111
112 1.2.   Sample mounting to TEM
113
114 1.2.1.   Mount the thin film prepared on a double-tilting TEM sample holder, followed by
115 inserting the holder into a TEM equipped with a scanning mode and an EDX detector (**Figure 1**).
116
117 **2.   TEM operation (specific to JEM2100 TEM with beam-rocking option attached)**
118
119 2.1.   TEM alignment for beam-rocking
120
121 2.1.1.   Start the TEM operation. After the routine TEM beam alignment procedure, go to STEM
122 mode by checking **Attachment Scanning Image Display (ASID)** in the ASID window in the TEM
123 control monitor (**Figure 1 & Figure 2**).
124
125 2.2.   Optical axis alignment
126
127 2.2.1.   Click the **Rocking** button in the ASID window of the TCM and then click the **Spot** button
128 in the Simple Image Viewer (SIV) to stop beam-rocking (**Figure 2**). Remove the sample from the
129 field of view. Set the beam-rocking range smaller than ±2° by clicking the **Mag**
130 **increment/decrement** buttons.
131
132 2.2.2.   Turn the **Brightness** knob on left operation panel (LOP: **Figure 3**) clockwise to the limit,

followed by turning the **OBJ FOCUS COARSE** knob of Right Operation Panel (ROP: **Figure 3**) counterclockwise to an underfocused condition: a caustic spot (**Figure 4**) appears on the fluorescent viewing screen.

2.2.3. Press the **BRIGHT TILT** function key (LOP) and move the caustic spot to the center of the fluorescent screen using a pair of **DEF/STIG X/Y** knobs (L/ROP).

2.2.4. Press the **Standard Focus** button (ROP), and then turn the **BRIGHTNESS** knob back counterclockwise so that an alternative caustic spot appears on the fluorescent screen.

2.2.5. Press the **F3** function key (ROP) (or click the **Spot** button in 'Alignment Panel for Maintenance' window on TCM) and move the beam spot to the center using a pair of **DEF/STIG X/Y** knobs.

2.2.6. Repeat steps 2.2.2-2.2.5 until the beam position stays at center even if the lens condition is switched at step 2.2.2 and 2.2.4.

2.3.   Incident beam collimation and setting its pivot point

2.3.1. Introduce the third largest condenser aperture at the center of the optical axis by turning the aperture knob clockwise with its position manually adjusted with two attached screws (**Figure 1**). Then, adjust the condenser lens stigmator to correct the beam shape to be coaxially defocused by turning the **BRIGHTNESS** knob both ways, using a pair of **DEF/STIG** knobs with **COND STIG** key on.

2.3.2. Press the **HT WOBB** key (ROP) and adjust the **BRIGHT TILT** knob to minimize the beam size fluctuation with the change in acceleration voltage. This process adjusts the beam convergence angle minimum. Press the **HT WOBB** key again to stop HT wobbler.

2.3.3. Activate maintenance mode (consult the manufacturer's manual). Select **JEOL** from the menu bar → **Scan/Focus window** → **Scan Control tab in TCM**. Then, click the **Cor** button and click the **Scan** button instead of **Spot** in the Image control panel of SIV.

2.3.4. To minimize the beam shift with beam-rocking, adjust a pair of **DEF/STIG** knobs, followed by turning the **OBJ FOCUS FINE** knob slightly counterclockwise. Finally, match the sample and pivot point height using Z control keys (ROP) so that the sample is focused on the fluorescent screen.

2.4.   Final beam alignment to obtain electron-channeling pattern of sample

2.4.1. Move the sample area of interest back to the center, and start beam-rocking by clicking the **Scan** button in the SIV window. Manually turn clockwise the annular dark field (ADF) detector cylinder (**Figure 1**) and insert the detector.

2.4.2. Set the ADF detector position at the center of the beam position by adjusting a pair of **DEF/STIG** knobs with **PLA** key on (LOP: **Figure 3**). Check the **STEI-DF** button in the **Image Select** menu of the **ASID** window and the **STEM** monitor in the **SIV** window displays an electron-channeling pattern (ECP). Adjust the **Brightness/Contrast** in the **ASID** window to best see ECP. Slightly turn the **BRIGHTNESS** knob to see the ECP contrast sharpest.

2.5. Data acquisition for HARECXS by EDX

2.5.1. By operating the STEM in beam-rocking mode, collect the EDX spectra by following the conventional spectral image method (using the spectral imaging function in **Figure 5**) as a function of beam tilting angles in the *x* and *y* directions and display elemental intensity distribution for specified elements, as shown in **Figure 5**.

NOTE: The intensity distribution pattern is called an ionization channeling pattern (ICP).

2.5.2. Use the **Line Scan** function in **Figure 5** for the 1D tilting measurement of a systematic row of reflections. Yellow arrow appears in the ECP preview to specify the measuring range, as shown in the upper left panel in **Figure 5**. Stop measurements when sufficient data statistics are obtained for ICPs.

3. Data analysis for quantification

3.1. Express X-ray intensity I_x for impurity x in the following form as a function of X-ray intensity I_i of host element i,[12]

$$I_x = \frac{c_x}{k_x} \sum_i \frac{f_i k_i I_i}{(n_i - \sum_x c_x f_{ix})} = \sum_i \alpha_{ix} I_i + \beta_x \qquad (1)$$

where

$$\alpha_{ix} = \frac{c_x}{k_x} \frac{f_{ix} k_i}{(n_i - \sum_x c_x f_{ix})} \qquad (2)$$

NOTE: Here, f_{ix} is the fractional occupancy of impurity x on the type i host site, c_x is the concentration of impurity x, and n_i is the fractional concentration of the type i host element among the total host sites prior to the accommodation of impurity atoms of type x. k_i is the k-factor of the type i host element, and F_i is the multiplicative factor per atom to scale the ionization cross-section under kinematic diffraction conditions to that observed under dynamical diffraction conditions. The additional constant offset β_x has been introduced as an extra fitted parameter to account for differences in interaction delocalization and errors in background subtractions. α_{ix} can be derived from Eq. (1) by multivariate linear regression for many sampling points of the ICP X-ray intensities.

3.2. Derive c_x and f_{ix} utilizing the condition $\sum_i f_{ix} = 1$ as[12]

217
$$c_x = \sum_i \frac{\alpha_{ix} n_i}{(\sum_x \alpha_{ix} + k_i/k_x)}, f_{ix} = \frac{\alpha_{ix} n_i}{c_x(\sum_x \alpha_{ix} + k_i/k_x)}. \qquad (3)$$

218 The uncertainties in c_x and f_{ix} for multiple impurities are readily derived from the error
219 propagation principle:

220
$$(\delta c_x)^2 = \sum_i \left[-\frac{\alpha_{ix} n_i}{(\sum_x \alpha_{ix} + k_i/k_x)^2} + \frac{n_i}{(\sum_x \alpha_{ix} + k_i/k_x)} \right]^2, \quad (4)$$

221 and

222
$$(\delta f_{ix})^2 = \frac{1}{c_x{}^2} \left[-\frac{\alpha_{ix} n_i}{(\sum_x \alpha_{ix} + k_i/k_x)^2} + \frac{n_i}{(\sum_x \alpha_{ix} + k_i/k_x)} \right]^2 (\delta \alpha_{ix})^2$$

223
$$+ \left(\frac{\delta c_x}{c_x{}^2} \right)^2 \left[\frac{\alpha_{ix} n_i}{(\sum_x \alpha_{ix} + k_i/k_x)} \right]^2, \qquad (5)$$

224 where $\delta \alpha_{ix}$ is the statistical error obtained in the linear regression from Eq. (1).
225

226 **REPRESENTATIVE RESULTS:**
227 The experimental ECP for $BaTiO_3$ and ICPs of Ba-L, Ti-Kα, and O-Kα near the [100] and [110] zone
228 axes are shown in **Figure 6A** and **Figure 6B**, respectively. Each constituent element exhibits a
229 specific ICP, indicating that the ICP is atomic site-specific[12].
230

231 As a fundamental application example, we examined Eu^{3+}-doped Ca_2SnO_4, which exhibits strong
232 red emission derived from the $^5D_0$–$^7F_2$ electric dipole transition of trivalent Eu ions (Eu^{3+}).
233 Considering the ionic radii similarity criterion, it would be more relevant to assume that Eu^{3+}
234 occupies the Ca^{2+} sites because Eu^{3+} is significantly close in size to Ca^{2+} than to Sn^{4+}. However,
235 Rietveld analysis of powder X-ray diffraction data revealed that Eu^{3+} equally occupied the Ca^{2+}
236 and Sn^{4+} sites, presumably because the local charge neutrality criterion dominates in this case.
237 An Eu and Y co-doped sample $Ca_{1.8}Y_{0.2}Eu_{0.2}Sn_{0.8}O_4$ was then synthesized because Y^{3+} ions with a
238 smaller ionic radius preferentially occupy smaller cation (Sn^{4+}) sites, expelling larger Eu^{3+} ions out
239 of the Sn^{4+} site into the larger Ca^{2+} site without changing the charge balance. As expected,
240 $Ca_{1.8}Y_{0.2}Eu_{0.2}Sn_{0.8}O_4$ exhibited a stronger emission than the $Ca_{1.9}Eu_{0.2}Sn_{0.9}O_4$ sample. The stronger
241 red emission in the co-doped sample is explained by the increased fraction of Eu^{3+} ions occupying
242 the asymmetric Ca site, coordinated by seven oxygen atoms, which enhances the electric dipole
243 moment compared to that of the symmetric six-coordinated Sn site.
244

245 A series of Eu and Y co-doped polycrystalline samples with nominal compositions of
246 $Ca_{1.9}Eu_{0.2}Sn_{0.9}O_4$ and $Ca_{1.8}Eu_{0.2}Y_{0.2}Sn_{0.8}O_4$ were prepared, and the site occupancies of the dopants
247 were determined by the present method.
248

249 **Figure 7** shows the ECP and ICPs of Ca-K, Sn-L, O-K, Eu-L, and Y-L for the $Ca_{1.8}Eu_{0.2}Y_{0.2}Sn_{0.8}O_4$
250 sample near the [100] zone. The Eu-L ICP was closer to the Ca-K ICP, whereas the Y-L ICP was
251 closer to Sn-L ICP. This suggests that the Eu and Y occupation sites could be biased, as expected.
252 The coefficients, α_{ix} for i = Ca, Sn, and x = Eu, Y derived using Eq. (1), where n_{Ca} = 2/3 and n_{Sn} =
253 1/3. The k-factors of the constituent elements are calibrated in advance using a reference
254 material with a known composition, the detailed discussion of which is found in [12]. The site
255 occupancies f_{ix} (Eq. (3)) of the impurities, and the impurity concentrations c of all the samples are

256 tabulated in **Table 1**.

258 In $Ca_{1.9}Eu_{0.2}Sn_{0.9}O_4$, Eu^{3+} occupied the Ca^{2+} and Sn^{4+} sites equally, consistent with the results of
259 the XRD-Rietveld analysis. In contrast, Eu^{3+} and Y^{3+} occupied the Ca^{2+} and Sn^{4+} sites at ratios of
260 approximately 7:3 and 4:6, respectively, in the co-doped samples, significantly biased as expected,
261 but also maintaining the charge neutrality condition within the present experimental accuracies[12].

263 **FIGURE AND TABLE LEGENDS:**
264 **Figure 1: Instrumental outlook.** Jeol JEM2100 S/TEM and its associated monitors, detectors, and
265 operation panel configurations.

267 **Figure 2: Layout of TEM control monitor (TCM).** Control windows necessary for the present
268 method are displayed and key functions and buttons are labeled.

270 **Figure 3: Left/right operation panels of the S/TEM.** (Left) Left operation panel (LOP). (Right)
271 Right operation panel. The function keys and operation knobs necessary for the present method
272 are labeled.

274 **Figure 4: Caustic spot image on the fluorescent screen.** The diameter of the spot ranges a few
275 centimeters on the screen, depending on the defocus value.

277 **Figure 5: Appearance of EDX control monitor.** Electron-channeling pattern (ECP) preview in
278 upper left panel specifies the area of measurement. For 1D tilting measurements, X-ray Linescan
279 is selected in the leftmost panel and the range of measurement is indicated by the yellow arrow
280 in the ECP preview. Periodic table in the lower left panel selects the elements of the ionization
281 channeling patterns (ICPs) to be displayed in upper right panel. Lower right panel displays the
282 accumulated EDX pattern in real-time.

284 **Figure 6: Experimental ECPs and ICPs.** (**A**: from left to right) ECP and ICPs of Ba-L, $T-K_a$, and $O-K_a$
285 emissions from $BaTiO_3$ obtained by beam-rocking near [100] zone axis. (**B**: from left to right) Same
286 as (A) near [110] zone axes. This figure has been modified from [12].

288 **Figure 7. ECP and corresponding X-ray ICPs from $Ca_{1.8}Eu_{0.2}Y_{0.2}Sn_{0.8}O_4$ by beam-rocking near the**
289 **[100] zone axis. (A)** ECP. (**B-F**) ICPs of $Ca-K_a$, Sn-L, $O-K_a$, $O-K_a$, Eu-L, and Y-L emissions, respectively.
290 This figure has been modified from [12].

292 **Table 1. Derived parameters (defined in text) of the samples of $Ca_{2-x}Eu_xSn_{1-y}Y_yO_4$ where (x, y) =**
293 **(0.2, 0.0) and (0.2, 0.2) respectively refer to Eu20 and Eu20Y20.**

295 **DISCUSSION:**
296 Critical steps in the protocol are the ability to accurately align the incident rocking beam that has
297 a small convergence angle with the pivot point, which is immobile at the specified area described
298 in steps 2.2–2.3. A collimated incident beam with a convergence semi-angle of approximately no
299 larger than 2 mrad was used. A beam size of 300 nm and diameter of 1 μm can be selected by

300 setting the condenser aperture #4 (10 μm in diameter) and #3 (30 μm) in the present hardware
301 system.
302
303 The advantages of the present method are that (i) no advanced STEM instruments such as
304 aberration-corrected STEM or even field emission electron gun is necessary; (ii) many sampling
305 points (e.g., ~4,000 points for a scan area of 64 × 64 pixels^2) can be automatically collected with
306 high efficiency, while operating the conventional STEM spectral imaging procedure on the
307 analyzer side, and (iii) multiple spectroscopic methods such as EDX, EELS, and
308 cathodoluminescence can be concurrently operated in a single integrated system, which enables
309 multimodal analysis[13].
310
311 Since the experimental ICPs can be precisely predicted by theoretical simulation, the method can
312 be applied not only to cases where the crystal of interest contains multiple inequivalent atomic
313 sites for a doped element[14]. Further extensions are ongoing, such as to detect the vacancy
314 concentrations and associated displacements of host elements, and even the ordering of dopants
315 segregated along the grain boundaries of ceramics. The present method can provide a significant
316 alternative technique applicable to relatively thick samples in contrast to atomic column-by-
317 column analysis using aberration-corrected STEM, which requires the preparation of very thin
318 high-quality samples (< 10 nm).
319
320 Atom site-selective electronic state analysis using TEM-EELS (HARECES) rather than EDX is
321 feasible[8-11]. For automatic measurement it is recommended to use 'ALCHEMI option' in a beam
322 controlling software 'QED,' running on the Gatan Microscope Suite, supplied by HREM Research
323 Inc[15]. In HARECES measurement, it is necessary to ensure that the transmitted beam is away from
324 the EELS detector position and perpendicular to the systematic row in the beam tilting sequence[8].
325
326 A limitation of this method is the minimum beam size of the incident electron beam, which limits
327 the minimum measured area to approximately 300 nm. This is due to the aberration of the TEM
328 lens system wherein the pivot center moves farther than the beam radius for a smaller beam size,
329 which could be amended in the future by modifying the TEM deflector lens current setting to
330 compensate for the beam wandering.
331
332 If the microscope used does not have beam-rocking mode, a very similar operation is achieved
333 using QED software, which also addresses the limitation, as the software can rectify the pivot
334 point moving even in the nano-beam mode. For S/TEMs manufactured by FEI Company (now part
335 of Thermo Fisher Scientific), TIA scripting, open-source code can manage all S/TEM functions and
336 attached detectors via a PC. Sequential EDX/EELS data acquisitions with successive incident beam
337 tilting were performed using the scripting program TIA running on the TEM imaging and analysis
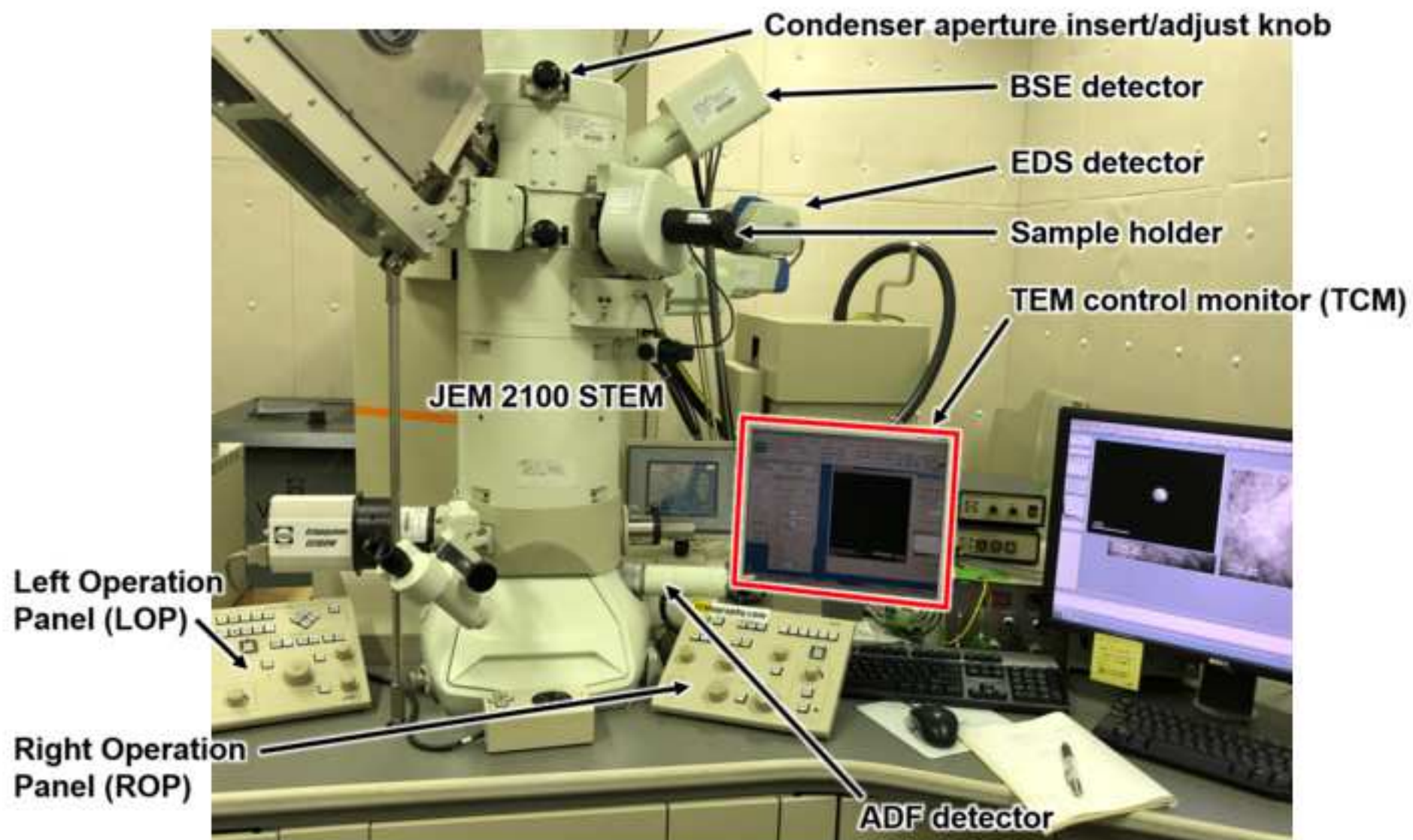338 platform[13].
339

344

DISCLOSURES:
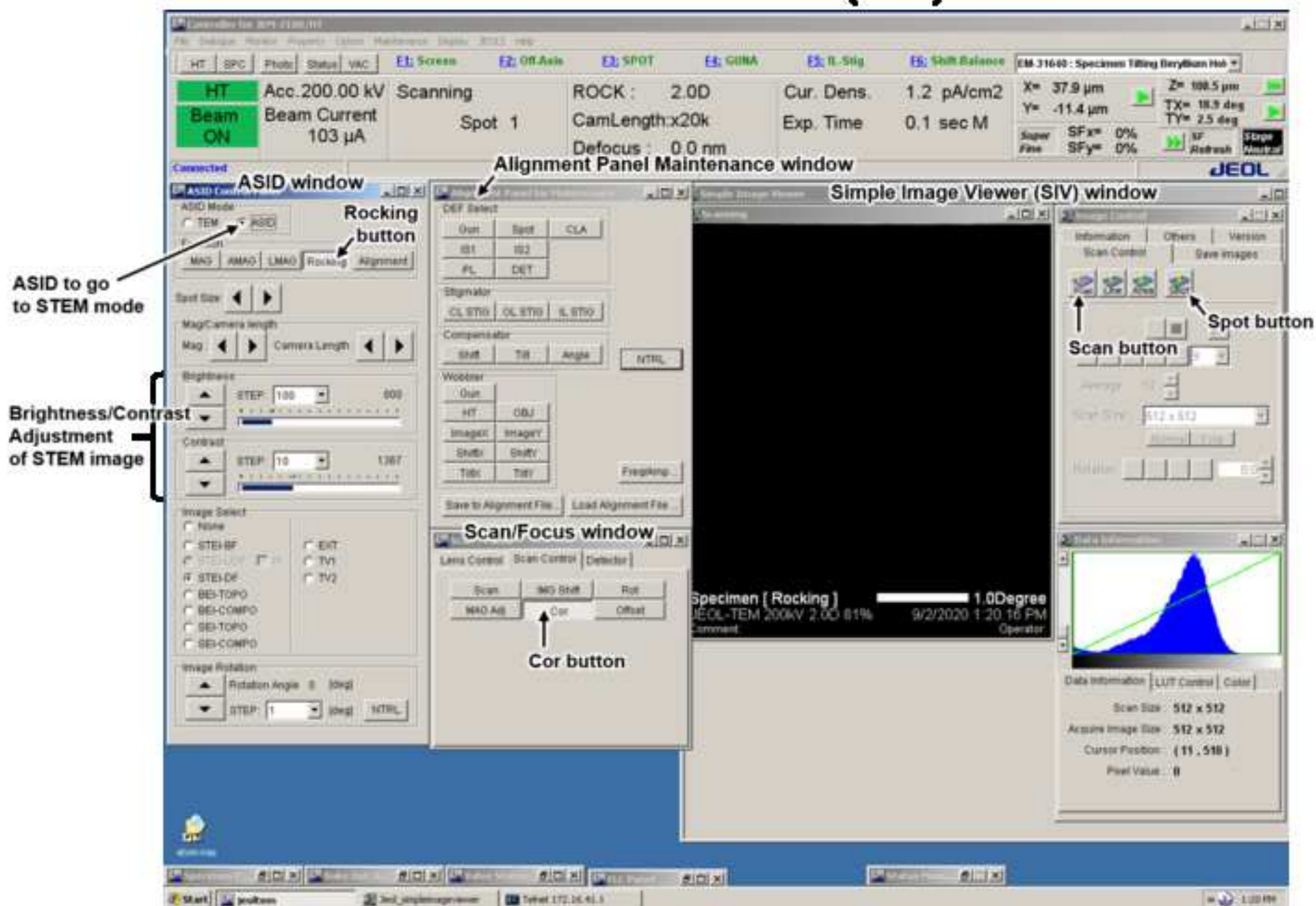
The authors have nothing to disclose.

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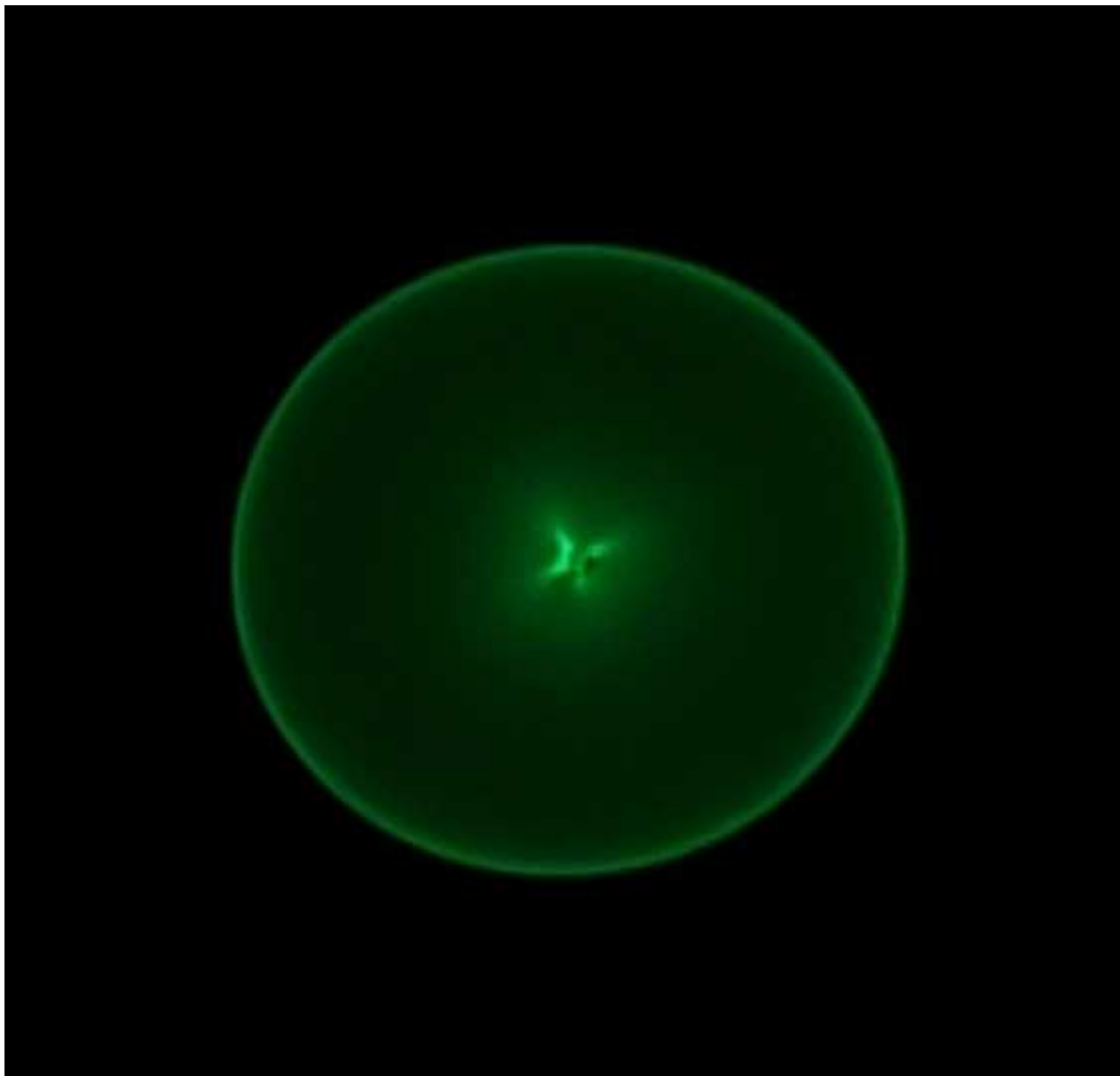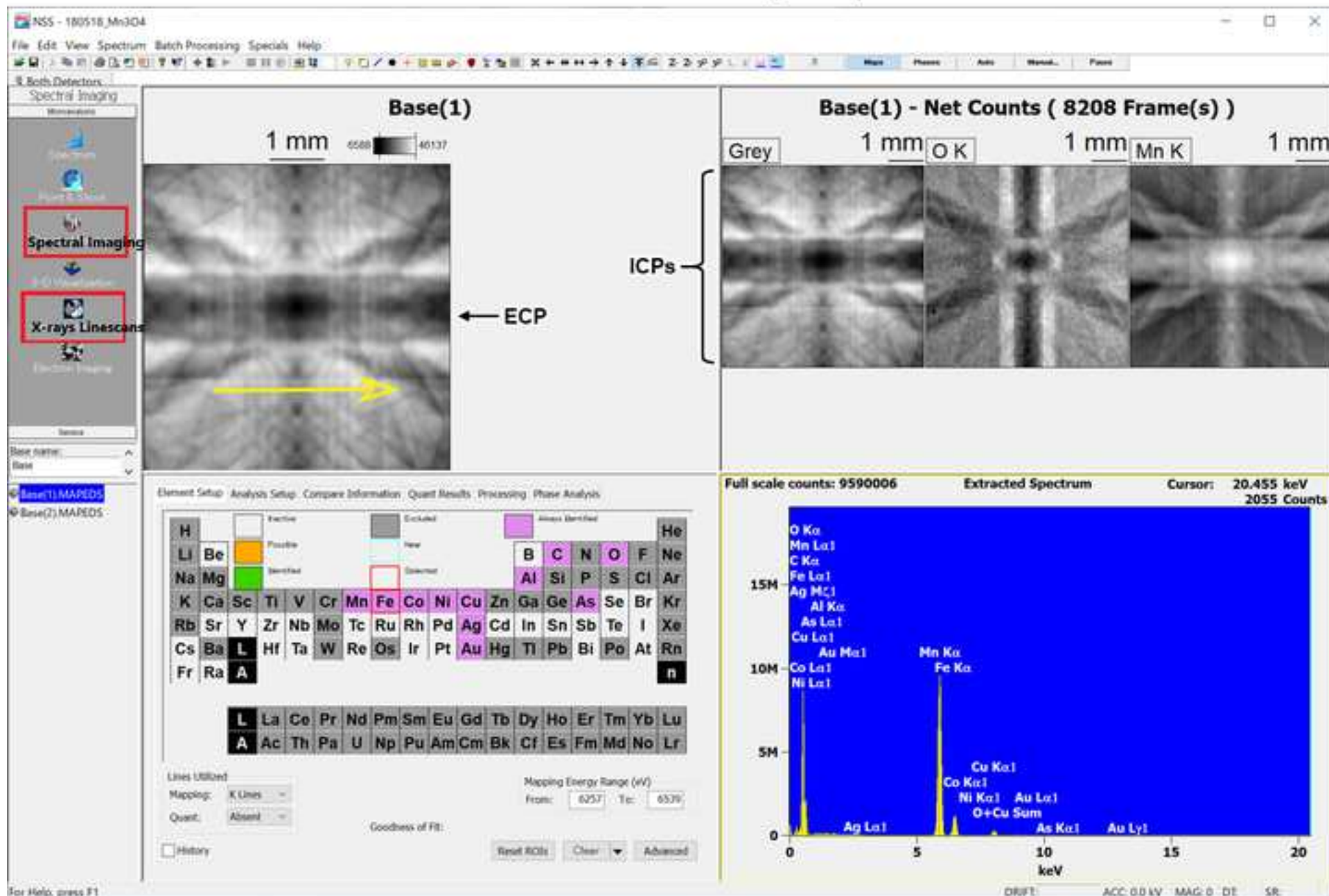15. https://www.hremresearch.com/Eng/plugin/QEDEng.html (2020).

382

Figure 1

Figure 1

Figure 2

Figure 3   Click here to access/download;Figure;Figure3.tif

Figure 3

Figure4

Figure5

EDS control monitor (ECM)

Figure6

Figure7
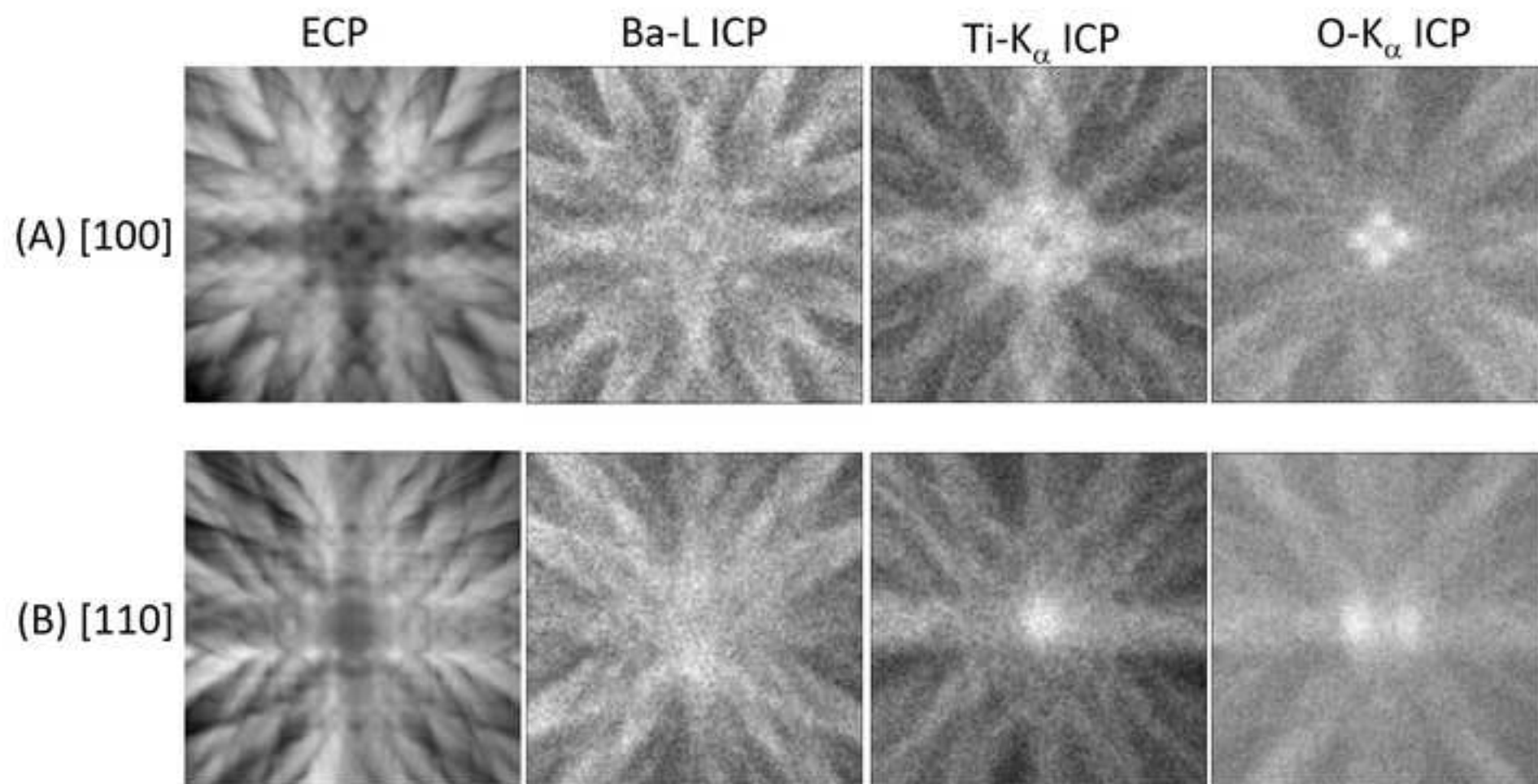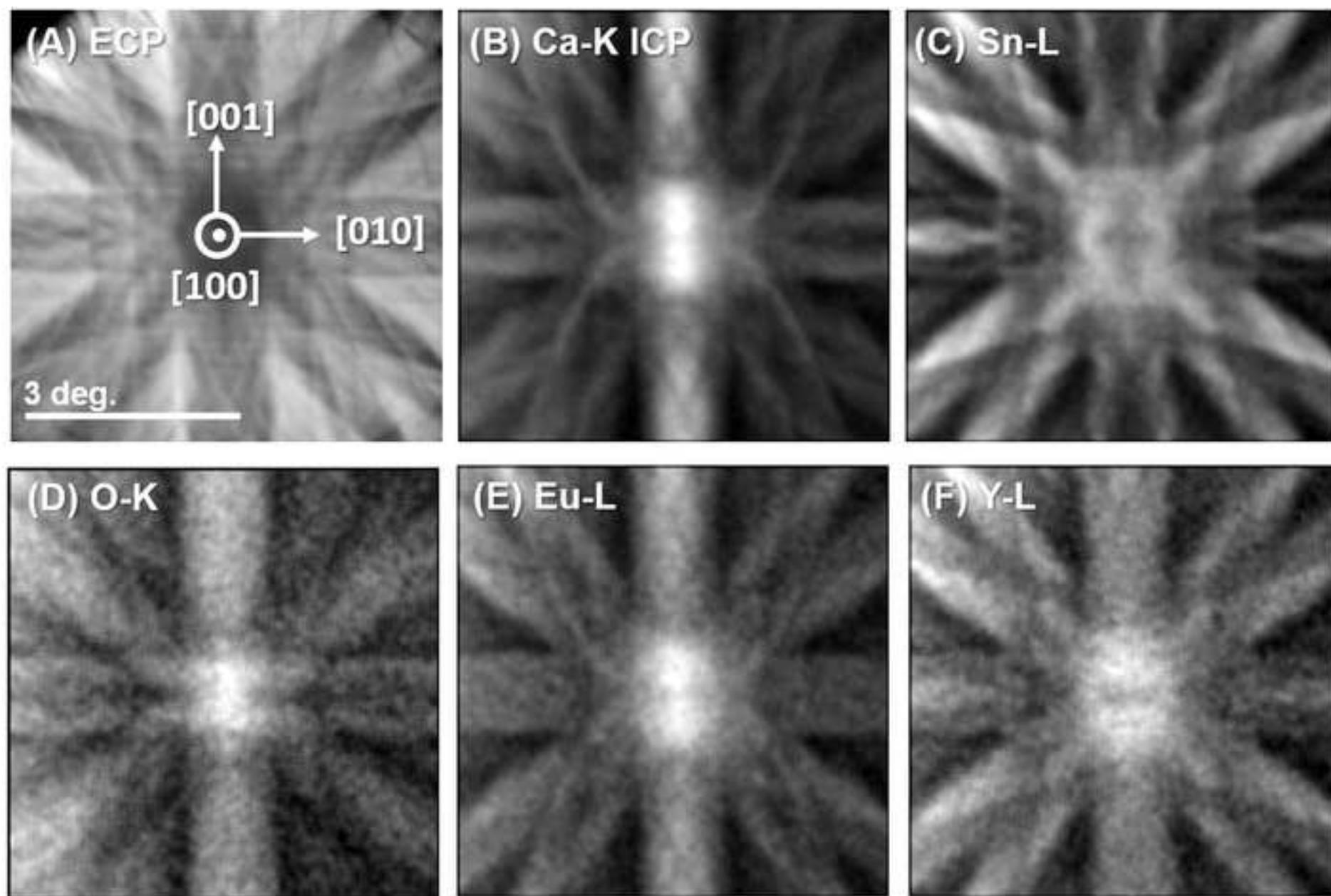
Sample	Dopant	α_{Ca}	α_{Sn}	f_{Ca}
$Ca_{1.9}Eu_{0.2}Sn_{0.9}O_4$	Eu	1.71±0.001	0.083±0.001	0.57±0.001
$Ca_{1.8}Eu_{0.2}Y_{0.2}Sn_{0.8}O_4$	Eu	0.162±0.001	0.077±0.001	0.78±0.003
	Y	0.040±0.002	0.265±0.009	0.28±0.002

f_{Sn}	c_x (x = Eu or Y)
0.43±0.002	0.061±0.001
0.22±0.008	0.088±0.006
0.72±0.001	0.118±0.004

Name of Material/ Equipment	Company	Catalog Number	Comments/Description
Electron Energy-Loss Spectrometer	Gatan Inc.	Enfina1000	Parallel EELS detector
Energy dispersive X-ray detector	JEOL Ltd.	SD30GV	EDS silicon drift detector
Gatan Microscope Suite (GMS)	Gatan Inc.	ver. 2.3.	Integrated software platform for controling cameras, detectors, S/TEM and data analysis
QED	HREM Research Inc.	for GMS 2.3 32bit	beam controlling software, running on the Gatan Microscope Suite
scanning transmission electron microscope	JEOL Ltd.	JEM-2100	Beam-rocking mode option in ASID controlling window
TEMCON	JEOL Ltd.		Control software for JEM 2100
Thermo NSS software	Thermo Fischer Scientific Inc., USA		EDS control software

JoVE62015R2

Quantitative atomic-site-analysis of functional dopants/point defects in crystalline materials by electron-channeling-enhanced microanalysis

by Masahiro Ohtsuka and Shunsuke Muto

Reply to editorial and reviewers' comments

Thank you so much for useful comments and we would like to reply to each comment in the following, described in red underneath each corresponding comment. We hope the present manuscript is now appropriate for publication.

<u>To Editorial comments:</u>

1. Please take this opportunity to thoroughly proofread the manuscript to ensure that there are no spelling or grammar issues.

We thank Editage (www.editage.com) for English language editing.

2. Please revise the lines 21-23, 47-50, 79-88, 242-261 to avoid overlap from previously published work "High-precision quantitative atomic-site-analysis of functional dopants in crystalline materials by electron-channeling-enhanced microanalysis"

We rephrased the specified texts to avoid overlaps. Please confirm if they are appropriate.

3. Please ensure that all text in the protocol section is written in the imperative tense as if telling someone how to do the technique (e.g., "Do this," "Ensure that," etc.). The actions should be described in the imperative tense in complete sentences wherever possible. Avoid usage of phrases such as "could be," "should be," and "would be" throughout the Protocol. Any text that cannot be written in the imperative tense may be added as a "Note." However, notes should be concise and used sparingly.

4. Line 111: Please define the abbreviations before use (ASID)

5. Line 111: Please ensure that the figure number mentioned is correct (TCM is loaded as Figure 3)

6. Line 119: Please elaborate on the fluorescent viewing screen.

7. Line 118: Please ensure that the figure number mentioned is correct (Uploaded Figure 2 has LOP and ROP)

8. Line 131: Please clarify the step mentioned to understand how the condenser is introduced.

9. Line 141: Please mention how the sample and the pivot point height are matched using the Z control keys.

10. Line 146: Please mention how is the annular dark-field detector placed at the beam position.

11. Line 228: Please use the following format for the figure and table legends. Identify the panel label before the panel description. Figure 1: Figure heading. (A) Panel description. (B) Panel description.

We revised the text according to the comments #3-11.

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We obtained copyright permission and uploaded the file to our account. The figures are cited in the corresponding legends, as suggested.

13. Please ensure that the figure numbers mentioned in the text and figure legends match with the uploaded figures.

We confirmed them.

_____

To Reviewers' comments:

Reviewer #1:

I have no major concerns with this manuscript. It gives a comprehensive background for the methodology and describes the motivation and potential interest to other scientists well. The protocol is described in detail and demonstrated in a sufficient manner. The description on the "protocol" section is very detailed, technical, and specific to the JEOL 2100 instrument. This is appropriate, but to make it more relevant to users of other microscopes,

I would consider prefacing this with a brief but more general discussion of the experimental considerations needed for a successful experiment.

Thank you very much for the positive comments to our manuscript. We prefaced about the present protocol specific to a JEM2100 STEM and provide some information in the final paragraph of Discussion section how users of other microscopes should realize the present protocol.

Reviewer #2:

Manuscript Summary:

This manuscript uses a rocking-beam transmission electron microscopy technique to perform quantitative, site-specific microanalysis. The chemical composition and occupancy of various lattice sites is investigated via energy-dispersive X-ray spectroscopy. The technique is applied to investigate preferential site occupation of dopant atoms in co-doped Ca_2SnO_4. This report appears useful, and I recommend publication. If the suggestions below can be incorporated, this work will be even more widely useful to the research community.

Major Concerns:

This manuscript could be improved by adding data that is mentioned but not shown. Specifically, I recommend to include a figure with the single-doped $Eu:Ca_2SnO_4$ sample in order for the reader to see the direct comparison with the data for the co-doped sample, which would more effectively illustrate the utility of the technique. Second, it is also mentioned that "The line scan function in the EDX controlling software enables 1D tilting measurements of a systematic row of reflections." It would be useful to show this in a figure so that the reader can see this directly. Finally, although not necessary for publication, adding an example using EELS (HARECES) would make this report even more useful to readers.

We thank so much reviewer#2 for the positive and useful comments. We can provide the ICPs of single-doped sample, though they were recorded around the different zone axis and the sample thickness was not the same, which we are afraid would not so effective nor obvious to show the differences between the two samples. This is another advantage of the present method because the analysis fully takes the dynamical effects into account, which ensures quantitative trustability of the results.

Secondly, we revised the protocol and associate figure to include description how 1D tilting experiment is achieved.

Finally readers can easily access several useful examples of HARECES by referring to our published papers cited in the text.

Minor Concerns:
The figure captions are mislabeled for Figs. 5 & 6.

Thank you so much for pointing out the mislabels. We revised the captions.

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