Identifying transient defects in exsolution of nanoparticles by semi-quantitative ABF STEM imaging

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Background

Exsolution enables direct growth of transition metal nanoparticles embedded in metal oxide supports, which are attractive for various electrochemical and catalytic applications for energy conversion and storage. In exsolution, the transition metal is first incorporated into the metal oxide matrix, and exsolve as metal nanoparticles under reducing conditions by diffusion, reduction, nucleation and growth. Foreign cations in perovskites usually substitute the A- or B-site depending on their relative size with respect to the host species. Small transition metals are thus commonly expected to prefer the B-site. However, the exsolution process is observed to be relatively fast, which is unexpected based on the low diffusivity of the B-site with strong covalent bonds to the oxygen octahedra. In similar perovskite systems, it has been suggested that small transition metals favor an interstitial position with square planar coordination adjacent to A-site vacancies [1], as illustrated in fig (a). In this work, the Ni position in A-site deficient La-doped $SrTiO_3$ in the initial stages of exsolution is explored using semi-quantitative STEM. The knowledge obtained will support the development of a microscopic model of the exsolution phenomenon, which can be applied for optimized process strategies for energy conversion and storage applications based on the anchored nanoparticles.

Method

Powders with nominal stoichiometry $La_{0.2}Sr_{0.7}Ti_{0.9}Ni_{0.1}O_3$ were synthesized by solid-state reaction. Exsolution of nickel metal particles were performed by reduction under 5% H_2 in Ar atmosphere at 800 °C for 30 minutes. The relatively large difference in atomic number (Z) between O (Z=8) and Ni (Z=28) is exploited in the STEM images by projecting the matrix along the <100> orientation to isolate the potential interstitial Ni position on the oxygen column. A FEI Titan G2 60-300 instrument with a DCOR Cs probe corrector was operated at 200 kV with a convergence angle of 33.1 mrad to obtain an ABF image from collection angles of 8-34 mrad, suitable to image the lighter element columns. The Z-dependency was identified using the multislice method as implemented in the abTEM package [2] by simulating STEM images with the experimental conditions for a thickness-defocus series of an ideal $SrTiO_3$ structure, and for an atomic model with an interstitial Ni and A-site vacancies. The experimental column intensities were determined by fitting 2D Gaussians using the Atomap package [3]. A statistical-model based approach based on Akaike and Bayesian Information Criterion (AIC, BIC) was utilized for fitting the intensity histogram to identify the most likely independent intensity contributions. The semi-quantitative approach proposed by Aarholt et al. [4] was adopted to identify the point defect from the relative intensities of the columns.

Results

As a rule of thumb, the intensity of ABF images is proportional to Z^a with a = 1.3 which originates from a balance between elastic and thermal scattering that are most dominant for lighter and heavier atoms, respectively.[5] However, changes in collection angle, thickness, defocus, and atomic number may alter this Z-dependency. By simulating a thickness-defocus map of ABF images of the ideal <100>-orientated $SrTiO_3$ structure with the employed collection angles, a linear Z-dependency is identified from the ratio between the intensities of the Ti- and Sr-columns, as seen in fig 1(b). From the simulated ABF image of the atomic models with interstitial Ni located on the O-column in fig (c), a split in a histogram of integrated intensities of the columns is expected to be observed in the experimental ABF image.

In fig (d), the experimental ABF image of the exsolved sample on the <100> orientation is presented with the inset illustrating the location of the 2D Gaussians fitted to the atomic columns. A statistical-model approach based on the integrated classification likelihood is adopted to avoid under- and overfitting the histogram of intensities, and to avoid biased interpretations. From fitting an increasing number of Gaussians, one calculates a score based on maximizing the log-likelihood function of the fit while penalizing the number of components and their complexity, which in our case, was done according to AIC and BIC. The log-likelihood function has a negative pre-factor, meaning a lower score indicates a higher likelihood of a valid physical description of the experimental data by the model. Both criteria agree on a three-component model for the optimized fit of the histogram of the integrated intensities of the 2D Gaussians of the O-column, seen in fig (e) and (f). There is, however, no guarantee of a physical validity of the model despite a good fit, but from the interpretation of the ratio of the mean value of component 2 and 3, the ratio becomes 1.23 ± 0.14 which results in an average Z of 9.83 ± 1.11 given a linear Z-dependency and interpreting component 2 as the O-column. The calculated value of 1 Ni for every 10 O provides an average Z of 9.82. While the absolute quantification of the number of Ni on the O-columns is challenging, the results indicate the presence of a foreign species on the columns which may be Ni. The first component can be interpreted as O-columns with a high number of oxygen vacancies generated due to the reducing environment.

Conclusion

A semi-quantitative approach utilizing the open-source packages abTEM and Atomap was adopted to identify the defect position of Ni in A-site deficient La-doped $SrTiO_3$ upon exsolution under reducing atmospheres. Simulated multislice images show a linear Z-dependency for the experimental conditions used. The intensity distribution of the O-columns in the experimental ABF image is best modelled using three Gaussians. The component of highest intensities holds a relative mean value to the main component that agrees with a calculated intensity ratio for the presence of Ni using linear Z-dependency. The interstitial defect position of Ni is expected to play an important role in the diffusion step of the exsolution process.

Graphic:

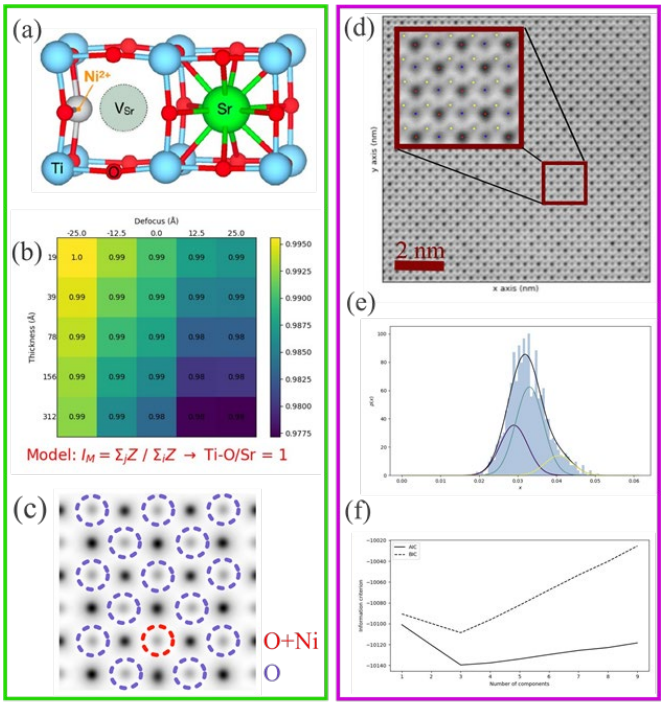

Fig: (a) Atomic model of interstitial Ni adjacent to an A-site vacancies in SrTiO3. (b) Quantification of relative intensity of Ti-O/Sr for a thickness-defocus map shows a linear Z-dependency. (c) <100> ABF STEM image of atomic model with the defects. (d) Experimental ABF STEM image with magnified image of fitted gaussians on the Sr- (red), Ti- (blue), and O-column (yellow). (e) Histogram of intensity from integration of 2D gaussians fitted to the experimental O-columns with the three optimized components identified using the (f) plot of the Akaike and Bayesian Information Criterion.

Keywords:

Point defects, Quantitative STEM, Open-source

Reference:

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