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Atomic imaging of $Ba_{0.6}K_{0.4}BiO_3$ using low-dose techniques

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Atomic resolution images of $Ba_{0.6}K_{0.4}BiO_3$ have been obtained at electron-dose levels of 10^2 $e^-/Å^2$ using a slow-scan CCD camera on a high-resolution electron microscope; at this dose level electron-beam damage can be avoided. The superconducting material is a clean perovskite without evidence for any distortions such as charge-density waves. At higher dose levels modulations appear which, from measurements of the desorbing species under low-energy electron radiation, are due to ionization damage and loss of oxygen.

1. Introduction

The family of materials $Ba_{1-x}K_xBiO_3$ is known to superconduct with an optimum doping level of $x=0.4$ leading to a transition temperature of 30 K [1]. Understanding the microstructure of this material has, however, proved to be exceedingly difficult. Standard diffraction analyses indicate that the material is a simple perovskite, see e.g. ref. [2], but some early experimental data using electron diffraction [3] suggested a more complicated structure. Further analysis showed that this was due to very rapid electron-beam damage [4]. Because of this damage it has proved impossible to date to obtain images of this material, and although all the available diffraction data are consistent with a simple perovskite, there are still some uncertainties in the literature.

In this note we report experimental high-resolution imaging of $Ba_{0.6}K_{0.4}BiO_3$ at total electron-dose levels much lower than those employed for conventional imaging using a slow-scan CCD camera. At these dose levels, of the order of 100 $e^-/Å^2$, we have been able to avoid electron-beam damage of the material. We confirm that this material is a simple perovskite. Oxygen-ion desorption under low-energy electron irradiation was observed, indicating that the relevant damage mechanism is radiolytic, i.e. due to low-energy electronic excitations.

2. Experimental methods

The samples used were conventional bulk samples which were crushed and mounted onto holey carbon films for electron-microscopy analysis. The slow-scan CCD camera used was a Gatan 679 which is a 1024×1024 array with 24 micron pixels. The overall conversion efficiency was two electrons per count, which can be compared to standard electron-microscope film which requires (based upon a recent calibration [5] using an optical density range of 2 and 25 micron pixels) about fourteen electrons per count. The camera was on a JEOL-4000 microscope which was operated at 400 kV, and the images were directly stored onto a Macintosh II computer. Standard minimum-exposure techniques were used with astigmatism corrected away from the area of interest with a magnification of $800\times$ on the camera corresponding to a pixel size of 0.3 Å.

The experimental work was performed at the Center for High Resolution Electron Microscopy at

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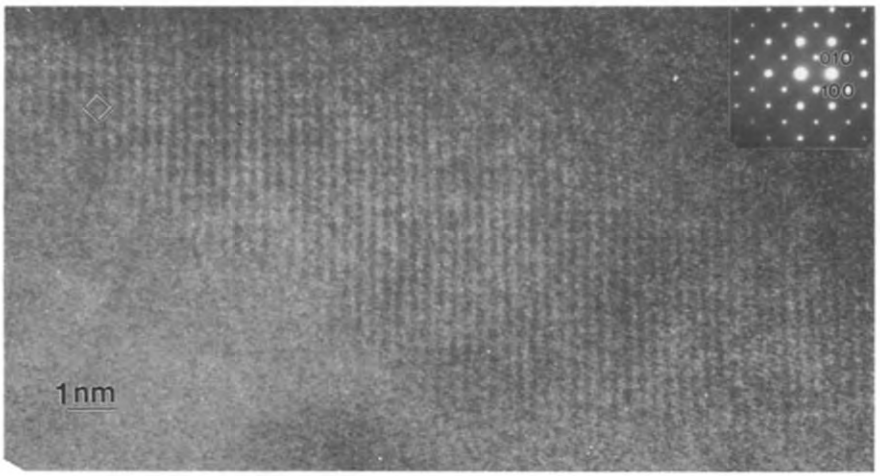

Fig. 1. [001] high-resolution image obtained under conditions of 1 s exposure and an average of 10 counts per pixel, corresponding to a beam dose of 250 $e^-/Å^2$. Neither the image nor the diffraction pattern (lower left) indicate modulations.

Arizona State University with some of the later analysis performed either at Northwestern or Argonne National Labs after transferring the images using ftp. The oxygen desorption measurements were performed using a SIMS mass spectrometer in a VG ESCA-SIMS lab, and irradiating the samples was done using a 1 kV electron beam.

3. Results

The normal electron-beam flux level used for high-resolution electron microscopy is about 10^4 $e^-/Å^2$ s with doses per picture of about 10^5 $e^-/Å^2$, although much lower doses can be used. At this level the material damaged within one second. Using diffraction patterns to investigate the onset of damage via the appearance of modulations, it was confirmed that the damage was very slow at a flux of 100 $e^-/Å^2$ s. It was not clear from the experimental data whether the damage was total dose dependent, or both dose and dose-rate dependent. From previous work [6–8] on materials which lose oxygen by an electronic excitation mechanism (see below) we have established that the dose rate is very important, and the process is highly non-linear. Approximately this flux level was used for the experimental images, with an exposure of one second corresponding to about ten counts per pixel. At this dose it was possible to obtain images

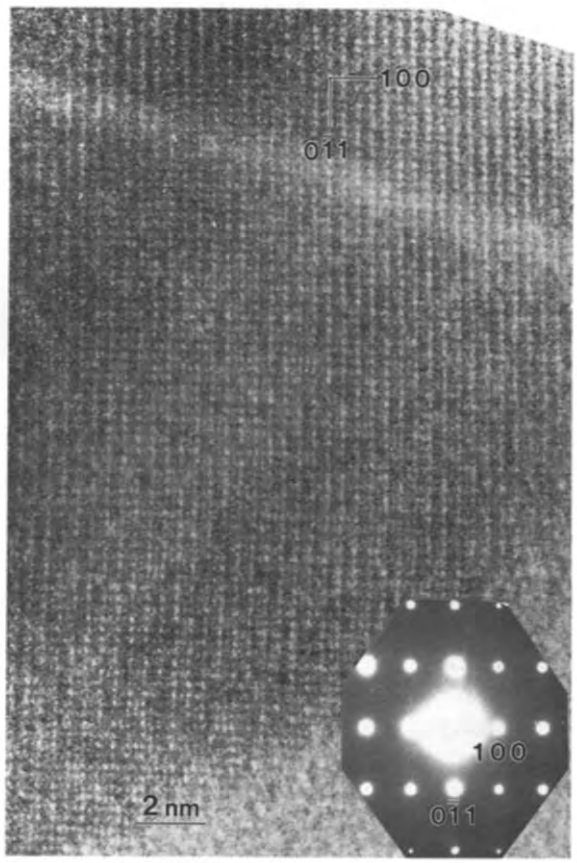

Fig. 2. A [011] high-resolution image at a beam flux of 550 $e^-/Å^2$ s showing a perfect structure.

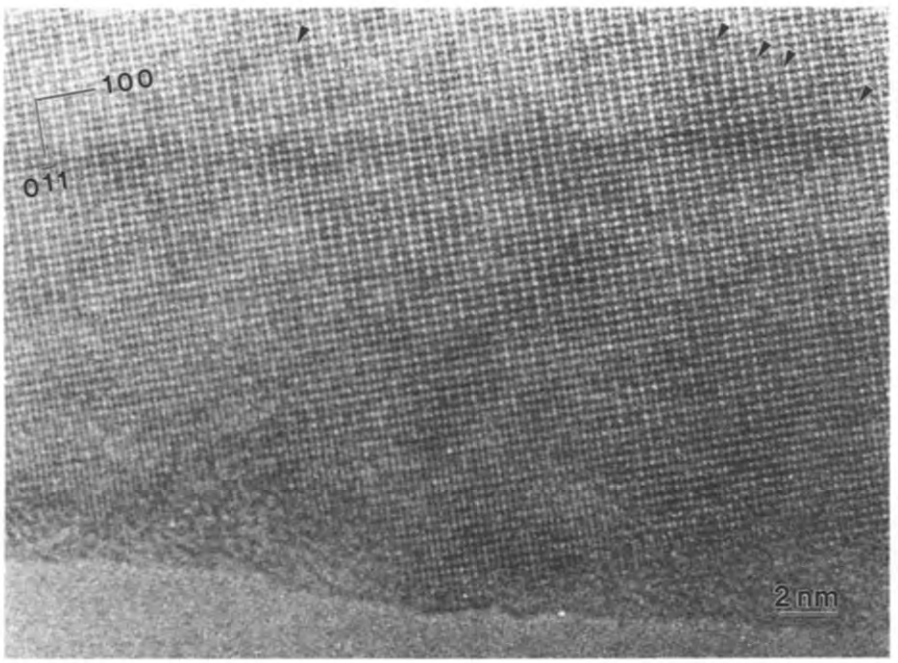

Fig. 3. At the higher dose rate of 1200 $e^-/Å^2$ s, the [011] image shows a slight modulation, as arrowed, after an exposure of several seconds.

from thin regions, but it was hard to use with the thicker regions because there was too little signal due to absorption effects, as shown in fig. 1 for the [100] zone.

The most informative zone is [110], where the barium (potassium) and bismuth (001) planes alternate with a separation of 2.1 Å as shown in fig. 2. For reference, we should add that at these dose levels it was possible to obtain focal series and obtain fairly good agreement with calculated images; these do not add significantly to the science and will therefore not be shown. No modulations, stacking faults or other defects such as planar defects were observed. At a slightly higher dose level of 10^3 $e^-/Å^2$ weak modulations in the thicker regions (where there is more total scattering) started to appear indicating the onset of damage as shown in fig. 3.

It has been suggested that the damage mechanism in these materials is due to knock-on [4]. As a simple test, we checked the ion-desorption spectrum using low-energy electron irradiation and detecting these using a SIMS mass-spectrometer, see e.g. refs [9] and [10]. It is very well established that positive oxygen ions desorb from many maximum valence oxides, see e.g. ref. [11], and the same processes lead to electron-beam damage in the microscope, see. e.g. refs. [6–9]. The data clearly showed oxygen ions, a signature of a low-energy excitation process rather than knock-on.

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