Three-dimensional atomic imaging of Y and (B\textsubscript{12})\textsubscript{13} clusters in YB\textsubscript{56} by HREM and crystallographic image processing

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Abstract

The three-dimensional atomic image of YB\textsubscript{56} was obtained by inverse Fourier transformation of three-dimensional phases and amplitudes in three high-resolution images along [100], [110] and [111] of YB\textsubscript{56} crystals. After crystallographic image processing, the image directly showed the three-dimensional potential map of the crystal, which showed (B\textsubscript{12})\textsubscript{13} clusters and Y atom positions. The present method would be useful for three-dimensional structure analysis in nanoscale regions.

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Keywords: High-resolution electron microscopy; Three-dimensional image; Boride; Image processing; Cluster

1. Introduction

High-resolution and radiation resistant monochromators are required for soft X-ray synchrotrons in the 1–2 keV energy region. Gadolinium gallium garnet and beryl are used for monochromators because of the d-spacing of these materials. However, crystal quality of these materials is low, and they suffer from synchrotron radiation damage. Recently, high quality YB\textsubscript{56} single crystals, with the YB\textsubscript{66} structure \cite{1,2}, have been synthesized for the use as high-resolution and synchrotron-radiation-resistant monochromators \cite{3,4}. After the discovery of the application of YB\textsubscript{56} as a soft X-ray monochromator, the crystal structure of YB\textsubscript{56} (\textit{Fm\textsubscript{3}}c, \textit{a}=2.34600 nm) has been determined using single crystal X-ray diffractometry \cite{5}. The boron framework of YB\textsubscript{56} is basically made of eight icosahedra (B\textsubscript{12})\textsubscript{13} and eight non-icosahedral B\textsubscript{80} clusters (totally 1584 boron atoms). The site occupancy of yttrium in YB\textsubscript{56} is 0.575, which suggests that the peanut-shaped ‘Y-sites’ (a pair of yttrium atoms) in the boron clusters should be occupied in most cases by only one yttrium atom \cite{1,2,5}.

High-resolution electron microscopy (HREM) is a powerful method for direct observation of the atomic structures of advanced materials and clusters \cite{6–8}. In the previous works \cite{9,10}, the Y-holes in the YB\textsubscript{56} were directly detected in the boron clusters by HREM, and the ‘local’ structure model was proposed for yttrium atom arrangements. In addition, a residual index (\textit{R}_\text{HREM} = \Sigma I_{\text{obs}} - I_{\text{calc}}/\Sigma I_{\text{obs}}) was used for image analysis to determine the crystal thickness and defocus value of the observed images, and differential images showed the atomic disordering of the boron atoms around the Y-holes \cite{11,12}. Although, surface structure and photoconductivity had been investigated \cite{13,14}, few observation have been reported yet on the three-dimensional potential distribution in the YB\textsubscript{56} crystals in nanoscopic region \cite{15}.

The purpose of the present work is to obtain the three-dimensional information of (B\textsubscript{12})\textsubscript{13}=B\textsubscript{156} clusters and Y atoms in the YB\textsubscript{56} crystals with nanoscopic sizes by using HREM. In the present work, crystallographic image processing and residual index were applied for image analysis, which is expected to provide quantitative three-dimensional atomic positions. A slow-scan CCD camera, which has high linearity and electron sensitivity was used to record HREM images digitally.
2. Experimental procedures

High quality single crystals of YB$_{56}$ were grown by an indirect heating floating-zone method [3,4]. The molten zone was heated by radiation from an inductively heated tungsten ring. The tungsten ring was placed between the work coil and the molten zone. A set of growth conditions for getting high quality YB$_{56}$ single crystals are as follows: growth direction $\langle 100 \rangle$, growth rate $10$ mm/h, rotation rate $6$ rpm (growth axis), atmosphere $\text{He} 0.3 \text{ MPa}$, composition of crystal $\text[B]/[\text{Y}] = 56$, and composition of the molten zone $\text[B]/[\text{Y}] = 40$.

3. Results and discussion

In order to get three-dimensional atomic arrangements, three-dimensional HREM observations have been carried out. The $\langle 100 \rangle$, $\langle 110 \rangle$ and $\langle 111 \rangle$ directions of the YB$_{56}$ crystals were selected in order to obtain the three-dimensional potential map of the YB$_{56}$. Fig. 2(a)–(c) show HREM images of the YB$_{56}$ recorded along the $\langle 100 \rangle$, $\langle 110 \rangle$ and $\langle 111 \rangle$ directions, respectively, using the slow-scan CCD camera. The right sides of the three images are the thinnest regions of the YB$_{56}$ crystals. To get an optimal resolution ($<0.016 \text{ nm/pixel}$), the digital images were recorded at microscope magnifications of $1.0 \times 10^6$. The images were recorded close to the Scherzer defocus condition ($-49 \text{ nm}$). Fourier transforms of Fig. 2(a)–(c) are shown in

![Fourier transforms of HREM images](image)

Samples for HREM observations were prepared by dispersing crushed materials on holey carbon grids. HREM observations were performed with a $400 \text{ kV}$ electron microscope (JEM-4000EX) having a resolution of $0.17 \text{ nm}$. The electron microscope is equipped with a slow-scan charge-coupled-device (CCD) camera (Gatan SSC model 694) and a LaB$_6$ cathode. The area of detection of the CCD camera is $1024 \times 1024$ pixels with a pixel size of $24 \times 24 \mu \text{m}$. Flowchart of image processing for three-dimensional imaging is shown in Fig. 1. For image processing of the observed HREM images, Semper (Synoptics Ltd), Digital Micrograph (Gatan Inc. CA, USA), TriView and CRISP (Calidris Corp. Stockholm, Sweden) software were used.
Fig. 2(d)–(f), respectively. Open circles indicate the resolution limit of the electron microscope of 0.17 nm.

In order to observe the potential distribution more clearly, crystallographic image processing was carried out for the Fourier transforms in Fig. 2. The reciprocal lattice was indexed, and the lattice distances were estimated using the positions of the strongest peaks in the transform. The local background and reflections below the resolution limit (0.17 nm) were subtracted, and the amplitudes and phases of the peaks were determined. The 46 independent reflections with errors of $\sim 10\%$ (residual indices) were obtained from the three HREM images, as listed in Table 1. Before correcting the phases, the phase origin was determined by investigating the origin shift that gave the best accordance with the phase conditions for the two-dimensional space group (plane group). The effect of the contrast transfer function of the objective lens was corrected. The defocus values were determined by using residual indices between experimental and calculated HREM images. The corrected phases refined by using crystallographic symmetrization [16,17], based on the plane groups, were used for the reconstruction of the Fourier transform.

**Table 1**

| Indices $(h\ell l)$ | Symmetrized phases | Amplitudes from Fourier transform |
|-------------------|--------------------|---------------------------------|
| 0 2 0             | 180                | 1217                            |
| 0 4 0             | 180                | 5679                            |
| 0 6 0             | 0                  | 9213                            |
| 0 8 0             | 0                  | 3502                            |
| 0 10 0            | 180                | 7079                            |
| 0 12 0            | 180                | 1215                            |
| 2 2 0             | 180                | 1014                            |
| 2 2 2             | 0                  | 2612                            |
| 2 2 4             | 180                | 2831                            |
| 2 4 0             | 180                | 2790                            |
| 2 4 2             | 180                | 1165                            |
| 2 4 4             | 0                  | 4745                            |
| 2 4 6             | 0                  | 1222                            |
| 2 6 0             | 180                | 546                             |
| 2 6 2             | 0                  | 4790                            |
| 2 6 4             | 180                | 1222                            |
| 2 6 6             | 180                | 1877                            |
| 2 6 8             | 0                  | 2551                            |
| 2 8 0             | 0                  | 962                             |
| 2 8 2             | 180                | 581                             |
| 2 8 4             | 180                | 443                             |
| 2 10 0            | 0                  | 235                             |
| 2 10 2            | 0                  | 1141                            |
| 2 12 0            | 0                  | 191                             |
| 2 12 2            | 0                  | 416                             |
| 4 4 0             | 0                  | 2093                            |
| 4 4 4             | 0                  | 1637                            |
| 4 4 8             | 0                  | 3643                            |
| 6 6 0             | 180                | 1027                            |
| 6 6 8             | 180                | 1735                            |
| 6 6 10            | 180                | 2776                            |
| 6 8 0             | 180                | 634                             |
| 4 8 0             | 180                | 1677                            |
| 4 8 4             | 0                  | 3847                            |
| 4 10 0            | 180                | 1077                            |
| 4 10 4            | 180                | 481                             |
| 4 12 0            | 180                | 398                             |
| 6 6 6             | 180                | 981                             |
| 6 8 6             | 0                  | 791                             |
| 6 8 0             | 180                | 2059                            |
| 6 8 4             | 0                  | 300                             |
| 6 10 0            | 180                | 1115                            |
| 6 10 6            | 180                | 225                             |
| 8 8 0             | 0                  | 1546                            |
| 8 8 8             | 0                  | 329                             |
| 8 10 0            | 180                | 175                             |

Pore structures in mesoporous materials were evaluated by a three-dimensional method [18], and the porosity was directly estimated from three-dimensional images in mesoscale. In the present work, a full three-dimensional reconstruction of YB$_{56}$ nanoscopic crystals with the size of $14\text{ nm} \times 14\text{ nm} \times \sim 4\text{ nm}$ was successfully carried out from HREM images by using crystallographic image processing. Structure analysis of single crystal X-ray diffractometry is the most important technique for studying periodic crystals with the size over several tens.
Fig. 3. (a) Three-dimensional potential map of $\text{YB}_{56}$ obtained by inverse Fourier transformation of three-dimensional phases and amplitudes. (b) Perspective view of $\text{YB}_{56}$.

Fig. 4. Projected images of three-dimensional image along (a,b) 100 and (c,d) 111 of $\text{YB}_{56}$, with different image intensities.
micrometers. However, nanoscopic crystals with the size down to a few nanometers can be studied only by electron microscopy and diffraction because of the strong interactions of electrons with matters.

4. Conclusion

The 46 independent phases and amplitudes were extracted from Fourier transform of high-resolution images, which were taken along the [100], [110] and [111] directions under the conditions of weak-phase objective approximation, of YB_{56} crystals with the size of 14 nm × 14 nm × ~4 nm. After the revision of the contrast transfer function by using residual index, inverse Fourier transformation was carried out, and the three-dimensional potential map of YB_{56} was obtained. The image directly showed the potential map of the YB_{56} crystal with ~1600 atoms in the unit cell, and positions of Y and (B_{12})_{13} clusters were directly imaged. The three-dimensional potential map will be useful for three-dimensional structure analysis in nanoscale regions of crystal materials.

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References

[1] S.M. Richards, J.S. Kasper, The crystal structure of YB_{56}, Acta Crystallogr. 25 (1969) 237–251.
[2] G.A. Slack, D.W. Oliver, G.D. Brower, J.D. Young, Properties of melt-grown single crystals of YB_{68}, J. Phys. Chem. Solids 38 (1977) 45–49.
[3] K. Kamimura, T. Tanaka, S. Otani, Y. Ishizawa, Z.U. Rek, J. Wong, Floating zone growth of monochromator grade crystals of YB_{66}, J. Cryst. Growth 128 (1993) 429–434.
[4] T. Tanaka, Y. Ishizawa, J. Wong, Z.U. Rek, M. Rowen, F. Schäfers, B.R. Müller, Development of a YB_{66} soft X-ray monochromator for synchrotron radiation, Jpn. J. Appl. Phys. Ser. 10 (1994) 110–113.
[5] I. Higashi, K. Kobayashi, T. Tanaka, Y. Ishizawa, Structure refinement of YB_{62} and YB_{68} of the YB_{66}-type structure, J. Solid State Chem. 133 (1997) 16–20.
[6] T. Oku, Direct analysis of atomic structures of advanced ceramics by high-resolution electron microscopy, J. Ceram. Soc. Jpn 109 (2001) S17–S24.
[7] T. Oku, S. Nakajima, Atomic structures of surface and interface in (Hg,Tl,Pb)-based superconductors studied by high-resolution electron microscopy, Solid State Commun. 124 (2002) 305–309.
[8] T. Oku, Direct observation of B_{44} and B_{116} clusters by high-resolution electron microscopy and crystallographic image processing, Solid State Commun. 127 (2003) 689–693.
[9] T. Oku, A. Carlsson, L.R. Wallenberg, J.-O. Malm, J.-O. Bovin, I. Higashi, T. Tanaka, Y. Ishizawa, Digital HREM imaging of yttrium atoms in YB_{56} with YB_{66} structure, J. Solid State Chem. 135 (1998) 182–193.
[10] T. Oku, Digital high-resolution electron microscopy of atomic disordering in YB_{66}, J. Electron Microsc. 49 (2000) 41–52.
[11] T. Oku, J.-O. Bovin, Atomic disordering in YB_{66} detected by high-resolution electron microscopy with residual indices, Phil. Mag. A 79 (1999) 821–834.
[12] T. Oku, J.-O. Bovin, I. Higashi, T. Tanaka, Y. Ishizawa, Atomic structures of YB_{66} studied by digital high-resolution electron microscopy and electron diffraction, J. Mater. Res. 16 (2001) 101–107.
[13] C.L. Perkins, M. Trenary, T. Tanaka, Structure and chemistry of the YB_{66}(100) surface, J. Solid State Chem. 133 (1997) 31–35.
[14] Y. Sakairi, M. Takeda, K. Kimura, T. Tanaka, Modulated photoconductivity in YB_{66}, J. Solid State Chem. 133 (1997) 195–197.
[15] T. Oku, Three-dimensional imaging of YB_{66} by high-resolution electron microscopy, Chem. Commun. 2002; 302–303.
[16] S. Hovmöller, A. Sjögren, G. Farrants, M. Sundberg, B.-O. Marinder, Accurate atomic positions from electron microscopy, Nature 331 (1984) 238–241.
[17] T.E. Weirich, R. Ramlau, A. Simon, S. Hovmöller, X.D. Zou, A crystal structure determined with 0.02 Å accuracy by electron microscopy, Nature 382 (1996) 144–146.
[18] Y. Sakamoto, M. Kaneda, O. Terasaki, D.Y. Zhao, J.M. Kim, G. Stucky, H.J. Shin, R. Ryoo, Direct imaging of the pores and cages of three-dimensional mesoporous materials, Nature 408 (2000) 449–453.