Quantitative strain-field measurement of 1:1 B-site cation ordered domains and antiphase boundaries in Pb(Sc$_{1/2}$Ta$_{1/2}$)O$_3$ ceramics by high-resolution transmission electron microscopy

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Quantitative strain measurements of the 1:1 B-site cation ordered domains, antiphase boundaries, and dislocations in a highly ordered Pb(Sc$_{1/2}$Ta$_{1/2}$)O$_3$ ceramic have been carried out by high-resolution transmission electron microscopy and geometric phase analysis. A phase shift of $\pi$ between two adjacent ordered domains across an antiphase boundary is determined unambiguously. The maximum in-plane strain and lattice rotation induced by a dislocation are 9.5% and 5.4°, respectively. In a defect-free antiphase boundary, the maximum in-plane strain and lattice rotation are 1.8% and 0.9°, respectively. The strain mainly concentrates inside the antiphase boundary.

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Lead scandium tantalate, Pb(Sc$_{1/2}$Ta$_{1/2}$)O$_3$ (PST), is a well-known order-disorder perovskite ferroelectric material. It has been studied extensively because of its pyroelectric property and order-disorder behavior. The Pb$^{2+}$ cations occupy the A-sites of the perovskite structure, while Sc$^{3+}$ and Ta$^{5+}$ cations occupy the B-sites at the center of the oxygen octahedra. The Sc$^{3+}$ and Ta$^{5+}$ cations may occupy the B-site sites randomly or can develop 1:1 NaCl-type order on the {111} planes. The disordered or intermediate ordered PST shows the ferroelectric relaxor behavior but becomes a normal ferroelectric below the Curie temperature in highly ordered state. The configuration of the two B-site cations strongly influences the physical properties of PST, such as electrical properties and phase transition behavior. In contrast, the elastic properties of PST are rarely reported. Besides polarization, the microscopic strain states and elastic energy are the important parameters in the theories of ferroelectric/relaxor. Besides chemical heterogeneity, strain is considered as a source of the random fields in relaxors.

The degree of 1:1 cation order ($S$) can be characterized by Raman spectroscopy, x-ray, neutron and electron diffraction. However, the spatial and size distribution of the ordered domains in a PST grain can be obtained by dark-field imaging and high-resolution transmission electron microscopy (HRTEM). In a Bragg-filtered HRTEM image, an antiphase boundary (APB) can be distinguished from the disordered domains. A phase shift of $\pi$ between the superstructure lattice fringes occurs across an APB. However, the above techniques are unable to give the quantitative structural information such as strain.

The geometric phase analysis (GPA) (Ref. 22) performs the measurement of local displacement with respect to a reference region in a HRTEM image and then calculates the corresponding strain tensor $e_{ij}$ and rotation $\omega_{ij}$. This method has already been applied to a number of quantitative HRTEM studies. A particular set of fringes in a HRTEM image can be selected by applying a filter on its Fourier component $g$ and the intensity is described as

$$ I_g(r) = A_g(r) \exp(iP_g(r)), $$

where the amplitude $A_g(r)$ and phase $P_g(r)$ represent the contrast level and location of the fringes. The relative phase shift induced by a small displacement of the fringes $u(r)$ with respect to a reference lattice can be measured,

$$ P_g(r) = -2 \pi g \cdot u(r). $$

The two-dimensional displacement field can be obtained by two noncollinear $g$,

$$ u(r) = -\frac{1}{2\pi} [P_{g_1}(r)a_1 + P_{g_2}(r)a_2], $$

where $a_1$ and $a_2$ are the lattice vector in real space corresponding to $g_1$ and $g_2$, respectively. The strain tensor and rotation for a small deformation is given by the derivatives of $u(r)$,

$$ \varepsilon_{ij} = \frac{1}{2} \left( \frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right) \quad \text{and} \quad \omega_{xy} = \frac{1}{2} \left( \frac{\partial u_x}{\partial y} - \frac{\partial u_y}{\partial x} \right). $$

Highly ordered PST samples ($S=0.86$) were fabricated using mixed-oxide route. TEM samples were prepared by polishing and then Ar$^+$ ion-milling. The HRTEM study was carried out at room temperature in a 200 kV FEI Tecnai F20ST microscope ($C_z=1.2$ mm). The quantitative analysis of the images was done by the package GPA phase (HREM Research Inc.). A Lorentzian filter with radius of 0.75 nm$^{-1}$ ($|g_{100}|/3$) was applied. HRTEM images of a Si crystal were used to evaluate the detectivity of our microscope. In a defect-free region in Si, the fluctuation in the measured in-plane strain and rotation are ±0.5% and ±0.2°, respectively. The images were carefully selected to avoid the influence of imaging artifacts on the GPA results, such as contrast reversals and thickness changes. Image delocalization does not contribute significantly to this study. It can be estimated by

$$ \Delta R = |\nabla \chi(g)| = \lambda |g| \Delta f + C_3 \lambda^3 |g|^3, $$

where $\chi$ is the aberration function, $\lambda$ is the electron wavelength (0.0025 nm), and $\Delta f$ is the defocus (~100 nm). If we
The power spectrum of the HRTEM image is shown in Fig. 1. The APB is revealed by the discontinuity of phase. A phase jump from 0 to 0° indicates no change in fringe spacing. The position of the APB is shown in the GPA. The maps of the in-plane strain fields are high intensity of two unit cells. The domains are separated by a 3 nm wide APB. It was indexed according to space group $Pm3m$. The high intensity of $g_{110}$ indicates the presence of the highly ordered domains. In the phase images shown in Figs. 1(c) and 1(d), a region in the OD1 far from the APB is selected as the reference in GPA. The value of the phase in OD1 is zero on average, and the fluctuation is less than $0.08\pi$, indicating no change in fringe spacing. The position of the APB is revealed by the discontinuity of phase. A phase jump from 0 to $\pi$ (or $-\pi$) is caused by the superstructure fringes in two adjacent ordered domains shifted relatively by half a period.

In order to characterize the local lattice deformation, the $(110)$ and $(001)$ lattice fringes ($g_{110}$ and $g_{001}$) are selected in the GPA. The maps of the in-plane strain fields ($e_{xx}$, $e_{yy}$, and $e_{xy}$) and lattice rotation ($\omega_{xy}$) are shown in Figs. 2(a)–2(d), respectively. The values of $e_{xx}$ and $e_{yy}$ in the defect-free regions, for example, in OD1, are fluctuated about $\pm 1.0\%$; whereas the $e_{xy}$ and $\omega_{xy}$ vary at $\pm 0.6\%$ and $\pm 0.2\%$, respectively. The values of the shear strain and rotation are close to the detectivity ($0.5\%$ and $0.2\%$). The observed average values of $e_{xx}$ and $e_{xy}$ indicate that a very small deformation occurred. It is highly likely related to the local distortions due to the random shifts in the Pb$^{2+}$ cations. The equivalent displacement calculated from $e_{xx}$ and $e_{xy}$ is about $0.20$–$0.40$ Å that is similar to the x-ray diffraction results. Zhukov et al. suggested that in a highly ordered PST, the Pb$^{2+}$ cations shift randomly away from the average center about $0.24$–$0.30$ Å. These nanoscale distortions reduce the crystal symmetry from cubic in the disorder phase or from rhombohedral in the low-temperature ordered phase to a lower one. Therefore, the interface between two different phases can contain local strain.

FIG. 1. (Color online) (a) HRTEM image of two ordered domains (labeled as OD1 and OD2). The APB is outlined by white dashed lines. (b) The power spectrum of the HRTEM image. $g_{121/21/2}$ and $g_{121/21/2}$ are indicated by the black and white arrows, and the corresponding phase images are shown in (c) and (d), respectively.

FIG. 2. (Color online) In-plane strain tensor components (a) $e_{xx}$, (b) $e_{yy}$, and (c) $e_{xy}$, and (d) lattice rotation $\omega_{xy}$. The region of the APB can be seen in (c) and (d).

FIG. 3. (Color online) Profile of (a) $e_{xx}$, (b) $e_{yy}$, (c) $e_{xy}$, and (d) $\omega_{xy}$ along $X$-$Y$ marked in Figs. 2(a)–2(d), respectively.

Consider $g_{110}$, the delocalization is $\approx 8$ Å, that is, less than two unit cells.

Figure 1(a) is a [110] HRTEM image of two ordered domains. The domains are separated by a 3 nm wide APB. The power spectrum of the HRTEM image is shown in Fig. 1(b). It was indexed according to space group $Pm3m$. The equivalent displacement calculated from $e_{xx}$ and $e_{xy}$ is about $0.20$–$0.40$ Å that is similar to the x-ray diffraction results. Zhukov et al. suggested that in a highly ordered PST, the Pb$^{2+}$ cations shift randomly away from the average center about $0.24$–$0.30$ Å. These nanoscale distortions reduce the crystal symmetry from cubic in the disorder phase or from rhombohedral in the low-temperature ordered phase to a lower one. Therefore, the interface between two different phases can contain local strain.

Several defects are observed on the strain-field maps. According to their characteristic strain fields, we deduce that those are dislocations. Such kind of crystal defect is often observed in the highly ordered domains because it acts as...
a fast diffusion channel during annealing to increase the degree of 1:1 order.\textsuperscript{7} Figures 3(a)–3(d) are the line-scan profile along “X-Y” marked in Fig. 2 in which a dislocation was included. The maximum value of $e_{x\text{xx}}$, $e_{x\text{xy}}$, and $\omega_{x\text{y}}$ are 7.5%, 9.5%, and $-5.4\%$, respectively.

In Figs. 2(c) and 2(d), the APB is recognized on the maps of $e_{x\text{y}}$ and $\omega_{x\text{y}}$. The line-scans across the defect-free APB along the mark “A-B” are shown in Figs. 4(a) and 4(b), respectively. The sinusoidal-like profiles are observed in both line-scans. This strain region is 6 nm across, that is, wider than the APB. The maximum values of $e_{x\text{y}}$ and $\omega_{x\text{y}}$ are about 1.5% and 0.9%, respectively, which are smaller than those in dislocations. The values of $e_{x\text{y}}$ and $\omega_{x\text{y}}$ outside APB diminish to the typical ones ($\sim 0.5\%$ and $0.2\%$) in the ordered domains. As a result, such small lattice deformation concentrates inside the APB and only extends to both sides of ordered domains about 1.5 nm (approximately four unit cells). Apparently, their influential strain field is shorter than that induced by dislocations. It is worthy to note that this kind of strain cannot be revealed by x-ray or neutron diffraction. However, our observation of strains in APB is consistent with the results of the convergent-beam electron diffraction (CBED) study\textsuperscript{19} in which small departures from the exact general symmetry of the second-order Laue-zone ring were observed in the defect-free APBs. It was concluded that the presence of a strain gives rise to the slight deviation in the symmetry in the CBED pattern.

The stress field can be obtained using the theory of elasticity.\textsuperscript{24,25} At the moment, it is not available because the measurement of elastic property in immediate or highly ordered PST lacks in the literature and several Brillouin scattering studies show that the elastic constants of disordered PST vary with the degree of cation order.\textsuperscript{9,10}

The present results deserve additional theoretical consideration and experimental studies. Strain or displacement field contributes to the parameters related to the energy gradient, elastic energy, and all electromechanical coupling. Those are essential to modeling the structure and growth of the macroscopic domain in ferroelectric/ferroelastic or the nanopolar regions in relaxors.\textsuperscript{11,12,14,31} It is also interesting to experimentally investigate the local strain in PST with different degrees of order and other order-disorder perovskite oxides.

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