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Raman spectroscopy evaluation of piezoelectric materials

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Recent instrumental progress, especially in data processing for a prompt, large-area screening (including non-destructive in-depth sampling), has made Raman spectroscopy a promising analytical tool for quantitative technological characterizations of piezoelectric materials. The Raman tool suits well quantitative assessments of structural changes and micromechanical behaviors. We show here a fully three-dimensional evaluation of domain textures and their statistical distributions in terms of of orientation angles, and a quantitative analysis of stress tensor in piezoelectric materials by polarized Raman spectroscopy.

1. Raman tensorial formalisms governing complex crystallographic structures

Practical applications of polarized Raman spectroscopy to quantitatively unfold three dimensional crystallographic information are yet in their infancy, mainly due to the complexity of the selection rules intrinsically governing the behavior of complex crystallographic structures. In this research, a three-dimensional Raman formalism is first put forward in order to determine the full set of Raman tensor elements for various structures, and then the Raman tensor elements are experimentally located through the characterization of the angular dependence of selected vibrational modes. **Figures 1**(a) and (b) show the experimentally determined angular dependence of intensities for the A_1(TO) and E(TO) Raman bands of tetragonal $BaTiO_3$ (BT), rspectively. Solid lines represent mathematical best-fitting curves, from which the Raman tensor elements are derived.

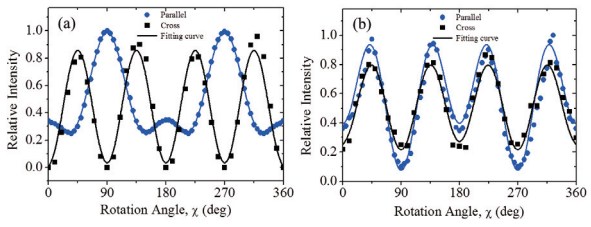

Fig. 1 Experimentally determined angular dependence of intensities for the (a) A_1(TO) and (b) E(TO) Raman bands of tetragonal BT under selected polarization geometries and their best-fitting curves.

A successive step to the determination of the Raman tensor elements resides in a spectroscopic algorithm enabling one to extract quantitative relationships that link the Raman tensor elements to Euler angles in space. The application of such algorithm entails a fully 3-D evaluation of domain texture can be experimentally provided for BT.

2. Domain structure analyses in barium titanate single crystals and multilayer ceramic capacitors (MLCC)

An example of application of the proposed Raman analysis is given here for the domain texture developed in the neighborhood of a Vickers indentation printed on the *a*-plane of a BT single-crystal. Experimental results of in-depth Raman mapping around the indentation print, shown in Fig. 2(a), are given in terms of relative band intensities (cf. the two sets of maps in (b) and (c) for $RI^{\parallel}_{270/305} = I^{\parallel}_{A_g} / I^{\parallel}_{B_g+E_g}$ and $RI^{\parallel}_{720/305} = I^{\parallel}_{A_g+E_g} / I^{\parallel}_{B_g+E_g}$, respectively) and in-plane and out-of-plane Euler angles (set of maps in (d) and (e) for χ and θ angles, respectively). Texture features were collected at depths of 0, 5, 10, 15, 20, and 25 μm from the surface of the crystal.

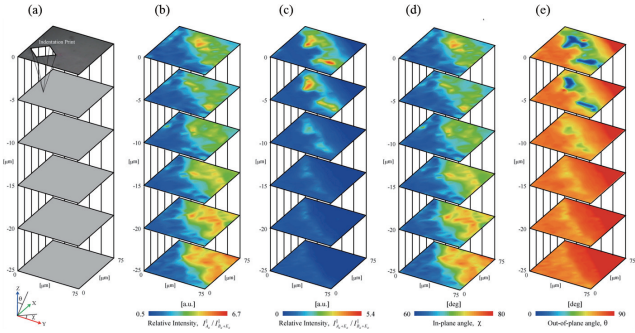

Fig. 2 Schematics of in-depth mapping results; (a) schematic draft of the domain texture in-depth; (b) and (c): in-depth mapping of relative intensities, $RI^{\parallel}_{270/305} = I^{\parallel}_{A_g} / I^{\parallel}_{B_g+E_g}$ and $RI^{\parallel}_{720/305} = I^{\parallel}_{A_g+E_g} / I^{\parallel}_{B_g+E_g}$, respectively; and, (d) and (e): maps of χ and θ angles, respectively.

In addition, an estimate of the convolutive effects expected in mapping domain textures owing to the transparency of BT is shown, according to a quantitative evaluation of the finite size of the optical probe. Experimental calibrations of the three-dimensional response functions of the optical probe along selected crystallographic directions of BT enabled a full spatially resolved probe deconvolution. Figure 3 shows an experimental

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profile of *c*-axis out-of-plane angular orientation as collected on the sample surface along a direction perpendicular to the indentation edge, and the deconvoluted profile of domain orientation corrected from probe convolutive effects on the detected Raman relative intensity.

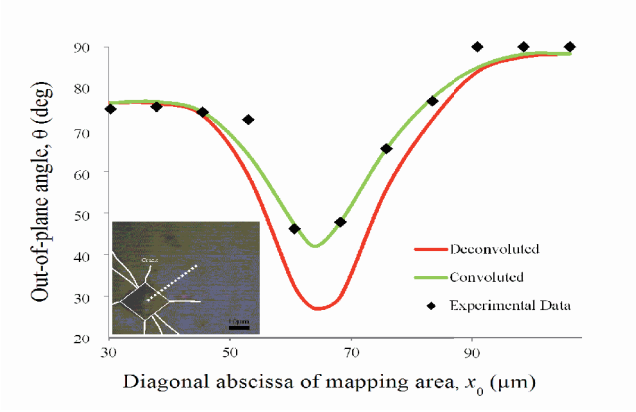

Fig. 3 Experimental, convoluted and deconvoluted profiles along the *c*-axis of out-of-plane angular orientation as collected on the sample surface along a direction perpendicular to the indentation edge (cf. dotted line in the micrograph shown in inset).

This application was chosen as a typical scenario encountered in domain orientation assessment, but the method can be easily extended to the analysis of polycrystalline samples with more complex domain configurations. Figure 4 shows the maps of Euler's angles in the interlayer zone and the corner zone of an MLCC device.

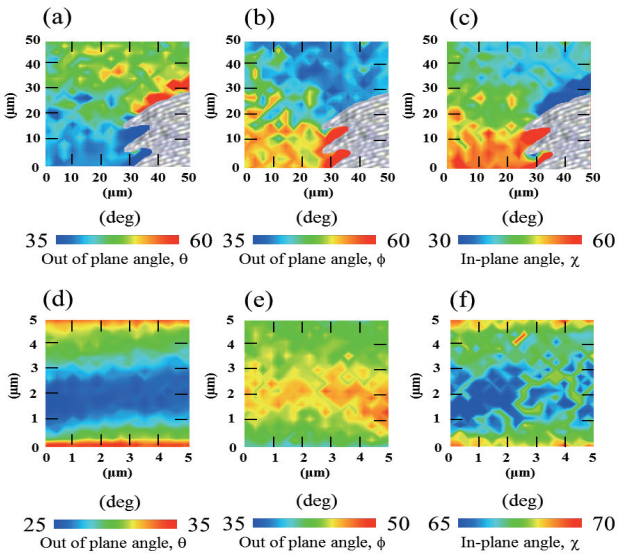

Fig. 4 Maps of Euler's angles in the interlayer zone ((a)-(c)) and the corner zone ((d)-(f)) of an MLCC

The angles define the average orientation in space of the *c*-axis of the tetragonal perovskitic lattice contained in the domain texture.

Both patterns and degree of alignment are a consequence of the complex residual stress field developed in the MLCC during cooling from manufacturing process. As can be seen, Raman assessments based on the presented algorithm quantitatively revealed the local domain structures.

3. Stress tensor dependence of the polarized Raman spectrum of tetragonal barium titanate

The stress tensor dependence of the polarized Raman spectrum of barium titanate in its tetragonal structure has been theoretically elucidated and the phonon deformation potential (PDP) constants of its A_1(TO) and E(TO) vibrational modes measured by means of a spectroscopic analysis of single crystalline samples under controlled stress fields despite the complications arising from the development of domain textures under stress and to phonon dispersion effects. Uncoupling the effects of crystallographic orientation and spatial convolution allows the establishment of a working algorithm for stress analysis in this perovskitic material. Figure 5 shows an example of analysis stress field surrounding an indentation crack tip in BT.

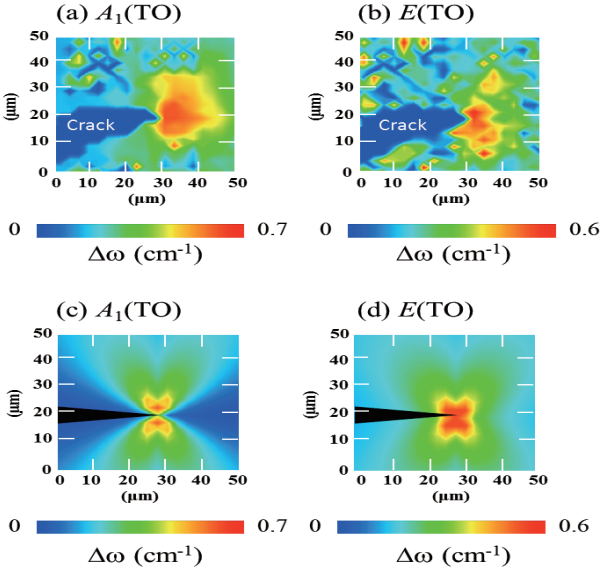

Fig. 5 Maps of experimental and calculated spectral shifts of the A_1(TO) ((a) and (c), respectively) and E(TO) ((b) and (d), respectively) modes around an indentation crack tip.

The highly graded (multiaxial) stress field stored at the crack tip required both rationalizing the dependence of oblique phonons on crystal orientation and applying a spatial deconvolution routine based on the three-dimensional response of the Raman probe. The present findings open the way to tensor resolved Raman analysis of the complex strain fields stored in advanced piezoelectric devices.