

In-situ observation on domain switching of PLZT via Raman spectroscopy

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Abstract: An in-situ and nondestructive technique was proposed and established for the study of domain switching in PLZT ceramics via observation of Raman spectrum changes based on the Raman light scattering principle and the soft mode theory. A Vickers indent was introduced into the polarized PLZT specimen so that the Raman spectrum change associated with the domain switching as induced either by an applied electric field or by a stress field surrounding the tip of the Vickers indent crack was in-situ measured and studied using this established technique. The relation between the domain switching and the measured Raman spectrum was discussed. It is well demonstrated that this technique can sensitively detect and measure the domain switching via the observation of Raman spectrum changes. The results confirm that Raman spectrum intensity is directly attributed to the change of the polarization direction of the incidence and scattered lights with respect to the direction of the average polarization direction of the domain in the polarized specimen. When the two directions are parallel, the induced polarizability tensor of the specimen would be enhanced and give rise to a higher intensity for Raman scattering light.

Key words: ferroelectric ceramics; Vickers indent; domain switching; Raman observation

1 Introduction

Domain switching is considered a major cause for degradation and failure of ferroelectric materials[1–3]. Observation of domain switching in the materials is an important way to investigate mechanism for degradation and failure of ferroelectric materials under applied electric or stress field. In order to understand the relationship between the property degradation and the domain switching during the service of the ferroelectric materials, some in-situ observation techniques have been established. For example, an in-situ XRD method was employed to quantitatively investigate the domain switching and corresponding strain field change under applied electric field as well as the relation between the domain switching and the macro property during fatigue[4]. An in-situ TEM technique was also employed to observe the domain switching[5]. All these techniques greatly enhanced our understanding of the domain switching in the ferroelectric materials. However, the spot of an X ray beam would normally cover many crystal grains in one time and thus an in-situ XRD

measurement can only give a sort of statistic domain information over a macro scale. On the other hand, because a TEM specimen must be prepared by cutting and being thinned down to be electron transparent, an in-situ TEM observation must thus be destructive and the data that observed cannot be directly correlated to bulk materials in real service. Moreover, TEM specimen must be placed in a high vacuum chamber and thus the observation is costly and inconvenient.

Raman spectroscopy is a promising and effective method to study ferroelectric phase transformation and ferroelectric properties[6, 7]. The spot of a laser beam used for Raman incidence light can be very small (typically of about 3 μm) and thus suits for the detection of the domain switching in a highly localized area of micro scale. Therefore, it is possible to obtain a uniform domain-switching signal within one single crystal grain of micrometers. In addition, Raman spectrum measurement does not need a high vacuum chamber or electron-transparent specimen for operation as does in TEM. Thus, an in-situ observation and measurement for ferroelectric domain switching can be realized easily with such a flexibility of Raman spectrum analysis.

In this study, we proposed and established an in-situ, nondestructive method for observation and measurement of domain switching via Raman spectrum technique based on Raman light scattering principle. A Vickers indent was introduced into the polarized PLZT ceramic specimen and the Raman spectrum change of the domain switching as induced either by an applied electric field or by a stress field surrounding the tip of the Vickers indent crack was examined and studied using our established technique. The relation between the domain switching and the measured Raman spectrum change was discussed.

2 Experimental

The dimension of PLZT (Pb(Zr_{0.53}Ti_{0.47})O₃) ceramic specimen was 8 mm × 8 mm × 0.8 mm. The specimen was prepared into in-plan polarized (polarized along the 8 mm × 8 mm plan). The measurement of Raman spectrum was performed on LabRam type from Dilor Inc., France. The laser excitation light source was Ar ion with a wavelength at 632 nm and a spot size about 3 μm. In addition, an in-situ observation via optical microscopy was used to determine the site illuminated by the laser so as to ensure that the laser beam illuminated in the middle of each crystal grain (the grain sizes in the ceramic specimen were 3–5 μm) and the effect of grain boundary was excluded. In order to fulfill the study on the domain switching as induced by Vickers indentation and the corresponding Raman spectrum change, the following sets of experiments were carried out.

For the sake of a facile in-situ observation and measurement of domain switching via Raman spectra, and a safety of the two electrodes were fabricated on surface of the specimens as follows: a groove of 0.2 mm wide was etched in the middle of the 8 mm × 8 mm surface on the specimen by lithography. The abruptness and flatness of the electrodes are fairly good, thus ensuring a uniform voltage to be applied between the two electrodes. When a voltage of 200 V is applied, a field strength of 1 000 V/mm, which is the coercing electric field value of the specimen, E_c , will be produced in the ceramic between the two electrodes.

In order to study the influence of the 90° domain switching that really occurs in the specimen on the Raman spectra, we consider 90° domain switching at crack tips as induced by an applied electric field. We chose a specimen originally in-plan polarized. As shown in Fig.1, we introduced an indentation of Vickers type on the part of the specimen surface where there is no electrode (the indentation of Vickers type was introduced using a HV-1000 type micro sclerometer with a load of 4.90 N and a loading time of 20 s). Firstly, we observed the original Raman spectrum around the crack tips,

including the front edges of the crack (from spot 1 to spot 6 as illustrated in Fig.2(a)) and the region surrounding the crack (from spot 7 to spot 13 in Fig.2(b)). When the electric field reapplied to the specimen is larger than E_c , the crack will propagate at the four corners of the indentation, and then we also in-situ observed and measured the change of Raman spectrum around the crack tip from spot 1 to spot 13 in the same specimen.

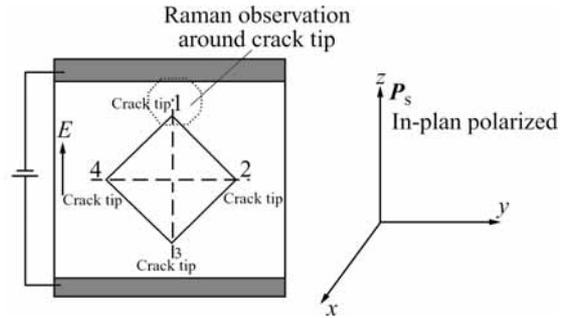


Fig.1 Schematic diagram of setup for measurement of Raman spectrum when specimen subjected to electrical field

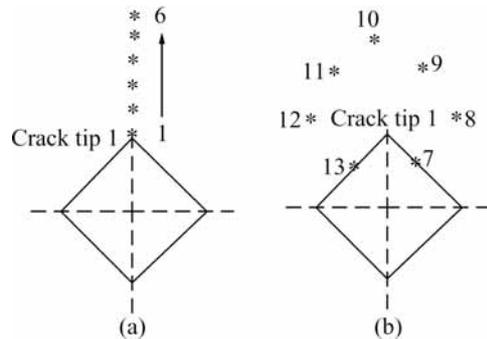


Fig.2 Schematic diagram of Raman observation with domain switching around crack tip from spot 1 to spot 13: (a) Spots 1–6; (b) Spots 7–13

3 Results and discussion

3.1 Raman spectrum intensity and soft mode theory

Raman spectrum is a kind of scattering spectrum [6, 7]. The intensity of induced polarization of the scattered light P_s can be approximately expressed as

$$P_s \approx \varepsilon_0 \left[\underline{\chi}(0) + \frac{\partial \underline{\chi}(\mathbf{u})}{\partial \mathbf{u}} \Big|_{\mathbf{u}=0} \mathbf{u} \right] \mathbf{E}_1 \tag{1}$$

It can be seen that P_s is related to the induced polarizability tensor of the scattering body $\underline{\chi}(\mathbf{u})$. Because domain switching in the scattering body may directly lead to a change in $\underline{\chi}(\mathbf{u})$, it can be seen that domain switching in the scattering body may lead to a variation in P_s and Raman scattered light intensity I_s .

Provided that z direction in Fig.3 is the direction for the spontaneous polarization in the material, the PZT material in tetragonal state will have two kinds of different basic modes for ZrO_3 torsion vibration: one torsion around z axis (O ZrO axis) and another around O ZrO (O ZrO) (i.e. $E(3TO+2LO)+B_1$ soft mode). For the same reason, the PLZT material in tetragonal state will have two kinds of different basic modes for O—Zr—O bending vibration: O—Zr—O bending and O—Zr—O (O—Zr—O) bending (i.e. $E(2TO)$ mode). Owing to the difference in the axis length, the wavelength and direction of the torsion vibration modes and bending vibration modes will be different accordingly. For example, The soft mode peak at the wave number of 212 cm^{-1} is associated with O—Zr—O bending vibration mode whereas the one at the wave number of 280 cm^{-1} is related to ZrO_3 torsion mode[8–12]. Because the optical entrance slit can be used to restrict the direction of light ray vibration, when domain switching (e.g. the orientation of electric domain changes from z direction to y direction) occurs at the specimen surface when being subjected to an electric field with an intensity exceeding coercing field intensity, the restriction from the optical slit will lead to the corresponding change in the peak intensity of the spectrum peaks of the two kinds of vibration modes as described above. In this way, when the orientation of specimen or scattering body with respect to propagation direction (including polarization direction) of incidence light, scattered light is appropriate, the Raman spectra can allow a nondestructive, in-situ observation and measurement of the domain switching [13].

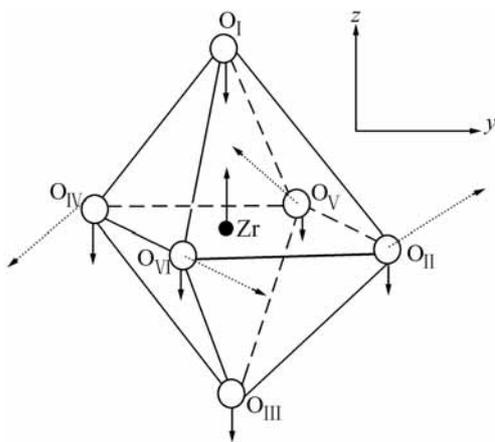


Fig.3 Instantaneous displacement of Zr and O atoms in optical mode

3.2 Raman observation for domain switching around crack tips

A concentration of tensile stress field in front of the tips of the crack may lead to domain switching in front of

the crack tips. In particular, for the geometry of the crack and the polarization orientation as shown in Fig.4, the concentrated tensile stress σ in front of the crack tips 1 and 3 will induce an migration movement of ions along the tensile stress field direction (that is, y axis direction), which is perpendicular to the original specimen polarization direction. Such a rearrangement movement of the ions will turn the original dipole P_s (or polarization direction) along z axis to the new direction along y axis and thus results in a 90° domain switching. On the other hand, due to the fact that their tensile stress field directions are parallel to the original polarization direction of specimen, the tensile stress field in front of the cracks tips 2 and 4 will not be able to induce such a 90° domain switching as in front of the tips 1 and 3.

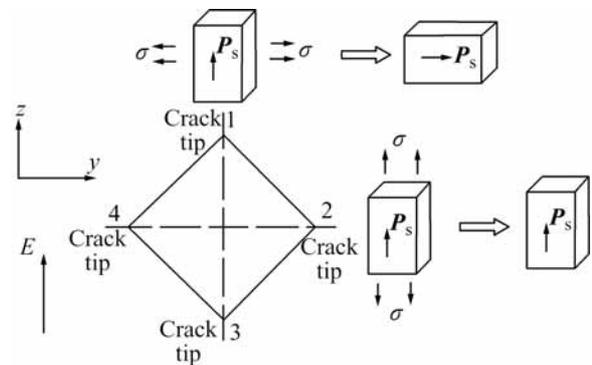


Fig.4 90° domain switching of ferroelectric unit cell in square phase[1]

As described above, after the stress-induced 90° domain switching occurred in front of the crack tips 1 and 3, a DC voltage was then applied, with the applied electrical field direction being parallel to z axis direction. In this way, when the strength of the applied electric field is larger than E_c , the electrical field-induced 90° domain switching would occur, and the domain direction would be redirected from y direction to z direction. This process thus reverses the stress-induced 90° domain switching in front of the crack tips 1 and 3.

The results of Raman observation around the crack tip before and after the electric field are shown in Figs.5 and 6. The polarization direction of the incidence and scattered lights is along y axis direction. It is obvious that the intensity of all Raman spectra around the crack tip after the application of electric field is weaker than that before the application of electric field, which confirms the applied electric field leading to a redirection of the local polarization direction from y axis direction to z axis direction. The results confirm that Raman intensity is directly attributed to the change of the polarization direction of the incidence and scattered lights with respect to the direction of the average polarization direction of the domain in the polarized specimen. When

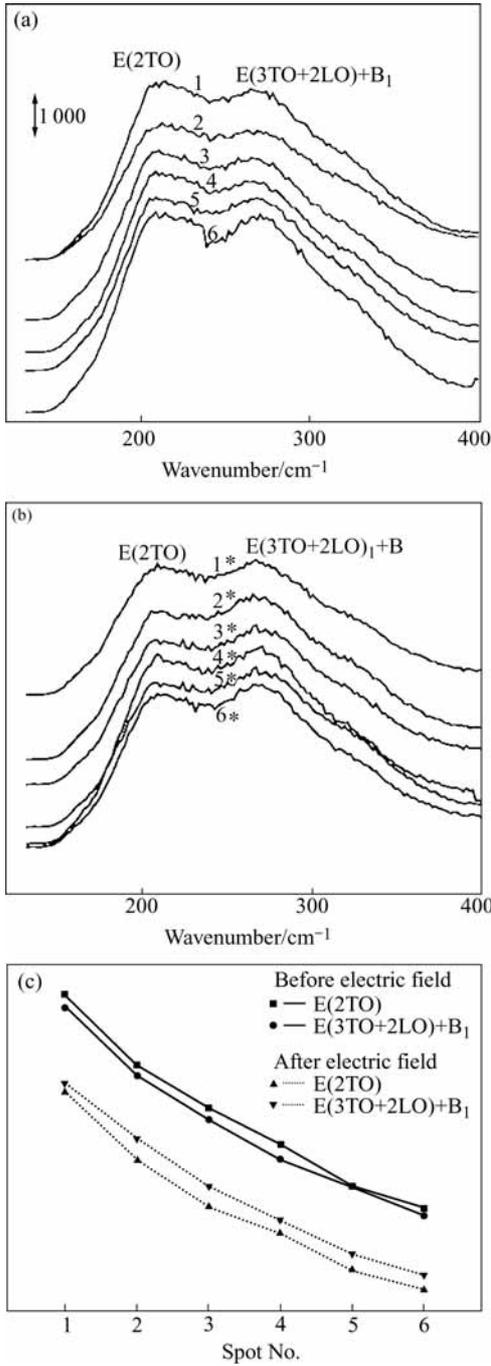


Fig.5 Raman spectra and comparison of corresponding intensities observed in spots 1-6 at crack tip before and after application of electric field: (a) Before application of electric field; (b) After application of electric field (indicated by *); (c) Comparison of intensities for two soft modes before and after application of electric field

the two directions are parallel (y axis direction) before the electric field, the induced polarizability tensor of the specimen $\underline{\chi}(\mathbf{u})$ would be enhanced and give rise to a higher intensity I_s for Raman scattering light. On the contrary, when the two directions are not parallel with the deflexion of the local polarization direction from

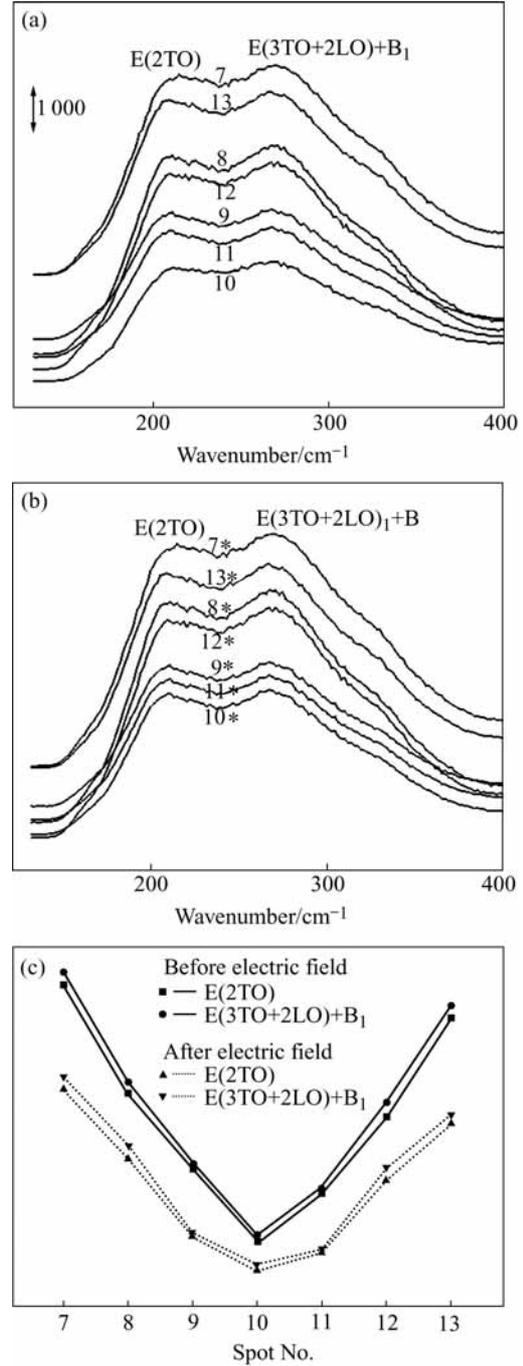


Fig.6 Raman spectra and comparison of corresponding intensities observed in spots 7-11 at crack tip before and after application of electric field: (a) Before application of electric field; (b) After application of electric field (indicated by *); (c) Comparison of intensities for two soft modes before and after application of electric field

y axis direction to z axis direction after the electric field, $\underline{\chi}(\mathbf{u})$ would be reduced to a lower value and thus I_s is lowered.

As the measurement moves from spot 1 to spot 6 (Fig.5), the intensity of Raman spectra either for the E(3TO+2LO)+B₁ soft mode or for the E(2TO) soft

mode is decreased steadily. The results indicate that when the strength of reapplied electric field is higher than E_c , the direction of the polarized dipole at tip 1 around the crack would be redirect to the direction of z axis and the polarized dipole vector along y axis which contributes to the intensity of Raman spectra would be decreased. However, from spot 1 to spot 6, the domain switching as induced by the stress field of the indent would be expected to gradually become weaker, that is, the vector of the polarized dipole along y axis as induced by the stress of the indent gradually became smaller. This leads to a gradual decrease in the intensity of Raman spectra as evident in Fig.5(c).

The changes in Raman spectra from spot 7 to 13 as shown in Fig.1 in the sample sample are presented in Fig.6. A systematic variation in the intensity of Raman spectric is demonstrated. When the measurement moves from spot 7 via spot 8 and spot 9, the Raman scattering intensity steadily decreases to the lowest value at spot 10. On the contrary, when the measurement moves from spot 10 via spot 11 and spot 12, the Raman scattering intensity increases steadily again and seems to resume to its original values on the positions of their symmetric opposite spots. It is intriguing here that the Raman spectrum intensities both for the $E(3TO+2LO)+B_1$ and for the $E(2TO)$ soft modes are varied in the almost same symmetric fashion as evident in Fig.6(c). This kind of symmetric variation in the Raman scattering intensity may reveal a symmetric distribution of the stress field as induced by the indent crack as expected, indicating that a higher indent stress would result in a higher intensity of Raman scattering as described in Figs.6(a) and (b). The lowest value in the Raman scattering intensity at the spot 10 indicates that there is a lowest indent stress at the tip 10, which is located on the extended crossing line of the indent crack.

4 Conclusions

Raman spectrum can be in-situ observed and measured for ferroelectric domain switching nondestructively at a micro scale. Using the established Raman technique, the variation of Raman spectra at the indent crack tips under a variation in the applied electric field intensity for the PLZT ceramic specimens were studied. The results confirm that Raman intensity is directly attributed to the change of the polarization

direction of the incidence and scattered lights with respect to the direction of the average polarization direction of the domain in the polarized specimen. When the two directions are parallel, the induced polarizability tensor of the specimen $\chi(\mathbf{u})$ would be enhanced and give rise to a higher intensity I_s for Raman scattering light. The variation in the Raman spectrum intensity at the different locations surrounding the crack tips was studied, it is confirmed that the indent stress field may have a systematic effect on the Raman scattering intensity. However, a full explanation and a quantitative modeling for the link between the soft mode theory in Raman spectra and the ferroelectric phase transition at microscopic level is still difficult and awaits for a further exploration.

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