

# Multivariate Curve Resolution for Angle-resolved polarized Raman Spectroscopy of Ferroelectrics

強誘電体の角度分解偏光ラマン分光における多変量曲線分解

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## 1. Introduction

Investigation of materials using Raman scattering is widely applied in sciences since it can label structures and compositions of materials based on inelastic scattering of laser light. In the field of solid state physics, a Raman spectrum provides rich information on vibration modes such as phonons with high accuracy, which can be used in both qualitative and quantitative analytical applications. Owing to the ability to detect changes in phonons, Raman spectroscopy has attracted much attention as a probe of structural phase transitions induced by softening of one characteristic phonon.<sup>1)</sup> In other words, Raman spectroscopy can shed light on microscopic pictures of structural phase transitions.

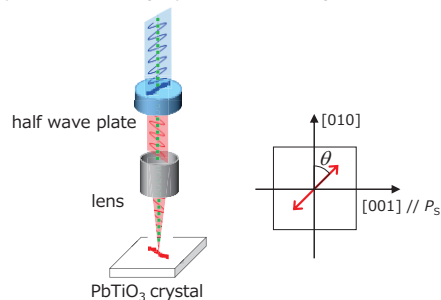
Raman scattering from optical phonons depends on Raman tensors derived from the point symmetry of crystals; thus polarized Raman spectroscopy has been performed to distinguish characteristic modes from others. However, there are difficulties in changing scattering geometries to probe various tensor components since it usually needs repositioning of optical elements in a measurement system. One powerful technique to overcome these difficulties is the angle-resolved polarized Raman spectroscopy in which a computer-controlled half-wave plate in the microscope changes the polarization direction of incident and scattered light with any angle  $\theta$  in order to change the observed Raman tensor components as shown in **Fig.1 (a)**.<sup>2)</sup> By the observation of angle dependence of Raman peak intensity, we can access the information of crystals such as a point group and the an optical axis. We have measured angle dependence of Raman peak intensity and have assigned soft modes to make clear the origin of structural phase transitions in ferroelectric materials.<sup>3)</sup>

One of the most important classes of structural phase transitions is a paraelectric–ferroelectric phase transition in which dielectric and piezoelectric responses are induced just below the phase transition temperature. Due to the enhanced responses, microscopic pictures of the phase transitions have been investigated from both fundamental and application viewpoints. An example of angle-resolved polarized Raman spectra

of a ferroelectric  $\text{PbTiO}_3$  crystal at room temperature is shown in **Fig. 1 (b)**,<sup>2)</sup> showing phonon peaks with different  $\theta$ . On the basis of the  $\theta$  dependence, modes can be assigned.<sup>2-3)</sup>

Although this mode assignment using angle-resolved polarized Raman spectroscopy seems to be simple and straightforward, it is often difficult to obtain each peak intensity correctly by least-square fitting with several Lorentzian functions when some peaks are overlapped as observed in Fig. 1 (b) around  $100 \text{ cm}^{-1}$ . Because soft modes of paraelectric-ferroelectric phase transitions are intrinsically broad, this problem appears so frequently. Therefore, sophisticated data analysis methods are necessary to extract underlying abundant information. In the present study, we show that multivariate curve resolution (MCR) is powerful for analysing angle-resolved polarized Raman spectra.

(a) System to change polarization angle  $\theta$



(b)  $\theta$  dependent Raman spectra of  $\text{PbTiO}_3$

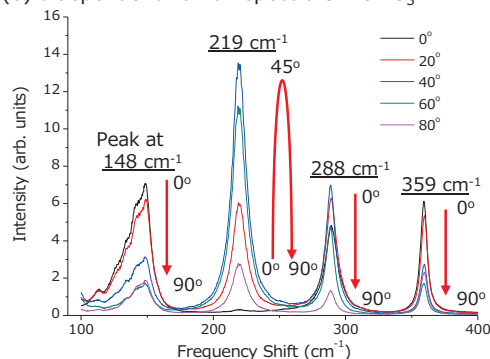


Fig. 1: (a) Polarized-angle rotation by half-wave plate for Raman scattering. In the present study, the angle  $\theta$  is set from  $[010]$  of tetragonal  $\text{PbTiO}_3$ . (b) Raman spectra of  $\text{PbTiO}_3$  at five  $\theta$  in a parallel nicol (HH) scattering geometry obtained from Ref. 2. The  $\theta$  dependence is roughly indicated by arrows.

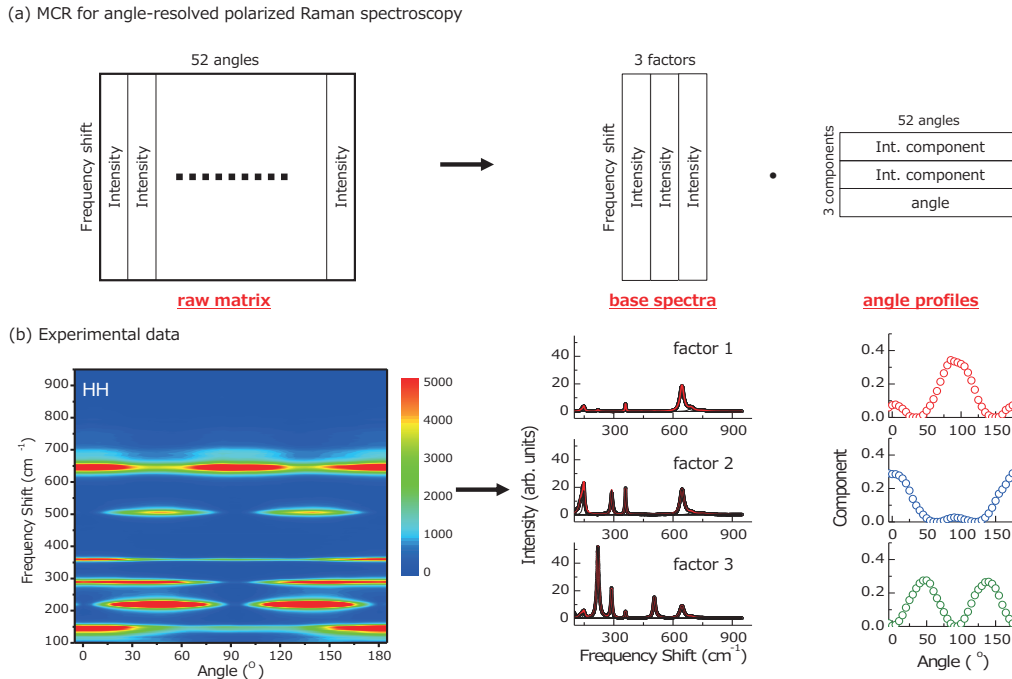


Fig. 2: (a) Concept of MCR for angle-resolved polarized Raman spectroscopy assuming three components. (b) Experimental and analyzed results for PbTiO<sub>3</sub>. In the present study, we acquired 52 spectra with different  $\theta$  in HH configuration. The spectra are resolved to 3 spectra and 3 component by using MCR.

## 2. Method

MCR, a matrix factorization technique, involves linear combination of a prescribed number of spectral components and their angle dependence under constraints.<sup>4)</sup> The concept is shown in **Fig. 2 (a)**.  $m \times n$  non-negative data matrix containing Raman spectra with different  $\theta$  are decomposable into three rows (base spectra) and three columns (angle profiles). The prescribed number is usually determined by principal component analysis. In the present study, MCR was performed by using a multivariate statistical analysis software, Unscrambler X (Camo Analytics).

## 3. Results and Discussion

**Figure 2 (b)** shows the raw data of PbTiO<sub>3</sub> and the results of MCR. Without any prior information concerning the nature of sample and any experienced fitting techniques, MCR extracts three types of spectra with different  $\theta$  profiles. The angle profiles should reflect the  $2 \times 2$  matrix of Raman tensor, and the peaks in one base spectrum belongs to the same mode. For example, all peaks in the third spectrum (denoted as “factor 3”) should be assigned to *E*-mode because the angle profile of “factor 3” is in good agreement with that expected by Raman tensor of *E*-mode of tetragonal  $4mm$  structure of PbTiO<sub>3</sub>. However, angle profiles of “factor 1” and “factor 2” could not be assigned simply on the basis of Raman tensor, which contains fundamental problems of “phase difference” of Raman tensor<sup>5,6)</sup> and should be solved as a next step.

It is worth noting that MCR enables us to

reduce the number of spectra to be analysed. As soft modes are intrinsically broad and overlapped with other peaks, all spectra obtained by this measurement are usually fitted one-by-one to determine the peak shift, width, and intensity, which is difficult and time-consuming for beginners to get reliable parameters. By analysing only three spectra obtained by MCR in Fig. 2 (b), we succeeded in reproducing the  $\theta$  dependent peak intensity reported in Ref. 2. Thus, by using MCR, we can handle a large amount of spectra obtained by angle-resolved polarized Raman spectroscopy efficiently. Because a large amount of spectra with different angles is acquired at various temperatures and pressures to investigate phase transitions, we consider it necessary to develop data analysis techniques more.

## Acknowledgment

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