Determination of Phase Transition by Principal Component Analysis Applied to Raman Spectra of Polycristalline $BATIO_3$ at Low and High Temperature

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ABSTRACT
This work describes the principal component analysis (PCA) applied to Raman spectra of polycrystalline $BaTiO_3$ as a function of temperature. During each experiment the samples was continuously heated and the Raman spectrum was registered every 0.5 °C at a rate of 0.1 °C min−1. This procedure is applied on samples $BaTiO_3$ compact powder to obtain their thermal behavior from -190 °C to 230 °C. The PCA method was able to distinguish spectral features to determine the phase transition temperature and the whole thermal history including the structural phase transition from rhombohedra to orthorhombic at -100 °C, orthorhombic to tetragonal at -5 °C and tetragonal to cubic at 121 °C.

Keywords: Phase transitions, $BaTiO_3$, principal component analysis.

RESUMEN
Este trabajo describe el análisis de las componentes principales (PCA) aplicados a los espectros Raman del $BaTiO_3$ como función de la temperatura. Durante el experimento las muestras fueron calentadas continuamente y los espectros Raman fueron registrados cada 0.5 °C a una razón de 0.1 °C por minuto. Este procedimiento es aplicado para muestras de polvo compacto de $BaTiO_3$ para obtener su comportamiento térmico de -190 °C a 230 °C. La técnica del PCA fue capaz de distinguir características espectrales para determinar la temperatura de la transición de fase y la historia térmica completa, incluyendo las transiciones de fase estructural: romboédrica a ortorrómbica at -100 °C, ortorrómbica a tetragonal at -5°C y tetragonal a cúbica at 121 °C.

1. Introduction

Polycrystalline $BaTiO_3$ is a well studied ferroelectric perovskite, this material has several phase transitions by temperature and also by pressure that have been extensively studied using several theoretical methods and experimental techniques [1-7]. In terms of temperature, $BaTiO_3$ has three phase transitions; from rhombohedral (R) to orthorhombic (O), O to tetragonal (T) and T to cubic (C). When these transitions are studied by Raman spectroscopy, the shift, disappearance and appearance of the Raman peaks are used for the determination of the phase transition region. However, sometimes it is difficult to determine the phase transition region using only the frequency Raman peaks plotted as a function temperature, the uncertainty increases when it is necessary to determine the phase transition temperature on a region. This behavior is more pronounced when the thermal distortions are close to 1% of cell volume, as is the case of $BaTiO_3$. For this reason, we present the application of the PCA statistical method to identify phase transition temperatures because PCA is a powerful statistical method that reduces the dimensionality of a data matrix. generating a new set of orthogonal variables called principal components (PCs). The first principal component (PC1) is a single axis in space. When we project each observation on that axis, the resulting values form a new variable; and their variance is the maximum among all possible

choices of the first axis. The second principal component (PC2) is another axis in space, perpendicular to the first one. The variance of this variable is the maximum among all possible choices of this second axis. The full set of PCs is as large as the original set of variables. It is recommended that for the sum of the variances of the first few PCs exceed 80% of the total variance from original data [8-9]. The PCA has been widely used for experimental data classification, for example, to investigate polycrystalline $BaTiO_3$ at high pressure [4], crystallization experiments [10], and analysis of narcotics in solid mixtures [11].

In this paper, we present the detection of phase transition temperatures by means of the analysis of the Raman spectra with PCA.

2. Experimental section

Barium titanate small samples of 2 mm diameter and ~ 500 μm thickness were obtained from compact powder (Aldrich, 99.9% purity and average particle size < 2 μm). Raman spectra were recorded with a Raman dispersive spectrometer (model Almega X) and a microscope (Olympus BX51) with a 50X objective (Olympus, NA = 0.80) was used for focusing the laser on the sample using a spot size of 1 μm, and for collecting the scattered light in 180° backscattering configuration. The Raman spectra were accumulated over 25 s with a resolution of ~ 4 cm^{-1} and the excitation source was 532 nm radiation from an Nd:YVO_4 laser (frequency-doubled). The temperature measurements were taken with Examina System – THMS600 (Linkam Scientific Instruments) with accuracy of 0.01 °C. The experiment was carried out five times in order to assure reproducibility and for assessment of the statistical significance of the results.

3. Results and discussion

During the continuous heating from -190 to 230 °C, three phase transitions take place: R→O, O→T and T→C. The Raman peaks are shifted and several frequency modes change or disappear as a result of temperature rise.

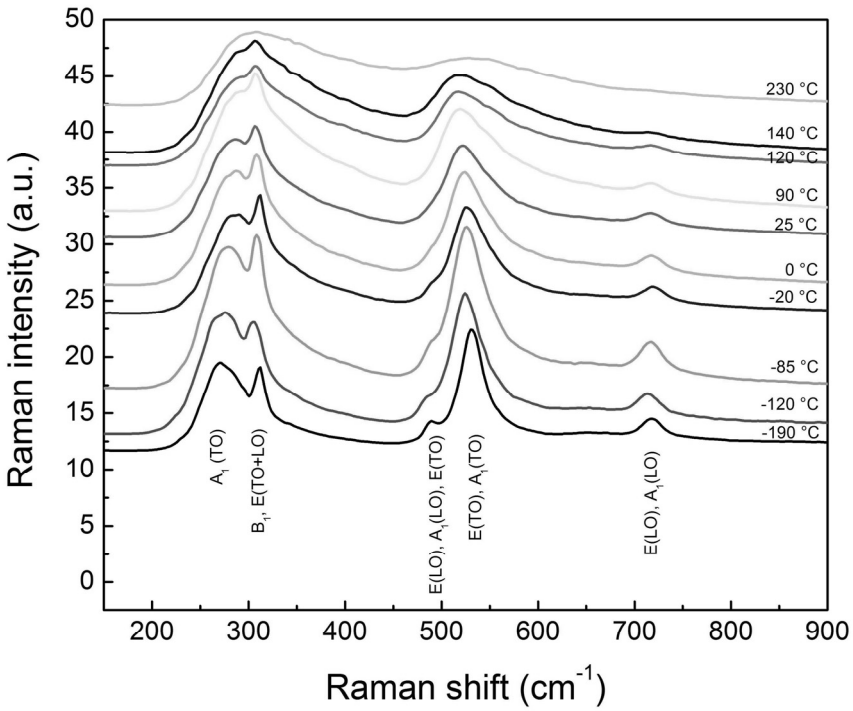

Figure 1. Raman spectra of polycrystalline $BaTiO_3$ as a function of temperature.

Figure 1 shows the polycrystalline $BaTiO_3$ Raman spectrum at different temperatures. At low temperature in phase rhombohedra (-190 ºC), the spectrum shows the following main lines: a broad peak near 271 cm^{-1} [A1(TO)], a sharp peak at 312 cm^{-1} [B_1, E(TO+LO)], a weak peak at 487 cm^{-1}, [E(LO), A_1(LO), E(TO)], asymmetric and broad peak near 532cm^{-1} [E(TO), A1(TO)], and a weak peak at 713 cm^{-1} [E(LO, A1(LO)], where the phonon assignment is given inside square brackets. When the temperature is increased until -100 °C, the Raman peaks disappeared or were shifted. The peak at 271 cm^{-1} is displaced to upper frequency, 279 cm^{-1}. The peak intensity at 487 cm^{-1} decreases when the temperature increases, this behavior is due to the rhombohedral to orthorhombic phase transition. The nex phase transition, orthorhombic to tetragonal, is carried out at -5 °C, where the Raman frequency in [A_1(TO)] shifted to 287 cm^{-1} and the Raman intensity decreases. The mode [E(LO), A_1(LO), E(TO)] disappears and modes [B_1, E(TO+LO)] and [E(TO), A_1(TO)] are shifted to 308 and 524 cm^{-1}, respectively. For phase transition T → C, at 121 °C, the several Raman modes have disappeared or diminished considerably. Cubic phase Raman response should not exist but for being a polycrystalline material its response is still present as shown in Figure 1.

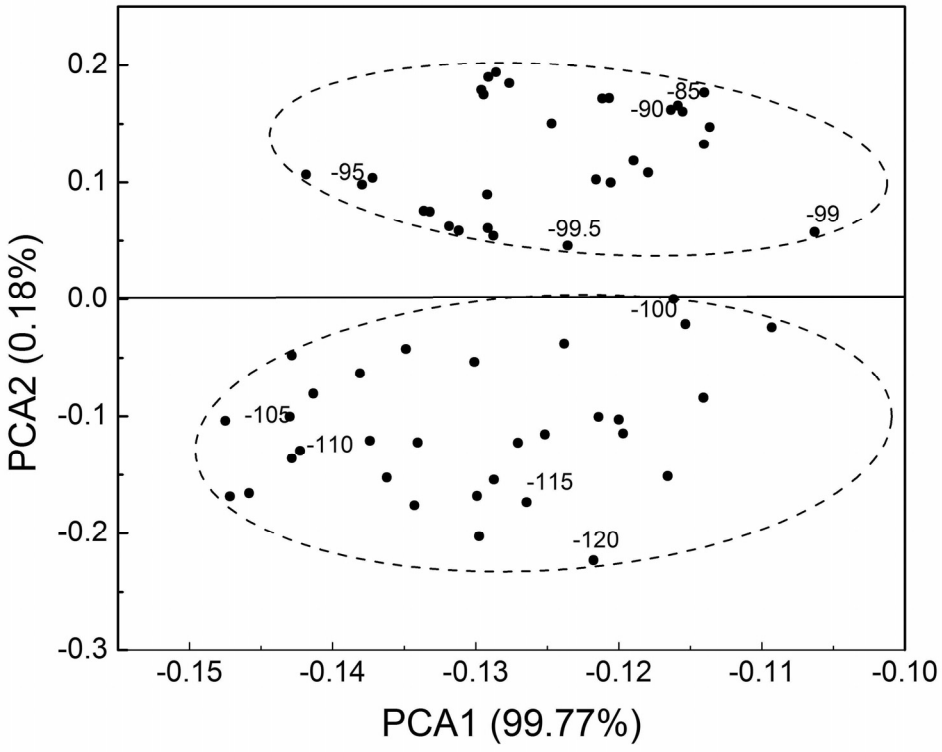

Figure 2. Score plot PCA1 vs. PCA2, phase transition temperature R → O at -100 °C.

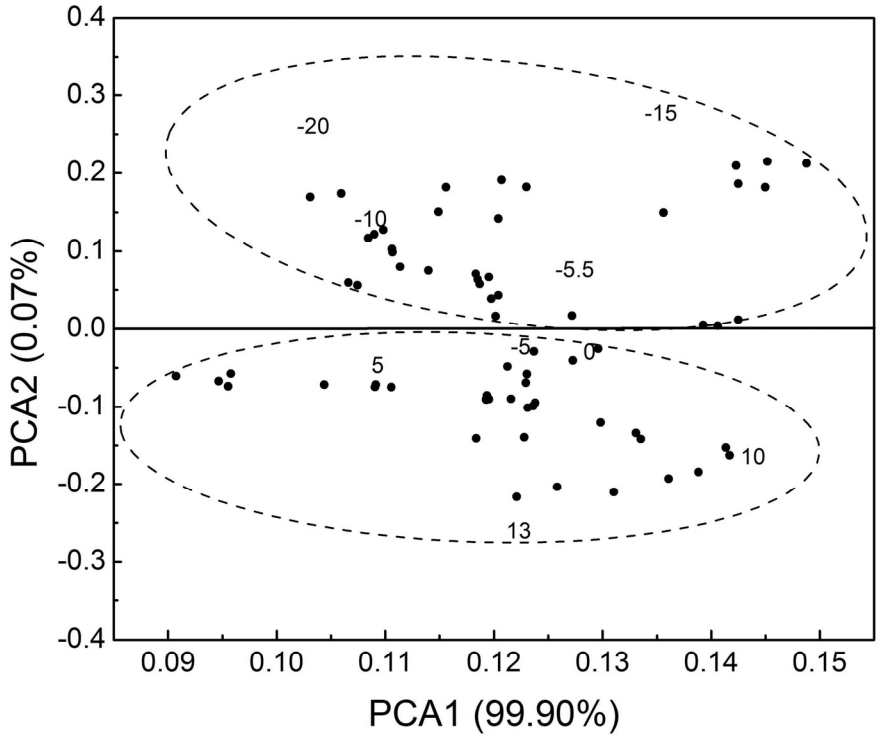

Figure 3. Score plot PCA1 vs. PCA2, phase transition temperature O → T at -5 °C.

Spectra per temperature were co-added, averaged and linealized for the evaluation by PCA method. For phase transition R → O, the data showed that 99.95 % of all the spectral variation could be accounted for two principal components; the loading plots are shown in Figure 2. The first principal component, PCA1, with an explained spectral variance of 99.77% and the second component, PCA2, with an explained spectral variance of 0.18 % shows the Raman vibration modes that have disappeared and changed in the Raman spectra. Applying PCA to the Raman spectra, the phase transition temperature is at ~ - 100 °C; from the figure, it can also be observed that before the phase transitions the values are in the negative part of the graph and, after it, in the positive side, the reference axis being zero.

Figure 3 presents the PCA analysis for phase transition O → T, at ~ - 5 °C. At low temperatures, phase transition O → T has a total weight according to the PCA analysis of 99.97 % with PCA1 99.9 % and PCA2 0.07 %. In the same figure, it is possible to see that the phase transition is fixed on the zero line in the graph of axis PCA2.

Phase transition T → C at 121 °C is shown in Figure 4, the peaks intensity decreases specially in [B_1, E(TO+LO)] and disappears in [E(LO, A1(LO),E(TO)]; this process is plotted in the PCA analysis with 99.98 % of whole the spectral variation. The values for PCA1 and PCA2 are 99.74 % and 0.24%, respectively. This behavior is similar to previous transitions, the values are in the negative part of the graph before the phase transition, and to perform it, it goes to the positive side.

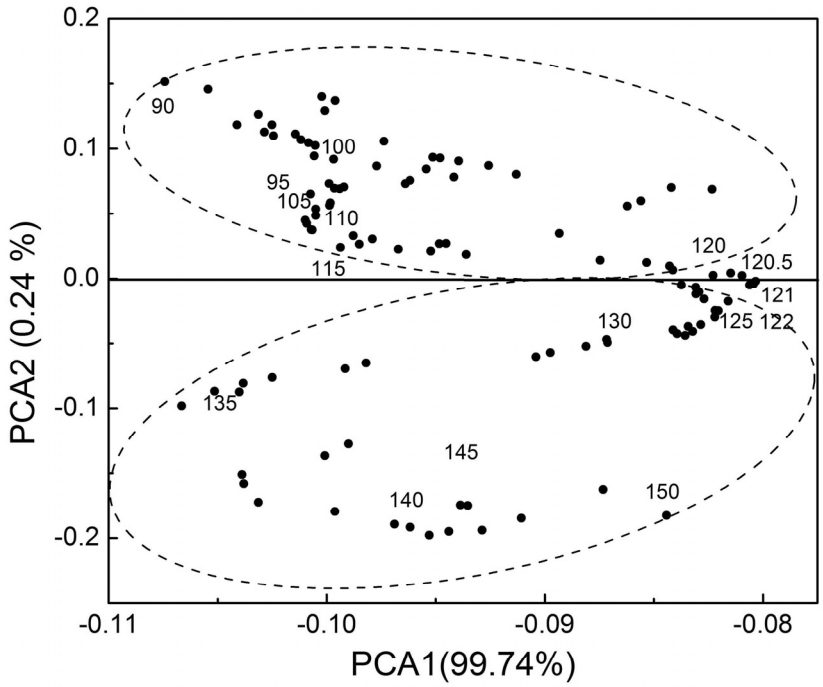

Figure 4. Score plot PCA1 vs. PCA2, phase transition temperature T → C at 121 °C.

It is believed that the spread of values is related to changes in volume during the transition. For example, in the rhombohedra to orthorhombic transition, where there are changes in angle and lattice parameter, the distance is larger between the positive and negative values, but when only the changes are associated to one lattice parameter, c, in the tetragonal to cubic phase transition, the values are very close to the zero axis of PCA2.

4. Conclusions

We have shown that applying the PCA analysis to the Raman spectra as a function of temperature is possible to determine the phase transition temperature by discrimination between the spectra. The temperature of the three phase transitions was determined in the negative region of PC2; this behavior shows the differentiation among the spectra data. Thus, we propose it as an alternative method for the analysis of phase transitions or structural changes in a sample with spectra appearing similar to each other. We consider that the principal contribution of this work is that is possible to determine differences among very similar spectra and know a specific value, not only a range.

References

[1] N. Baskaran, A. Ghule, Ch. Bhongale, R. Murugan and Hua Chang, Phase transformation studies of ceramic BaTiO3 using thermo-Raman and dielectric constant measurements, Journal of Applied Physics, Vol. 91, Issue 12, June 2002, pp. 9461-10231.

[2] I. Hatta, Potentiality of an ac calorimetric method in the study of phase transitions, Thermochimica acta, 304/305, 1997, p.p. 27-34.

[3] Y. Shiratori, C. Pitham, J. Dornseiffer and R. Waser, Raman scattering studies on nanocrystalline BaTiO3, Part I – isolated particles and aggregates, J. Raman spectroscopy, Vol. 38, June 2007, p.p. 1288-1299 and Part II – consolidated polycrystalline ceramics, J. Raman spectroscopy, Vol. 38, June 2007, p.p. 1300-1306.

[4] R.Y. Sato-Berrú, E.V. Mejía-Uriarte, C. C. Frausto-Reyes, M. Villagrán-Muniz, Medina-Gutiérrez, H. Murrieta S y J.M. Saniger-Blesa. Applications of principal component analysis and Raman spectroscopy in the analysis of polycristalline BaTiO3 at high pressure, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 66, N° 3, March 2006, p.p. 557.

[5] M. Villagrán-Muniz, M. Navarrete and E.V. Mejía-Uriarte, Photoacoustic determination of phase transition in BaTiO3 induced by high pressure at room temperature, Rev. Sci. Instrum. Vol. 74. No. 1, January 2003, pp. 732-734.

[6] E.V. Mejía-Uriarte, M. Navarrete, M. Villagrán-Muniz, Signal processing in photoacoustic detection of phase transitions by means of the autospectra correlation-based method: Evaluation with ceramic BaTiO3, Rev. Sci. Instrum. Vol. 75, Nº 9, September 2004, pp. 2887-2891.

[7] E. V. Mejía-Uriarte, R.Y. Sato-Berrú, M. Navarrete M. Villagrán-Muniz, C. Medina-Gutiérrez, C. Frausto-Reyes and H. Murrieta S. Phase transition of polycrystalline BaTiO3 at high-pressure detected by a pulsed photoacustic technique, Measurement science and technology 17, N° 6, May 2006, p.p. 1319-1323.

[8] NIST/SEMATECH e-Handbook of Statistical Methods: http://www.itl.nist.gov/div898/handbook, 2005.

[9] R.A. Johnson, D.W. Wichern, Applied Multivariate Statistical Analysis, Prentice Hall, Inc., USA, 1999, p. 458.

[10] J.A. Falcon, K.A. Berglund, In situ monitoring of antisolvent addition crystallization with principal components analysis of Raman spectra, Crys. Growth Des. Vol. 4. 2004, p.p. 457-463 (2004).

[11] A.G. Ryder, G.M. O'Connor, T.J. Glynn, Quantitative analysis of cocaine in solid mixtures using Raman spectroscopy and chemometric methods, J. Raman Spectrosc. 31, Vol. 221 No 3, March 2000, p.p. 21-227.

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