Hindawi Publishing Corporation
Journal of Spectroscopy
Volume 2015, Article ID 276537, 6 pages
http://dx.doi.org/10.1155/2015/276537

Research Article

Monitoring of Spectral Map Changes from Normal State to Superconducting State in High-T_C Superconductor Films Using Raman Imaging

J. L. González-Solís,[1] R. Sánchez-Ruiz,[1] I. A. Arana-Zamora,[1] J. C. Martínez-Espinosa,[2] M. L. Pérez-Arrieta,[3] and C. Falcony-Guajardo[4]

[1] *Biophysics and Biomedical Sciences Laboratory, Centro Universitario de Lagos, Universidad de Guadalajara, Enrique Díaz de León S/N, Paseo de la Montaña, 47460 Lagos de Moreno, JAL, Mexico*
[2] *Mathematics and Biotechnology Academy, Instituto Politécnico Nacional-UPIIG, 36275 Silao de la Victoria, GTO, Mexico*
[3] *Unidad Académica de Física, Universidad Autónoma de Zacatecas, Calzada Solidaridad Esq. Paseo, La Bufa s/n, 98060 Zacatecas, ZAC, Mexico*
[4] *Departamento de Física, Centro de Investigación y Estudios Avanzados-IPN, Apdo., Postal 14-470, Del. Gustavo A. Madero, 07000 México, DF, Mexico*

Correspondence should be addressed to J. L. González-Solís; jluis0968@gmail.com

Received 16 July 2014; Revised 23 September 2014; Accepted 24 September 2014

Academic Editor: Jie-Fang Zhu

We have explored the chemical structure of $TlBa_2Ca_2Cu_3O_9$ high-T_C superconductor films with Tl-1223 phase to monitor spectral map changes from normal state to superconducting state using the technique of Raman imaging. Raman images were performed for 12 different temperatures in the 77–293 K range. At room temperature, the Raman images were characterized by a single color but as the temperature dropped a new color appeared and when the temperature of 77 K is reached and the superconducting state is assured, the Raman images were characterized by the red, green, and blue colors. Our study could suggest that the superconducting state emerged around 133 K, in full agreement with those reported in the literature. A cross-checking was done applying principal component analysis (PCA) to other sets of Raman spectra of our films measured at different temperatures. PCA result showed that the spectra can be grouped into two temperature ranges, one in the 293–153 K range and the other in the 133–77 K range suggesting that transition to the superconducting state occurred at some temperature around 133 K. This is the first report of preliminary results evaluating the usefulness of Raman imaging in determination of transition temperature of superconductor films.

1. Introduction

The scientific applications of superconductivity in commerce and industry have been broadened by the discovery of ceramic superconductors or high-T_C superconductors [1]. Creating high-T_C superconductor films with high current densities (~106 A/cm^2) in long kilometer lengths has become the major goal to be achieved for industrial and commercial applications. The creation of high-T_C superconductor films with high current densities has been achieved in laboratories with smaller lengths of films but has not yet been achieved for longer lengths of film. Some of the superconducting films preparation techniques used include metal organic chemical vapor deposition (MOCVD), pulsed laser deposition (PLD), sol-gel, metal-organic deposition (MOD), chemical vapor deposition (CVD), electrophoresis, electrodeposition, and aerosol/spray pyrolysis. Because only films of high quality are useful in industrial and commercial applications, several parameters of the films as crystal orientation, oxygen concentration, morphology, grain size, and layer thickness must be monitored to insure that films with high current density and transition temperature are being manufactured [2]. In order to determine the current density and transition temperature of the films, crystal orientation, oxygen concentration, and layer thickness play major roles [2–5]. Current flow in a high-T_C superconductor film is directly related to the crystal orientation and layer thickness of the films, so that the better aligned the axes of the crystal for the appropriate layer thickness, the higher the current density in the film. Furthermore, the transition temperature is directly related to the oxygen concentration of the crystal; the higher the oxygen concentration, the higher the transition temperature. Previously published works show that these three important characteristics of these films can be monitored using Raman spectroscopy technique [6]. In addition, the temperature dependence of the Raman line shapes can indicate changes in the electronic density of states and help in the search for superconducting mechanisms. The analysis of temperature dependence of the phonon frequencies is also a means to determine which phonons could be directly associated with the superconducting transition. Almost all aspects of high-T_C superconductivity have been addressed by Raman scattering because of its experimental versatility and the coupling of the elementary excitations to electron-hole pairs. Small samples have been nondestructively investigated at low temperatures, under electric or magnetic fields, as a function of excitation energy, and under high pressure. Thus, the effects of external parameters on superconductivity can be studied [7].

Raman scattering is the inelastic scattering of photons creating or annihilating an elementary excitation (phonons, plasmons, excitons, or spin fluctuations) in the solid. All of these excitations have been observed and studied in high-T_C superconductors, which is why Raman scattering has contributed so much to their understanding [8]. Raman spectroscopy is a powerful analytical investigation technique for studying phonons in solid with relatively simple instrumentation [9]. Therefore, Raman spectroscopy is an excellent tool for acquiring information on properties of high-T_C superconductor films in situ; however, the technique of Raman spectroscopy could be even more powerful if it allows us to know the spatial distribution of the chemical composition in high-T_C films. In a Raman image, each pixel is assigned the Raman spectrum recorded in the same position obtaining a spatial distribution of colors (red, green, or blue) where each color indicates a specific chemical component [10].

Furthermore of the Raman imaging, recently multivariate analysis has been applied to Raman spectroscopy to classify a wide variety of biological samples becoming a very promising tool to be used in biomedical research. In particular, PCA has been used to differentiate between epithelial precancers and cancers [11] and leukemia, cervical cancer, and control samples [12, 13]. PCA is a way of identifying patterns in data and expressing the data in such a way as to highlight differences. When the principal component loadings are plotted as a function of different variables, they reveal which variable accounts for the greatest difference. Other techniques widely used in data analysis are linear discriminant analysis (LDA) and hierarchical clustering analysis (HCA), allowing identifying in a natural way the classes present in data and depicted by a tree diagram or dendrogram. These techniques have been used in a large 5 variety of engineering and scientific disciplines such as gene expression [14, 15], stock indices [16], and astrophysics [17].

In this work, we characterized the chemical structure of $TlBa_2Ca_2Cu_3O_9$ high-T_C superconductor films with Tl-1223 phase and monitored spectral map changes from normal state to superconducting state by using the technique of Raman imaging. A cross-checking was done applying PCA to other sets of Raman spectra measured at different temperature of the films obtaining the same Raman imaging result. The transition temperature reported for these films using the standard technique of the strong fall in the electrical resistance is 133.5 K [18]. It is the first report of preliminary results evaluating the usefulness of Raman imaging and PCA in the determination of transition temperature of $TlBa_2Ca_2Cu_3O_9$ high-T_C superconductor films with Tl-1223 phase.

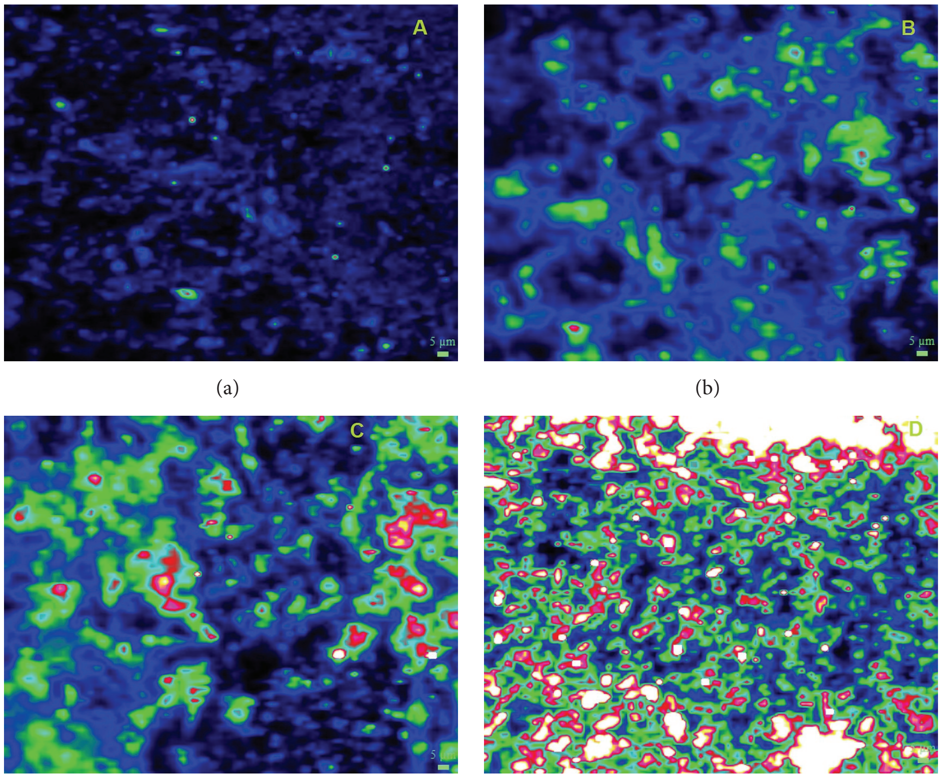
2. Experiment

In this work, we explored three $TlBa_2Ca_2Cu_3O_9$ high-T_C superconductor films with Tl-1223 phase processed by Pérez-Arrieta et al. through a two-step novel synthesis [19]. The films of average size of about 0.5 cm^2 and a thickness of ~3 μm were labeled as M74, M89A, and M98A. Raman images were obtained using a Horiba Jobin-Yvon LabRAM HR800 Raman system, constituted by an Olympus confocal microscope which focuses with a 50X Leica long-range objective, a laser of 830 nm, and 17 mW power irradiation (spot size of approximately 1 μm diameter) on the surface of the superconductor film and collects the Raman backscattered radiation.

The control of the Raman system, spectra recording, and images processing were performed with the LabSpec 5.0 software. We used the Raman peak at 520 cm^{-1} of a silicon semiconductor for instrument calibration. In order to measure temperature-dependent Raman spectra, each superconductor film covered by a pair of quartz sheets was placed inside a Linkam THMS600 heating and cooling microscope stage coupled to Raman system. Microscope stage or cryostat allows that the Raman measurements can be performed within the 77 to 900 K temperature range. The cryostat is attached to a Linkam TMS94 temperature programmer whereby the desired temperature and laser exposure were programmed. Temperature programmer and the cryostat are connected to a tank, which supplies liquid nitrogen to cryostat. The cryostat is placed on the X-Y stage of microscope and its window positioned under the microscope objective allowing point to point automatic mapping of the interest region on the film.

All Raman spectra were recorded with spectral resolution of 0.6 cm^{-1}. By using LabSpec software, a region of 100 × 100 μm^2 was selected to characterize the films. Once desired temperature is reached, X-Y stage automatically moves across the selected region in step of 1 μm with laser exposure of 0.5 seconds. For each temperature, the data acquisition time for a single Raman image of a superconductor film was 90 minutes, on average.

Raman images of the three superconductor films were obtained for 12 different temperatures within 77–293 K range. The resolution for each Raman image was 100 × 100 pixels by containing a total of 10,000 Raman spectra.



(a) (b) (c) (d)

Figure 1: Raman images of M74 $TlBa_2Ca_2Cu_3O_9$ high-T_C superconductor films with Tl-1223 phase. (a) Raman image at 293 K. (b) Raman image at 153 K. (c) Raman image at 133 K. (d) Raman image at 77 K.

For the PCA, we measured an average of 2.5 spectra for each of the 12 temperatures within 77–293 K temperature range using the same Raman system. PCA and all the algorithms for data analysis were implemented in MatLab commercial software.

3. Results and Discussion

We analyzed three $TlBa_2Ca_2Cu_3O_9$ high-T_C superconductor films with Tl-1223 phase. These superconductor films have a tetragonal (*D4h*) unit cell with $a = 0.38429$ and $c = 15.871$ Å and belong to the *P4/mmm* space group. They have one insulating TlO layer, two spacing BaO layers, two separating Ca layers, and three conducting CuO_2 planes making them *"1223"* type. The transition temperature measured in these films using standard techniques is about 133.5 K [3, 4, 18, 20].

Raman images were constructed by plotting spectral intensities of superconductor films versus the coordinates of points from where spectra were recorded and, according to this, the red, green, or blue colors are assigned. Each film was analyzed according to the methodology described in the previous section.

In order to obtain the Raman images, we measured a large number of spectra in a programmed manner. Figure 1 shows four of twelve Raman images of M74 superconductor film measured at 293, 153, 133, and 77 K. Raman image measured at 293 K (see Figure 1(a)) is characterized only by the blue color and its representative spectrum is given in Figure 2(a). At room temperature, the blue color dominates and as temperature drops and approaches the transition temperature, T_C, new green regions appear and increase considerably (see Figures 1(b) and 2(b) and Table 1). Figures 1(c) and 1(d) show Raman images of M74 superconductor film measured at 133 and 77 K, respectively. At 133 K, we observed that the red color started to appear inside green regions and its Raman spectrum is shown in Figure 2(c) (see Table 1). At 77 K, where it is known that the superconducting state is already expressed in our type of films, the Raman image is characterized by the red color showing that its appearance shows us the emergence of the superconducting state, determining T_C. This monitoring of spectral map changes from normal state to superconducting state in $TlBa_2Ca_2Cu_3O_9$ high-T_C superconductor films with Tl-1223

Table 1: Experimental Raman bands for $TlBa_2Ca_2Cu_3O_9$ high-T_C superconductor films with Tl-1223 phase.

Banda (cm^{-1})	Symmetry	Atoms mainly involved
104	A_{1g}	Tl, Ba, Cu
152	A_{1g}	Cu, Ba
238	B_{1g}	O(1) CuO_2 plane-O(4)
260	A_{1g}	Ca-Ca
526	A_{1g}	Bridge O(3), O(4)

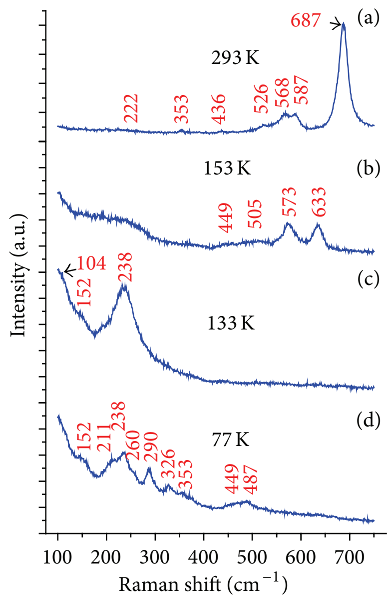


FIGURE 2: Raman spectra of the $TlBa_2Ca_2Cu_3O_9$ high-T_C superconductor films with Tl-1223 phase measured at different temperatures.

phase using Raman imaging could allow us to suggest that the emergence of the superconducting state occurred around $T_C = 133$ K. In Raman spectra at 133 and 77 K (Figures 2(c) and 2(d)), we observe that the strong band at 238 cm^{-1} (B_{1g} modes) is the one that best characterizes this red region of the Raman images and it is assigned to O(1) in CuO_2 planes, where the superconducting charge carriers are thought to be localized.

In Table 1, we observe that the A_{1g} modes of T1-1223 involve motion of Ca, Ba, Cu(2), O(2), and O(3) atoms along the c-axis [21–25]. Other Raman bands, whose origin is not clear, are shown in the Raman spectra; however, some of the bands at 293 and 449 cm^{-1} could be assigned Cu planes O(1,2) and O(2,3) [25] and the bands at 587 and 633 cm^{-1} could be a B_{1g} O(4) motion (oxygen atom of TlO plane) [26].

Raman images and spectra obtained for superconductor films, M89A and M98A, showed the same behavior as the Raman images and spectra for M74 film.

In this paper, we present the spatial distribution of the high-T_C superconductor film's major chemical components during the transition to the superconducting state.

We have reported in this paper the first spectral maps of superconductor films during superconducting transition. Raman imaging could provide us with information about which phonons could be directly associated with the superconducting transition and the regions on superconductor films where there is a greater concentration of oxygen as temperature approaches the transition temperature.

The exact sequence of events during superconducting transition is, of course, well understood from studies of fall in the electrical resistance of the superconductor films. Unlike this method, highly limited by the grain boundaries, spectral imaging methodology affords the advantage of monitoring the distribution of chemical components using only their inherent vibrational fingerprints and therefore without these limitations of granular type. Furthermore, spectral recognition of $TlBa_2Ca_2Cu_3O_9$ high-T_C superconductor films is necessary for an application of vibrational imaging methodology to aid in the detection of the superconducting phase in high-T_C films.

The main advantages of Raman imaging over other techniques include the high spatial resolution achievable, which is in the same order as visible microscopy, and the compositional sensitivity of vibrational spectroscopic methods.

As a cross-checking, we applied PCA to other sets of spectra from each film. The average of Raman spectra taken per temperature was 3 obtaining a total of 30 spectra for each film. Raw spectra were processed by carrying baseline correction, smoothing, and normalization to remove noise, sample fluorescence, and shot noise from cosmic rays. This spectral processing was performed through a filter based on the Baseline Correction with Asymmetric Least Squares Smoothing algorithm [27]. Unlike other algorithms, it is fast and simple (even for large signals) and asymmetric weighting applies everywhere. Each acquired spectrum was normalized to the highest peak. Upon processing the spectra, PCA was implemented, where the main information is described by the first principal components.

PCA was implemented based on the temperature dependence of Raman spectra. The PCA results for the M74, M89A, and M98A films are shown in Figure 3. In PCA plots, each point represents a Raman spectrum measured to a given temperature.

In each plot, clearly, the 30 points can be grouped into two temperature ranges, one in the range of 293–153 K (black points and normal state of films) and the other in the range of 133–77 K (red points and superconducting state of films) suggesting that the transition to the superconducting state occurred at some temperature around 133 K. Our result of the transition temperature using the Raman imaging technique is strongly supported by a cross-checking applying PCA. PCA was able to distinguish between spectra of the normal state and superconducting state of high-T_C superconductor films with 100% sensitivity and 100% specificity allowing us to obtain a highly reliable value for the transition temperature, T_C. This temperature value, around $T_C = 133$ K, obtained using PCA agrees perfectly with the value obtained using the technique of Raman imaging.

In this paper, we demonstrate that the recognition of the superconducting transition using methods of vibrational spectral imaging is possible, although the instrumentation utilized may not have been optimal for this purpose. In Raman spectroscopy, the high spatial resolution reveals details of the spatial distribution of chemical components in high-T_C superconductor films. The use of somewhat higher laser power and more efficient optical components will reduce the data acquisition time and improve the signal quality to such an extent that this methodology may be useful for screening applications of all types of thin films.

4. Conclusions

In this paper, we presented the first spectral maps of the distribution of the high-T_C superconductor film's major chemical

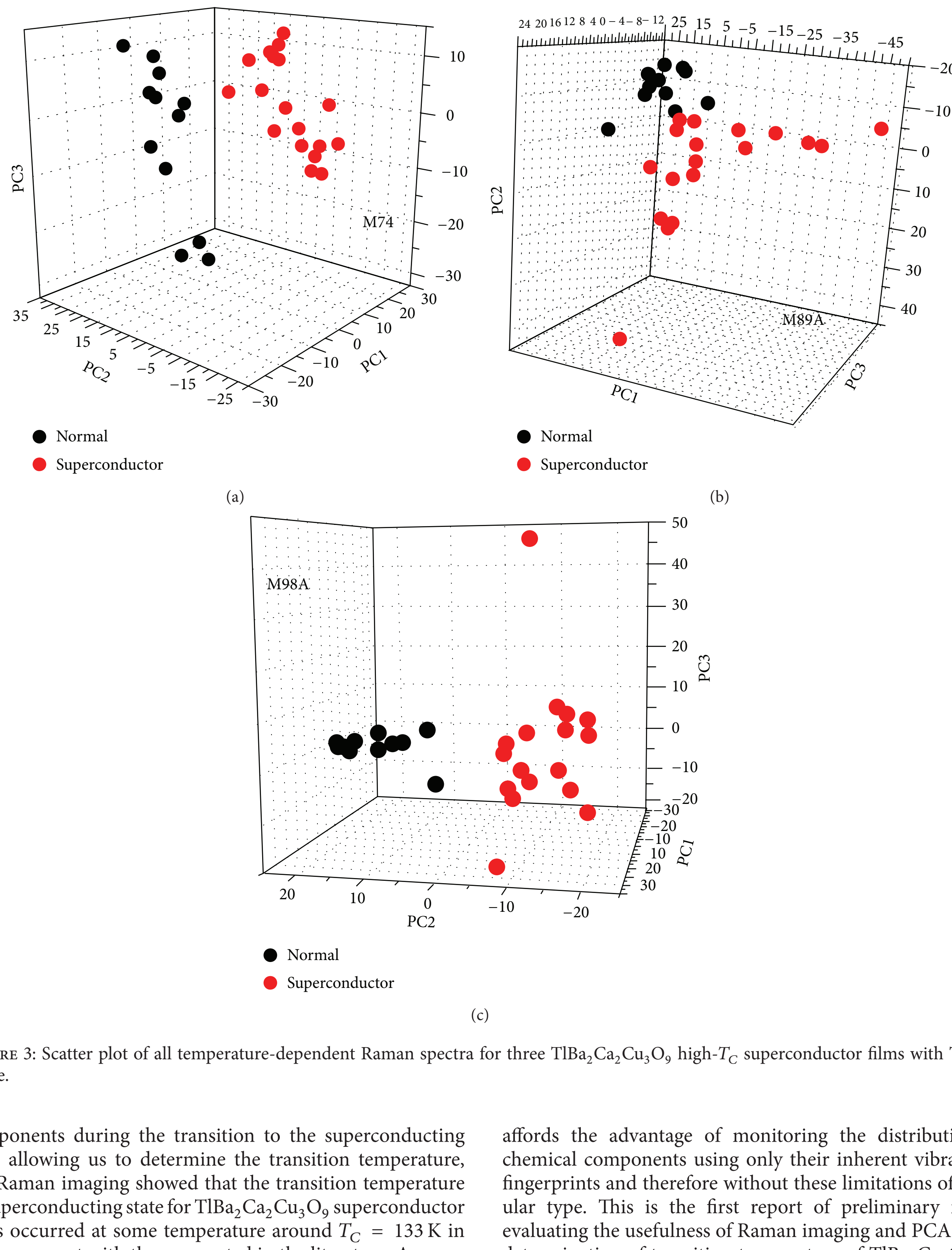


Figure 3: Scatter plot of all temperature-dependent Raman spectra for three $TlBa_2Ca_2Cu_3O_9$ high-T_C superconductor films with Tl-1223 phase.

components during the transition to the superconducting state allowing us to determine the transition temperature, T_C. Raman imaging showed that the transition temperature to superconducting state for $TlBa_2Ca_2Cu_3O_9$ superconductor films occurred at some temperature around $T_C = 133$ K in full agreement with those reported in the literature. A cross-checking was done applying principal component analysis to other sets of spectra of the superconductor films measured at different temperatures and obtaining same value for the transition temperature. Unlike other methods to measure this critical temperature in high-T_C superconductor films, highly limited by the grain boundaries, Raman imaging technique affords the advantage of monitoring the distribution of chemical components using only their inherent vibrational fingerprints and therefore without these limitations of granular type. This is the first report of preliminary results evaluating the usefulness of Raman imaging and PCA in the determination of transition temperature of $TlBa_2Ca_2Cu_3O_9$ high-T_C superconductor films with Tl-1223 phase.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

The authors wish to thank CONACYT for financial support under Grant no. 45488. Also, they are thankful to Intercovamex Company in Mexico for the financial aid to show this work in XXII International Material Research Congress, IMRC 2013.

References

[1] T. P. Sheahen, *Introduction to High-Temperature Superconductivity*, Plenum Press, New York, NY, USA, 1994.

[2] A. Goyal, D. P. Norton, J. D. Budai et al., "High critical current density superconducting tapes by epitaxial deposition of $YBa_2Cu_3O_x$ thick films on biaxially textured metals," *Applied Physics Letters*, vol. 69, no. 12, pp. 1795–1797, 1996.

[3] N. Dieckmann, A. Bock, and U. Merkt, "Spatially resolved analyses of epitaxial and electrical properties of $YBa_2Cu_3O_7$ devices," *Applied Physics Letters*, vol. 68, no. 25, pp. 3626–3628, 1996.

[4] A. Bock, R. Kürsten, M. Brühl, N. Dieckmann, and U. Merkt, "Desorption of oxygen from $YBa_2Cu_3O_{6+x}$ films studied by Raman spectroscopy," *Physical Review B - Condensed Matter and Materials Physics*, vol. 54, no. 6, pp. 4300–4309, 1996.

[5] C. Thomsen, R. Liu, M. Bauer et al., "Systematic Raman and infrared studies of the superconductor $YBa_2Cu_3O_{7-x}$ as a function of oxygen concentration ($0 \leq x \leq 1$)," *Solid State Communications*, vol. 65, no. 1, pp. 55–58, 1988.

[6] R. Feile, U. Schmitt, and P. Leiderer, "Raman experiments on YBaCuO-Superconductors," *Physica C*, vol. 153–155, no. 1, pp. 292–293, 1988.

[7] S. B. Dierker, M. V. Klein, G. W. Webb, and Z. Fisk, "Electronic raman scattering by superconducting-gap excitations in Nb_3Sn and V_3Si," *Physical Review Letters*, vol. 50, no. 11, pp. 853–856, 1983.

[8] C. Thomsen, "Light scattering in high-$T_c$superconductors," in *Light Scattering in Solids VI*, M. Cardona and G. Güntherodt, Eds., vol. 68 of *Topics in Applied Physics*, pp. 285–359, Springer, Berlin, Germany, 1991.

[9] E. Faulques and R. E. Russo, "Characterization of high temperature superconductors with Raman spectroscopy," in *Applications of Analytical Techniques to the Characterization of Materials*, D. L. Perry, Ed., Plenum Press, New York, NY, USA, 1991.

[10] C. Matthäus, S. Boydston-White, M. Miljković, M. Romeo, and M. Diem, "Raman and infrared microspectral imaging of mitotic cells," *Applied Spectroscopy*, vol. 60, no. 1, pp. 1–8, 2006.

[11] N. Stone, C. Kendall, N. Shepherd, P. Crow, and H. Barr, "Near-infrared Raman spectroscopy for the classification of epithelial pre-cancers and cancers," *Journal of Raman Spectroscopy*, vol. 33, no. 7, pp. 564–573, 2002.

[12] J. L. González-Solís, J. C. Martínez-Espinosa, L. A. Torres-González, A. Aguilar-Lemarroy, L. F. Jave-Suárez, and P. Palomares-Anda, "Cervical cancer detection based on serum sample Raman spectroscopy," *Lasers in Medical Science*, vol. 29, pp. 979–985, 2014.

[13] J. L. González-Solís, J. C. Martínez-Espinosa, J. M. Salgado-Román, and P. Palomares-Anda, "Monitoring of chemotherapy leukemia treatment using Raman spectroscopy and principal component analysis," *Lasers in Medical Science*, vol. 29, no. 3, pp. 1241–1249, 2014.

[14] Q. Zhang and Y. Zhang, "Hierarchical clustering of gene expression profiles with graphics hardware acceleration," *Pattern Recognition Letters*, vol. 27, no. 6, pp. 676–681, 2006.

[15] P. D'Haeseleer, "How does gene expression clustering work?" *Nature Biotechnology*, vol. 23, no. 12, pp. 1499–1501, 2005.

[16] L. Kullmann, J. Kertesz, and R. N. Mantegna, "Identification of clusters of companies in stock indices via Potts super-paramagnetic transitions," *Physica A*, vol. 287, no. 3-4, pp. 412–419, 2000.

[17] A. Dekel and M. J. West, "On percolation as a cosmological test," *The Astrophysical Journal*, vol. 288, pp. 411–417, 1985.

[18] A. Iyo, Y. Tanaka, Y. Ishiura et al., "Study on enhancement of Tc (≥ 130 K) in $TlBa_2Ca_2Cu_3O_y$ superconductors," *Superconductor Science and Technology*, vol. 14, no. 7, pp. 504–510, 2001.

[19] L. Pérez-Arrieta, M. Aguilar-Frutis, J. L. Rosas-Mendoza, C. Falcony, and M. Jergel, "Two step synthesis of $TlBa_2Ca_2Cu_3O_x$ films on *Ag* substrates by spray pyrolysis of metal-acetylacetonates," *Revista Mexicana de Fisica*, vol. 54, no. 6, pp. 446–450, 2008.

[20] S. S. P. Parkin, V. Y. Lee, A. I. Nazzal, R. Savoy, R. Beyers, and S. J. La Placa, "Tl_1 Ca_{n-1} Ba_2 Cu_n O_{2n+3} ($n = 1, 2, 3$): a new class of crystal structures exhibiting volume superconductivity at up to ~110 K," *Physical Review Letters*, vol. 61, no. 6, pp. 750–753, 1988.

[21] C. Thomsen and G. Kaczmarczyk, "Vibrational Raman spectroscopy of high-temperature superconductors," in *Handbook of Vibrational Spectroscopy*, J. M. Chalmers and P. R. Griffiths, Eds., John Wiley & Sons, Chichester, UK, 2002.

[22] D. L. Perry, *Applications of Analytical Techniques to the Characterization of Materials*, Springer Science+Business Media, LLC, 1990.

[23] K. F. McCarty, B. Morosin, D. S. Ginley, and D. R. Boehme, "Raman analysis of $TlCa_2Ba_2Cu_3O_{19}$ and $Tl_2Ca_2Ba_2Cu_3O_{10}$ crystals," *Physica C: Superconductivity and Its Applications*, vol. 157, no. 1, pp. 135–143, 1989.

[24] C. Thomsen and M. Cardona, "Light scattering in high-T_c superconductors," in *Physical Properties of High Temperature Superconductors I*, D. M. Ginsberg, Ed., p. 409, World Scientific, Singapore, 1990.

[25] A. D. Kulkarni, F. W. de Wette, J. Prade, U. Schröder, and W. Kress, "Lattice dynamics of high-Tc superconductors: optical modes of the thallium-based compounds," *Physical Review B*, vol. 41, no. 10, pp. 6409–6417, 1990.

[26] E. Faulques, P. Dupouy, and S. Lefrant, "Oxygen vibrations in the series $Bi_2Sr_2Ca_{n-1}Cu_nO_{4+2n+y}$," *Journal de Physique I*, vol. 1, pp. 901–916, 1991.

[27] H. F. M. Boelens, P. H. C. Eilers, and T. Hankemeier, "Sign constraints improve the detection of differences between complex spectral data sets: LC-IR as an example," *Analytical Chemistry*, vol. 77, no. 24, pp. 7998–8007, 2005.