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Colorimetry technique on $BaTiO_3$ and $KNbO_3$ ceramics to determine the phase transition

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Abstract

In this work, colorimetry was used in order to identify the phase transition of $BaTiO_3$ and $KNbO_3$ ceramic. The transition of the structure produces a change of color of the ceramic bulks because their optical properties change. The transition phase was detected with a color sensor and reflectance method on ceramic bulks. *CIE L*a*b** and *CIE L*u*v** color spaces were used to measure the color changes reported. Experimental results showed that the changes of color are suitable for detecting the phase transition in both perovskite structures. The phase transition in the proposed ferroelectric materials was also measured by means of the dielectric constant method and the results obtained were in agreement with the temperatures reported for phase transition changes on $BaTiO_3$ and $KNbO_3$. Therefore, the colorimetry technique proposed in this paper proved to be suitable for detecting structure changes as a relationship between color properties and temperature.

Keywords: Colorimetry; Ferroelectric ceramics; Phase transition

1. Introduction

The optical properties of materials have been used as an indirect method to obtain information of their physicochemical properties. The light reflected by an object is modified according to these properties, and in many cases, these variations contribute to a change in the perception of the color of the materials.[1] This occurs generally when metals are heated or when they have been subjected to chemical reactions.[2–6] When ferroelectrics are heated, an internal change of their chemical structure occurs; these changes, known as phase transition (PT), produce an alteration on their optical properties. The temperature at which PT occurs can be indirectly measured by techniques such as reflectance [7] which, through the material optical properties, measures microscopic changes on the PT that modify the ceramic reflective properties. Other optical properties can also be used to determinate curie temperature (T_C) in ceramics of $BaTiO_3$ and $KNbO_3$ and other compounds.[8–15]

The colorimetric technique proposed in this paper also applies the reflectance principle to measure color changes on ceramic bulks. These color changes are due to alterations in reflection and absorption properties. Refractive index and absorption coefficient are the indicators that change when the PT occurs.[16,17] In photopic conditions, the human eye can appreciate the variation of color caused by the temperature increase of the ceramic; however, it is necessary to use a color sensor to quantify the changes on a conventional color space. Internationally, *CIE L*a*b** and *CIE L*u*v** are two color spaces that allow measuring color properties.[18] They were developed with the purpose to obtain more uniform color spaces[19] and both use three parameters to quantify colors: *Lightness*, *Hue* and *Chroma*, as shown in Fig. 1.

2. Method

The color of bulks made of ferroelectric ceramics of barium titanate ($BaTiO_3$) and potassium niobate ($KNbO_3$) was measured.[20,21] Aldrich provided the raw materials for the bulks, $BaTiO_3$ and $KNbO_3$. The powders were ball-milled with an electronic mill until the grains were fine. Some drops of polyvinilic alcohol, at a rate of 1.5 drops per gram, were added. Later, pow-

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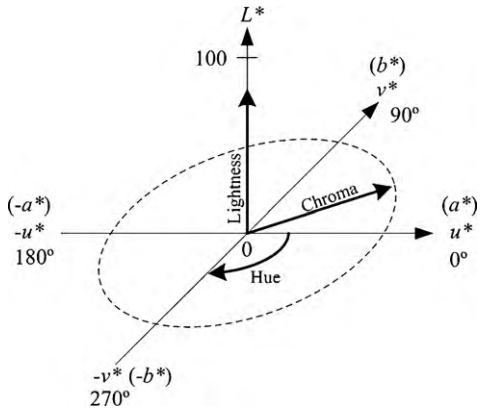

Fig. 1. Three-dimensional coordinate system representation of the *CIE L*u*v** color space. Distribution of coordinate system (illustrated in quotes) for *CIE L*a*b** color space is similar to *CIE L*u*v**.

ders were pressed, by applying 3500 kg/cm^2, into discs of 10 mm diameter and 2 mm of thickness. Sinterization was performed as follows: $BaTiO_3$ discs were heated with a rate of 5 °C/min until they reached 600 °C, then the rate was increased to 10 °C/min until they reached 1200 °C; thereafter temperature was kept stable for 2 h. $KNbO_3$ disks were heated in three intervals with a rate of 10 °C/min each: from room temperature to 130 °C, and then from 130 °C to 280 °C; the final temperature of each interval was kept stable for 10 min. Thereafter, heating continued uninterruptedly until temperature reached 800 °C; then temperature was kept stable for 60 min.

The ceramic bulks were heated by a controlled heater as it is shown in Fig. 2. Thus, it was possible to ensure that the temperature rate did not increase faster than 0.5 °C/s. This requirement allowed the color sensor to obtaining at least 10 measurements per each centigrade degree. The color sensor was located over one side of the ceramic bulk with a separation distance of 3 mm. The distance between the sensor and the ceramic was the same for all the measurements. The sensor was protected from thermal induction with isolating material in order to avoid possible measurement errors caused by the heat of the sensor circuitry. Based on the reflectance technique, the color sensor used was the MTCS-ME1 mainboard with the modEVA-TOP plug-in module of Jencolor. A beam of white light illuminated the ceramic surface with a slope of 45° and returned through a round aperture to the color sensor. The light reflected contained information of the changes of color that occurred in the ceramics. The disturbances of the photopic environment were reduced with this setup. The sensor mainboard sent the coordinates of both CIE spaces aforementioned to the computer and they were synchronized with the temperature measurements. Afterwards, measures were averaged for each grade.

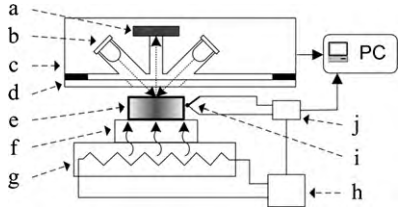

Fig. 2. Experimental setup to measure the color parameters based on *CIE L*u*v** and *CIE L*a*b** spaces of $BaTiO_3$ and $KNbO_3$ ceramics: (a) color sensor, (b) light source, (c) MTCS-ME1 mainboard with modEVA-TOP module, (d) thermal isolation, (e) ceramic bulk, (f) aluminum base, (g) heater, (h) temperature control, (i) thermocouple and (j) digitizer.

3. Theory

Lightness, *Hue* and *Chroma* ease the distinction between different wavelengths and luminance of sources of color. *Lightness* (L^*) is related to the luminance of grays; therefore, a value of $L^* = 0$ denotes a perfect black. The scale of the color is defined by *Hue* (h). According to Fig. 1, *Hue* angle denotes the dominant wavelength of the color. Last, *Chroma* (C) is directly related to the spectral content of the wavelengths that are merged and thus conform a particular color. Absence of color produces a zero value in *Chroma*. In addition, it is the magnitude of the resultant vector on a bidimensional plane for a specific color represented in the coordinate systems for CIE color spaces, as it can be seen in Fig. 1. In *CIE L*a*b**, *Hue* and *Chroma* can be calculated with the following equations:

$$h_{ab} = \tan^{-1}\left(\frac{b^*}{a^*}\right) \quad (1)$$

$$C_{ab} = [(a^*)^2 + (b^*)^2]^{1/2} \quad (2)$$

and for *CIE L*u*v**:

$$h_{uv} = \tan^{-1}\left(\frac{v^*}{u^*}\right) \quad (3)$$

$$C_{uv} = [(u^*)^2 + (v^*)^2]^{1/2} \quad (4)$$

where a^* and b^* are *CIE L*a*b** coordinates; u^* and v^* are coordinates of *CIE L*u*v**. However, there is no simple relationship between the scales of a^*, b^* and u^*, v^*. Data can only be transferred from one color space to another going back to X, Y, Z tristimulus values.[19] *Lightness* L^* is the third coordinate for both color spaces and it is defined by Eq. (5). L^* describes the changes of blackout and has the same value for *CIE L*u*v** and *CIE L*a*b**:

$$L^* = 116\left(\frac{Y}{Y_n}\right)^{1/3} - 16 \quad (5)$$

*CIE L*a*b** and *CIE L*u*v** color spaces are more focused on color measurements over surfaces; therefore, they are more suitable for the purpose of this study.

4. Results

The dielectric constant method[22] was used to compare the results obtained by the colorimetry technique proposed in this paper. Fundamentally, this method consists in measuring the dielectric constant of the ceramic bulks while they are being heated; Fig. 3 shows the dielectric constant for $BaTiO_3$ as a function of temperature. The $BaTiO_3$ phase transition from tetragonal to cubic structure occurred at about 130 °C, and for $KNbO_3$, the transition from orthorhombic to tetragonal occurred

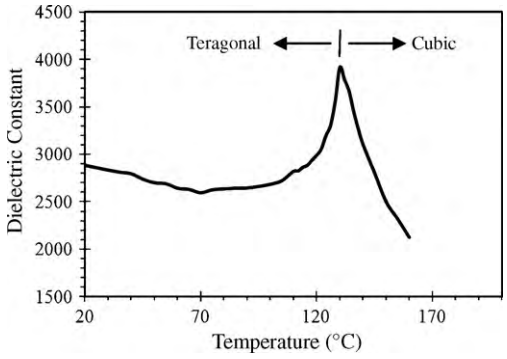

Fig. 3. Dielectric constant of $BaTiO_3$ as a function of temperature. Phase transition from tetragonal to cubic was reached at 130 °C.

at about 200 °C. In the case of the colorimetry technique, the measurements of *L*a*b** and *L*u*v** were used in Eqs. (1)–(5) to calculate the variations of *Lightness*, *Hue* and *Chroma* that occurred during the phase transition for $BaTiO_3$. The most evident changes were found for *Lightness* and *Chroma*. The change on the tendency of *Lightness* agreed with the absorption coefficient increment reported by DiDomenico and Wemple[23,24]. In other words, the body of the ceramic absorbed different spectral components of light before PT occurred. Changes in *Chroma* also confirmed that the light reflected was modified by the changes in the optical properties produced by PT. Moreover, the ceramic tended to become more reflective during the interval of heating. The $KNbO_3$ *Lightness* followed a similar behavior as that for $BaTiO_3$ ceramic. The changes on *Chroma* for both ceramics were different; however, it was evident that the behavior of color changes was analog for these two compounds.

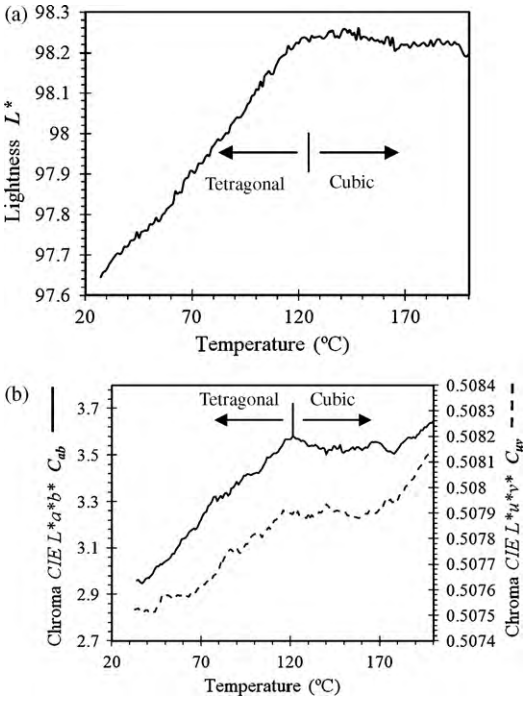

Fig. 4. Tetragonal to cubic phase transition detected by colorimetry technique occurred at about 120 °C on $BaTiO_3$ ceramic as indicated by abrupt changes on: (a) *Lightness* and (b) *Chroma* based on the *CIE L*u*v** and *CIE L*a*b** spaces.

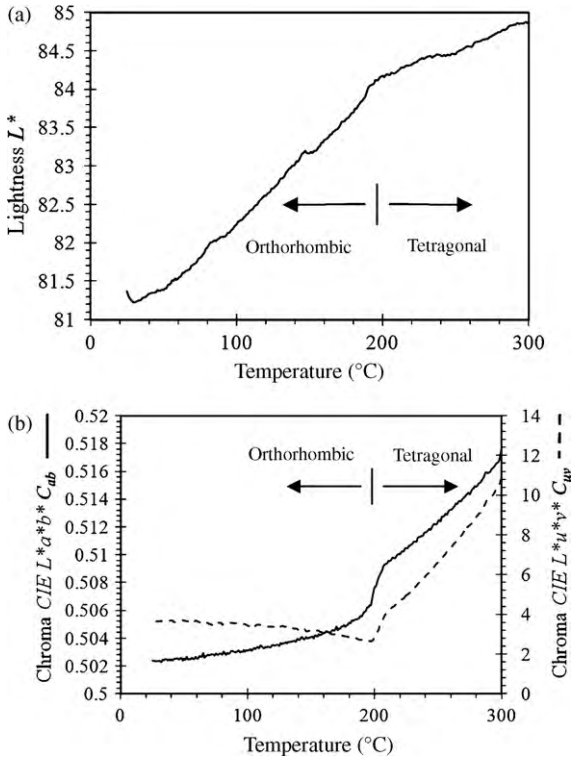

Fig. 5. Orthorhombic to tetragonal phase transition detected by colorimetry technique occurred at about 200 °C on $KNbO_3$ ceramics as indicated by abrupt changes on: (a) *Lightness* and (b) *Chroma* based on the *CIE L*u*v** and *CIE L*a*b** spaces.

Thereby, the *Lightness* increment ratio was reduced; the *Hue* angle diverged in the same direction for $KNbO_3$ and $BaTiO_3$ in the case of *CIE L*a*b** or *CIE L*u*v**, and the magnitude in *Chroma* increased its value after the phase change. Finally, the results presented here show that the PT in $BaTiO_3$ occurred at 120 °C (Fig. 4); while for $KNbO_3$, it occurred at 200 °C (Fig. 5). The phase transition was detected by colorimetry technique due to the significant changes in color variation tendency.

It is important to mention that the measurements can be disturbed by the pollution caused by thermal evaporation of the materials used to mount the setup. During one of the experiments performed in this work, the pollution caused by particles evaporated from other elements, like polymers nearest to the ceramic during the heating, produced a film over the ceramic surface, which disturbed the results severely. However, under conditions of minimal ceramic pollution during the process of heating, it was possible to confirm that the changes in color reported in this paper were completely reversible for both types of ceramics.

5. Conclusions

The results of colorimetry technique confirmed the data found with traditional techniques of dielectric constant and other methods that connect alterations in optical properties of $BaTiO_3$ and $KNbO_3$ with the temperature at which PT occurs.[25–30] An advantage of using the technique proposed here is that it does not require electrodes or a highly controlled environment during the

measurements; it only requires a free surface over the ceramic bulk where to direct the light beam. This is very convenient when thin films of ceramics are used and it is necessary to characterize them. However, depending on the ceramic composition, orthorhombic to tetragonal phase transition detection, as in the case of $KNbO_3$, a better thermal isolation would be needed in order to avoid any color sensor damages. Thermal isolation also reduces disturbances on the color sensor circuits, which otherwise may produce false phase transition detections. Additionally, color measurements based on two color spaces produced clearer evidence of the fact that changes in the structure of these types of ferroelectric ceramics also modify their surface optical properties. Finally, these experimental results suggest that the colorimetric technique described in this paper would be appropriate to obtain the PT of ferroelectric ceramics made of other compounds.

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