QUANTUM MECHANICAL AND EXPERIMENTAL STUDY OF THE ADDITION OF Ni TO THE $BaTiO_3$ MATRIX FOR OPTICAL APPLICATIONS

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1. INTRODUCTION

In general pigments consist of a host network, matrix, in which the pigmenting component is integrated, usually involving a transition or internal transition cation, and the possible stabilizing modifier constituents, thus achieving the pigmenting properties. A ceramic pigment is an inorganic compound, which in turn needs to display a stable crystalline structure at high temperatures, be insoluble in the material in which it is applied, have an appropriate particle size, be resistant to acids, alkalis or abrasives, and not to release gases into the glaze[1]. In order to assure that these properties are reproducible, rigorous control is required of the synthesis materials, and their heat treatment (calcination).

$BaTiO_3$ was used as a matrix for Ni in this study. This compound has been widely studied due to its interesting electric properties: ferroelectricity, high dielectric constant, piezoelectricity and pyroelectricity, however with regard to its pigmenting applications, hardly anything was found in the literature[2].

The $Ni_xBa_{1-x}TiO_3$ powders for the study of the optical properties were prepared by the Pechini method. Ni was added to the matrix in different percentage (X= 1.0; 5.0 and 10.0% by moles). These powders were calcined at temperatures of 380°C for 90 min and 600°, 800° and 1000°C for 2h. The samples were characterized by X-ray diffraction, Raman spectroscopy, UV-visible spectroscopy and colorimetry. To better understand the experimental results, quantum mechanical calculations were made using the CRYSTAL98 computational package for the periodic system.

2. EXPERIMENTAL RESULTS

The X-ray diffraction analyses enabled verifying the formation of barium titanate with a tetragonal structure for all the synthesized compounds, without detecting any other phase, thus involving a monophase material ($H_{Tetragonal}$). Based on XRD, by means of the Scherrer equation, we calculated the size of the crystallites for the samples; these displayed sizes between ~ 20-60 nm. The tetragonality factor (c/a) was calculated, verifying a reduction in the tetragonality of the compounds with the addition of Ni, which was consistent with the Raman spectroscopy results, in which no Raman vibrational modes were verified, and the compounds were assumed to have a pseudocubic structure.

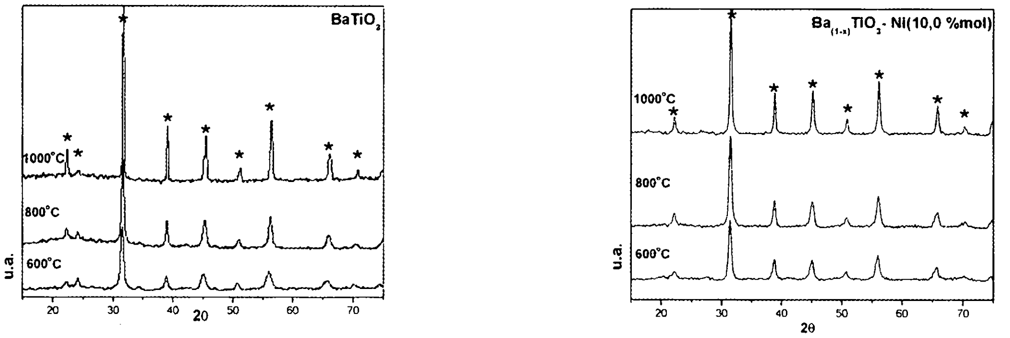

Figure 1. DRX of $BaTiO_3$ (a) and of $Ba_{(1-x)}TiO_3$-Ni (10.0 mol%) (b) calcined at 600, 800 and 1000°C for 2h.

The colours were characterized by measuring their wavelength (l) in the UV-visible region, comparing the standard white with three different sources of illumination (A), (C) and (D50), where (A) was a tungsten light, (C) midday light of illuminant (A) modified by filters, and (D50) midday light. The colorimetric coordinates (L a* b*) displayed an activation for the green and yellow colours (a*< 0) and (b* >0).

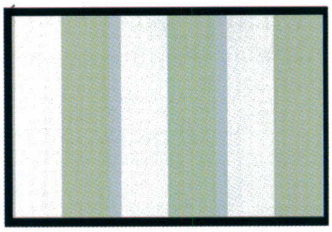

Figure 2. Comparison of the colour of $Ba_{(1-x)}TiO_3$*-Ni(10.0 mol%) calcined at 1000°C for 2h with the standard white using the three different illuminants (A), (C) and (D50).*

UV-vis spectroscopy showed a greater reflectance in the 500-800 nm region, which corresponds to the green region. Using these spectra, it has also been possible to verify the experimental gaps of the compounds, which displayed values between approximately 3.5 and 3.0 eV for the pure and Ni-doped $BaTiO_3$ respectively.

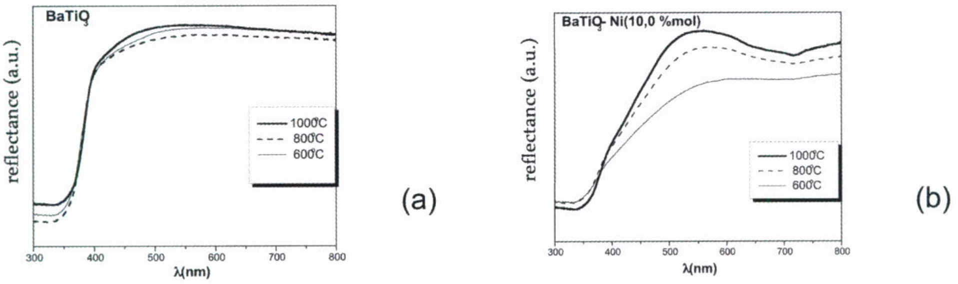

Figure 3. UV-visible spectrum of sample $BaTiO_3$ *(a)* $Ba_{(1-x)}TiO_3$*-Ni(10.0 mol%) (b) calcined at 600, 800 1000°C for 2h.*

For greater support of the research and quantum mechanical understanding of the compounds, calculations were performed using the CRYSTAL98 computational base for periodic systems. In the first place, calculations were made for the optimization of the parameters as Figure 4 shows. These calculations enabled verifying the values of the "gap" of the material in its tetragonal structure; in accordance with the experimental results these were approximately 3.5 eV. For the doped material, some adjustments in the calculations still remain pending.

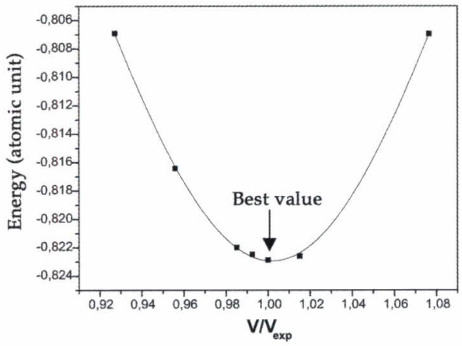

Figure 4 . Optimization curve of the theoretical calculations.

3. CONCLUSIONS

BT exhibited an excellent matrix for Ni; XRD analysis indicated that the powders were monophase, and all the compounds displayed nanometric crystallite sizes. The Raman spectra presented no vibrational modes for any of the Ni-doped compounds, and it was assumed that these compounds had a pseudocubic structure. The quantum mechanical calculations were shown to be tools of great importance for obtaining better structural conclusions in the future in relation to the compounds studied for their application as pigments.

REFERENCES

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