Study of Phase Transition in $(Ba_{0.6}Sr_{0.4})(Ti_{1-x}Ni_x)O_3$ Ceramics by Dielectric Measurements.

N. Leguedani[1], S. Mouden[1], M. Hafid[1] and T. Fukami[2].

[1]*LPVC-Departement of Physics IBN Tofail University, Faculty of Sciences,14000 Kenitra, Morocco.*

[2]*Departement of Electronic Engineering, Faculty of Engineering, Shinshu University, Nagano 380, Japan.*

A dielectric measurements study of the phase transitions in(Ba0.6Sr0.4)(Ti1-xNix)O3 transitions in ceramics with x ranging from 0.0 to 3.0 is reported. Both temperature transitions of respectively cubic-tetragonal and tetragonal-orthorhombic phase transitions are shifted to lower temperature with increasing Ni content. A change from normal to diffused phase transition is also observed in Ni-doped samples.

I. INTRODUCTION

The study of the ferroelectric materials like $BaTiO_3$, $(Ba_xSr_{1-x})TiO_3$ (BST) and doped BST is of a great interest, since there are quite a lot of important properties to be investigated. Indeed desirable properties include low-temperature Curie peak, high dielectric constant and low dielectric losses are requested in diverse technology devices[1-4]. Its known that the curie temperature of barium strontium titanate (BST) can be changed by adjusting the Ba:Sr ratio [5,6]. Several studies have been reported on BST with various dopants [1,7-10]. In order to contributed to the comprehension of the role played by dopants like Ni^{2+} on the phase transitions and its influence on the dielectric properties, we report in this paper recent dielectric investigation on $(Ba_{0.6}Sr_{0.4})(Ti_{1-x}Ni_x)O_3$ with x ranging from 0 to 3%.

II. EXPERIMENTAL METHODS

The investigated materials have been prepared from pure brium titanyl oxalate, chemically pure strontium carbonate, and nickel and titanium oxides. The required amounts of these materials were wet-mixed for 10h in a high-alumina mill and calcinated at 1150°C for 1h in air to provide starting powders with desired compositions.The milling with 5 mm diameter ZrO_2 balls after calcination continued for some 20h. After drying, the powders were pressed into pellets, 20 mm in diameter and 2 mm thick, under a pressure of 300 kg/cm^2 and then sintered at 1350°C for 2 h in air. X-ray diffractometry using a SIEMENS D500 with a Cu anti-cathod (λ_{Cu}= 1.5419 Å) has been performed in order to confirm the crystal structure of the studies ceramics. Their morphology was observed throught a cambrige Stereoscan 100 scanning electron micrograph (SEM. Fig 1(a) and (b) show an example of the obtained SEM pictures for ceramics with 0.5% and 1% Ni-doped.

For dielectric measurements, vacuum-evaporated gold electrodes have been deposited on both faces of each ceramics. For low-temperature measurements, the prepared samples were introduced in a nitrogen-cryostat controlled with a TBT400 temperature to above 420K, a furnace have been used. The dielectric constant has been then obtained using an HP 4194A Impedance Analyzer linked to a computer for data analysis.

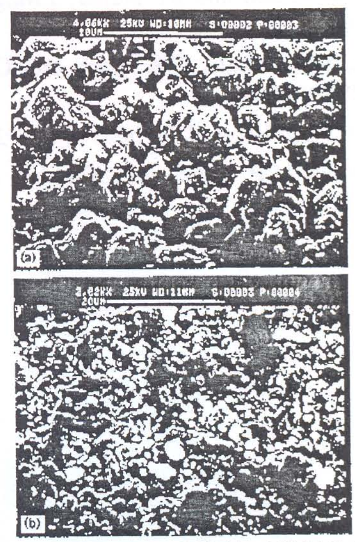

FIG. 1 : SEM micrographs of 0.5% (a) and (b) Ni doped $(Ba_{0.6}Sr_{0.4})(Ti_{1-x}Ni_x)O_3$.

III. RESULTS AND DISCUSSION.

Figure 2 represents, the dielectric ε for $(Ba_{0.6}Sr_{0.4})TiO_3$ (BST) and BST-Ni doped ceramics (x_{Ni}= 0.2-3%), measured under 1 kHz and in a temperature range from 100 to 450K.

The results show that in contrast to pure $BaTiO_3$, the well known Curie temperature [11] takes place at about 280K for BST sample. When introducing nickel ions, both cubic-tetragonal (C-T) and tetragonal-orthorhombic (T-O) temperature transitions are shifted to lower temperatures. Figure 3, where Tc_1 and Tc_2 referred to the C-T and T-O respectively, shows the Ni-influence on both temperature transitions. On the other hand it is worth to note that the introduction of Ni ions in BST leads to a dispersion of curie temperature, which gives a diffused nature to a cubic-tetragonal transition (fig. 4).

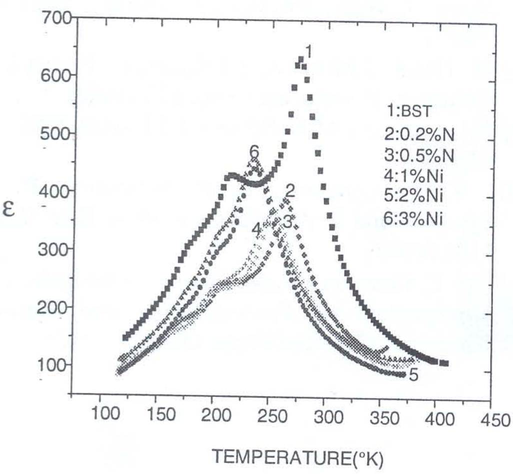

FIG 2. Dielectric constant as function of temperature for

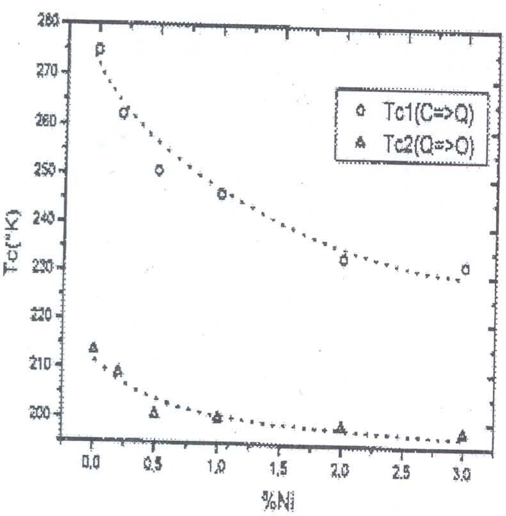

Fig. 3. Curie temperature vs. Ni content in (Ba...

FIG 3. Curie temperature vs Ni content $Ba_{0.6}Sr_{0.4})(Ti_{1-x}Ni_x)O_3$.

Theoretical analysis [9] has been developed to explain the origin of both the appearance of the diffused phase transition and the shift of the Curie temperature to lower temperature. The main features

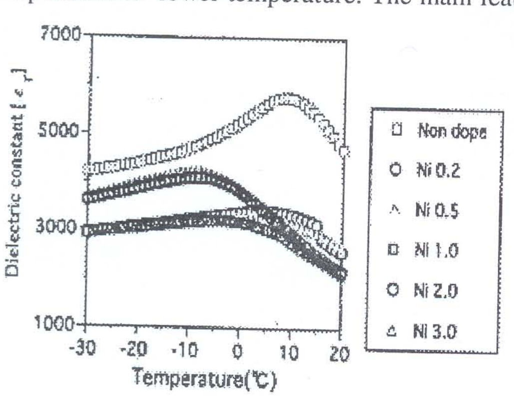

Fig. 4. Temperature dependence of ε_r near the C-T transition.

of this analysis consider the substitutional ions as defect of the ''Random Local Temperature Transition'' type, and the concept of the soft mode to describe the displacive nature of the phase transition. Equation (1) included parameters a, b and c which are adjusted to give the best fit to the experimental data figure 5.

$$Tc=[a(N(r)+1)Tci-(a+bN(r)+c)T]/[(a-b)N(r)-c)] \quad (1)$$

Where N(r) is a random function having a different form for various system (here $N(r) \equiv n = \%$ Ni), and Tci is the Curie temperature in non-doped system (BST).

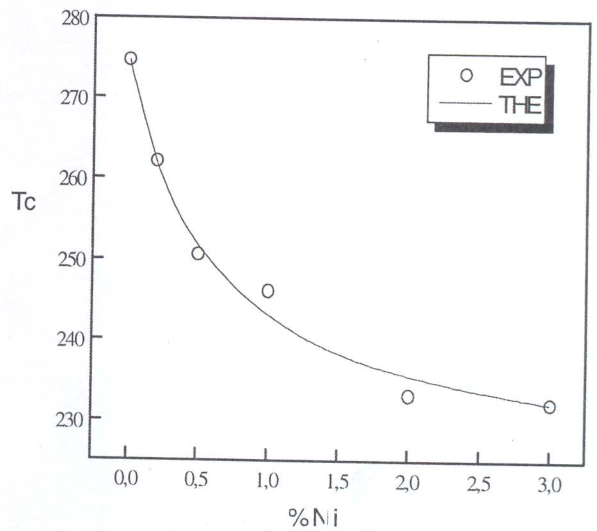

FIG 5. Tc decrease vs the amount of Ni, experimental data represented with open circle and the linear curve correspond to the fit using formula (1)

IV. CONCLUSION

The obtained results show clearly that the dielectric properties and the Curie temperatures are mostly dominated by the introduction of Ni^{2+} ions which leads to a diffused phase transition in the $(Ba_{0.6}Sr_{0.4})TiO_3$ ceramics.

ACKNOWLEDGMENT

This work was supported by the PARS grant N°: physique 01.

[1] S. B. Herner, F. A. Selmi, V. V Varadan and V. K. Varadan, Mater. Lett. 15, 317 (1993).
[2] D. A. Johnson, Microwave Laboratory of Stanford University, M. L Report No. 825 (July, 1961)
[3] L. M Sherppard, Bull. Am. Ceram. Soc. 71, 85 (1992).
[4] F.Selmi, D. K. Ghogaonkar, R. Hughes, V. V. Varadan and V. K. Varasan, *SPIE,* Vol 1489, *Structure, Sensing and Control* (1991), p.97.
[5] Y.Syamaprasad. R. K. Gagali and B. C. Mohanty, Mater. Lett. 7, 197 (1988).
[6] L. Zhou, Z. Jiang and S. Zhang, J. Am.Ceram. Soc. Commun. 74 2925 (1991)
[7] T. Fukami, M. Kusunoki and H. Tsuchiya, Japan. J. Appl. Physics 26, (Supp. 26-2) 46 (1987).
[8] M. Hafid, S.Mouden, T.Fukami, C. Proust and E.Husson, Feroelectrics 186, 173 (1996)
[9] N.Leguedani, M.Hafid and S.Mouden RNJCP[2] 97.p.41.
[10] V. V. Lemanov, E. P. Smirnova, P. P. Syrnikov and E. A.Tarakanov, Phys. Rev. B 54, 3151 (1996).
[11] M. E. Lines and A. M. Glasses, *Principles and Applications of Ferroelectrics and Related Materials* (Claredon Press, Oxford, 1977).