Available Online

JSR Publications

J. Sci. Res. **1** (2), 192-199 (2009)

JOURNAL OF SCIENTIFIC RESEARCH

www.banglajol.info/index.php/JSR

Ferroelectric Phase Transition in Cu-doped $BaTiO_3$ Crystals

A. Ouedraogo[1*], K Palm[1], and G. Chanussot[2]

[1]Laboratory of Applied Organic Chemistry and Physics, UFR/SEA University of Ouagadougou BP 7021 Ouagadougou 03 Burkina Faso

[2]Laboratory of Dielectrics University of Dijon 21000 Dijon France

Received 23 January 2009, accepted in final revised form 6 April 2009

Abstract

The paper examines the ferroelectric-paraelectric phase transition in Cu:$BaTiO_3$ single crystals. Using thermo-currents and dielectric measurements, we found for pure samples the phase transition temperature to be close to Curie temperature (T_c=120°C) with an anisotropy of the dielectric constantε.The lowering of temperature T_m, corresponding to the maximum of pyroelectric signal, with the increase of concentration of impurities is confirmed by measurements of ε. Moreover, the $\varepsilon(T)$ curves show progressive broadening as well as higher peak with the increase of impurity concentration, and the transition becomes more and more diffuse**.** The same effect occurs when the samples are subjected to a laser irradiation (λ=5145Å). During annealing, crystals lose copper and T_m is thereafter observed to increase again. $BaTiO_3$ is a displacive ferroelectric (having high permittivity k-values) which undergoes a first order phase transition. Ions substitutions have an effect on the lattice dynamics attributed to charge transfer to Ti and a lowering of elastic forces in $BaTiO_3$.

Kewwords: Ferroelectric transition; $BaTiO_3$ single crystals; Thermo-currents; Dielectric constant.

DOI: 10.3329/jsr.v1i2.1876

1. Introduction

The remarkable impact of Fe, Co and Mn concentrations on the ferromagnetic and ferroelectric properties is attributed to the effective exchange coupling interaction between oxygen vacancies and the doping ions [1, 2]. It is also known that the unusual dielectric properties of $BaTiO_3$ make this ferroelectric compound at ambient temperature (Curie temperature T_c=120°C) an important material for electrical engineering. Its photorefractive character is very useful in nonlinear optics for holographic storage [3]. Indeed $BaTiO_3$, $SrTiO_3$ and $CaTiO_3$, the best-known perovskites of the ABO_3 type, find

* *Corresponding author*: alioue@univ-ouaga.bf

their way in the manufacture of multi-layer capacitors, thermistors and also transducers for their piezoelectricity [4, 5]. The ferroelectric materials are promising for microwave applications (capacities with strong permittivity, tunable filters and resonators) and modulators of frequency due to their strong permittivity (high-k) and their weak dielectric losses. The large variation of the dielectric permittivity at ambient temperature also proves to be an important characteristic. Indeed the reliability, effectiveness and improvement of these electronic devices are related to the structure and microstructure of thin-layers-ferroelectric materials [6]. This paper examines the effect of Cu concentration on the ferroelectric properties such as the temperature of the phase transition and the dielectric constant in barium titanate ($BaTiO_3$).

2. Materials and methods

The entire measurements [7] of the thermo-currents and the dielectric permittivity presented here are developed in the Laboratory of Dielectrics of the University of Dijon where the single crystals are prepared using the method of KF flow [8]. Crystallization was made during the cooling of a molten mixture of barium carbonate ($BaCO_3$) and titanium oxide (TiO_2) in a bath of potassium fluoride (KF). The crystals have the shape of triangular thin blades whose thickness varies between $6x10^{-5}$m and $15x10^{-5}$m according to the rate of doping. Known as butterfly wings with a surface area of about 0.5cm^2, the ferroelectric axis *c* is generally perpendicular to the large face.

The samples doped with copper look yellow, becoming darker and darker, with the percentage x of impurities. Doping is carried out during the growth of crystallization. For doping with copper, $Cu(NO_3)_2,3H_2O$ is added and then TiO_2 subtracted, whereas doping with iron, Fe_2O_3 is added and then TiO_2 subtracted. The operation is controlled by spectrophotometric analysis. Temperature T of the crystal rises linearly (with a rate $b=dT/dt$) through the ferroelectric-paraelectric phase transition and the current i_p leads to the pyroelectric coefficient: $f = dP/dT = i_p/Sb$. It is linked to a global polarization P, higher than the spontaneous polarization P_s which is a characteristic of ferroelectric materials. This is due to the other kinds of polarization taking place in the sample: dipolar, and by space charge. At $T=T_m$ there occurs a maximum in the thermal variation of the current i_M ; this maximum of i_M corresponds to an inflection point in the curve of the polarisation versus temperature. The measurement of dielectric constants is performed using an impedence meter 1613-A, an audio-frequency oscillator of the type 1311-A, an amplifier and a detector of zero type 1232-A. Two very thin electrodes in silver paste are deposited on the crystal. The cooling of the oven is achieved by means (electric floodgates) of a temperature regulated cold nitrogen jet directed onto the tube of a steel cell on which the sample is located within the tube at 4mm from the sample. Temperature is measured by means of a chromel-alumel thermocouple and the rate of heating is programmed. Temperature accuracy is then about 0.5°C [7].

3. Results and Discussion

The samples, made of single domain *c* by a field *E*=500V/cm, are assembled according to one of the directions *a* or *c* for measurement. Let us call T_M as the temperature at which the maximum of ε occurs. It corresponds to the passage of the quadratic to cubic symmetry phase. For the Cu-doped crystals, T_M decreases according to concentration as shown on Fig. 1. We observe in Fig. 2 that on increasing the Cu concentration in the crystal, the value of ε at maximum increases whereas the $\varepsilon(T)$ curve appears to exhibit a broader peak. Measurements of the thermo-currents provide results consistent with these data. The temperature corresponding to maximum of permittivity is observed to practically coincide with that of the maximum of thermo-current i_p. We therefore identify both quantities, T_M and T_m.

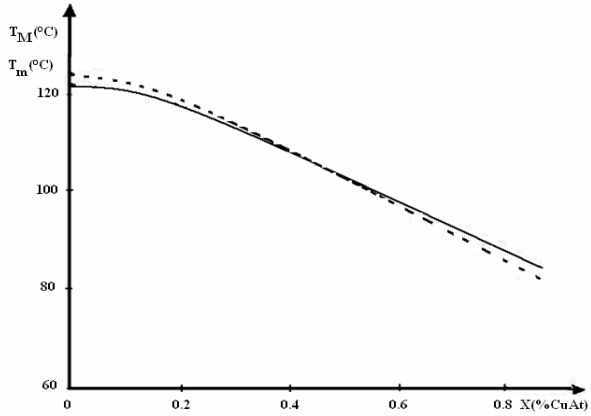

Fig. 1. Variation of T_M (dashed line) and T_m (full line) against Cu concentration.

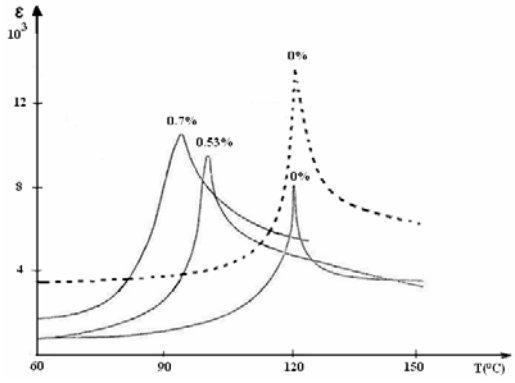

Fig. 2. Dielectric constant of Cu:$BaTiO_3$ (1kHz) as a function of *T*. Broken line – ε_a; solid line – ε_c.

For two pure crystals from the same bath and assembled according to *a* and *c* axis, equal values of $T_M \approx 120°C$ are measured (Fig. 1) and an anisotropy of ε is observed. The dielectric constant measured in the crystallographic *a*-direction, $\varepsilon_a^{(T)}$ is larger than $\varepsilon_c^{(T)}$ at any temperature (Fig. 2). The ratio $\varepsilon_a/\varepsilon_c$ decreases from 16 at ambient temperature to 2 at the transition temperature and reaches its lowest value (1.1) in the non-polar phase. Merz [9] had found, for very thin crystals with a single field, a value $\varepsilon_a/\varepsilon_c=20$ and noted that this factor takes the value 1 at the transition at Curie point (120°C). Thus, the anisotropy is the largest in the region of the ambient temperatures.

The calculated difference ΔT between the temperatures T_m for the pure crystal and the doped crystals, varies linearly with the percentage of Cu from $x \approx 0.3$ (Fig. 3). A broadening and flattening of the maximum of $\varepsilon(T)$ and a shift of the Curie temperature T_C have also been observed in Fe-doped $BaTiO_3$ ceramics [10, 11]. Similar effects also exist in the potassium tantalite niobate [12] and in several oxides with perovskite structure: Nb:$KTaO_3$, Cu,La:$PbTiO_3$ [13]. After annealing at 1300K for 150 hours, there is a loss of copper (% Cu becomes: $y \sim 0.55x$) and temperature T_m increases in Cu:$BaTiO_3$ crystals (Fig. 3). For a concentration $y=0.2\%$, $\Delta T=12°C$. Oxygen vacancies are created by heating, the gap is reduced as a result, and the Curie temperature increases T_c [1].

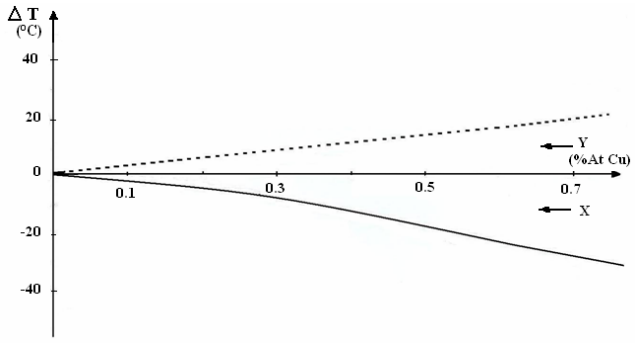

Fig. 3. Variation of $\Delta T = T_m(x\%\ \text{Cu}) - T_m(x=0)$ for Cu:$BaTiO_3$) ---- before annealing; …. after annealing.

From $\varepsilon^{-1}(T)$, Ouedraogo *et al.* [11] determined the Curie constants as 13×10^4K in ferroelectric phase and 25×10^4K in paraelectric phase (i.e., a ratio of 2 for 1.6% Fe:$BaTiO_3$). These values are not affected when the samples are subjected to a laser irradiation (λ=5145Å). Photo-thermo-currents show a more diffuse transition with the discontinuity of dielectric constant $\varepsilon_a(T)$ less acute and a lowering of the temperature T_M. These results are confirmed by Fe:$BaTiO_3$ with high percentages of doping (iron penetrates the samples more easily than copper) (Fig. 4). Irradiation influences the transition, the domains structure and thus the ferroelectric properties [1]. The existence of an electric field induces a variation of the optical index in photo sensitive crystals which is the case during laser irradiation where charges transports take place.

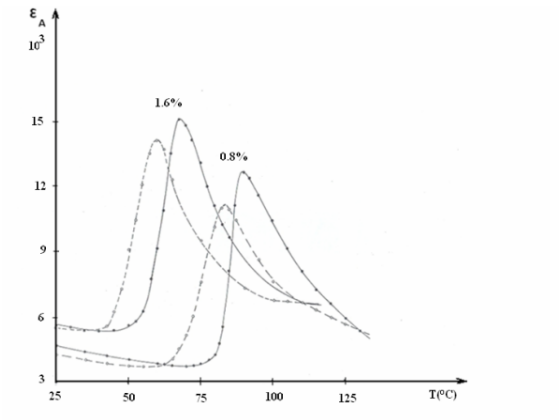

Fig. 4. Dielectric constant of Fe:$BaTiO_3$ (1 kHz). Laser: λ =5145Å, 800mW ($\varepsilon_A = \varepsilon_a$).

It is possible to suppress the phase transition at strong concentrations in the case of La: $BaTiO_3$. The effect of La was observed by Raman diffusion, for which an additional mode appears with an increase of intensity with the concentration of La [14]. The study confirmed the increase in conductivity under reduction treatment as due to the exponential increase in Cu^{2+} defects. Substitution induces a transfer of charges of oxygen towards titanium (partial reduction of titanium) [15]. Chen *et al.* [16] also concluded that Cu doping might be responsible for the metallic behaviour observed in Cu-doped $BaTiO_3$. There is thus an influence of heterovalent substitutions on the dynamics of the lattice and conduction in perovskites [15].

For percentages higher than 0.3%, the determination of concentrations of various ions made it possible to deduce that the most probable site for the Cu^{2+} ion is the Ti^{4+} site [7]. This results in a very marked Jahn-Teller effect with a distortion of the lattice [7]. For high concentrations, the disorder increases by doping, giving a decrease in the activation energy *W*. In reduced crystals, *W* drops to zero when the conductivity increases. This could be understood on the basis of correlated electron hopping or of band broadening [18].

Displacements of ions are associated with a particular mode of vibration. In the Cochran theory of the soft mode, this mode is linked to the order parameter (the polarization) which in $BaTiO_3$ transforms like the irreducible representation T_{1u} of the high temperature symmetry group. The cancellation of an eigen-frequency of vibration of the solid at temperature T_c corresponds to the disappearance of the force to which the atoms are subjected, that drives them to the equilibrium position in high temperature phase. The solid becomes "soft" (i.e. unstable) for this mode. A stability can be found only when the system is moving to a new phase.

The existence of the soft mode is characteristic of structural transitions [19]. In the case of $BaTiO_3$, the transition is displacive and the thermal variation of spontaneous

polarization presents a discontinuity. In any case, the various models must take into account the modifications in the couplings between electrons and vibrations if the doping ion is located in the titanium site. This situation induces local symmetry changes and modifications of the couplings [20] and thus affects the properties of $BaTiO_3$ [21].

In view of miniaturization in microelectronics, perovskite materials with very high permittivity are interesting candidates to replace dielectrics currently used in the development of Metal/Insulator/Metal (MIM) capacitors. High dielectric constant porcelain composition contains mainly $BaTiO_3$, but also contains by weight 1 to 5% of $LaTiO_3$ and 2 to 5% of Ta_2O_5 providing a high dielectric constant of at least 3000. The maximum of ε is found when the size of grains is about 700 nm when $BaTiO_3$ is quadratic, i.e. ferroelectric and is thus not derived from the phase transition quadratic-cubic [22].

The origin and the microstructure of the material are important in the dielectric behaviour of barium titanate. T_C and ε decrease with the size of grains when the diffusivity increases until it disappears for grains of about 100 nm [23, 24].

Taking the polarization $\vec{P}$ associated with the vectorial representation T_{1u} of the group O_h (cubic phase) as the order parameter (following the Landau theory of second order phase transitions), it appeared in fact experimentally that $\vec{P}$ exhibits a discontinuity at the transition point : the transition is then known to be of first-order [25], but close enough of second order to be still described by a Landau-type approach.

4. Conclusion

Experimentally, the Curie temperature T_c can be determined by measuring the pyroelectric current i_p or the dielectric permittivity ε versus temperature: T_c is identified with the temperature T_m of the maximum of i_p and to the temperature T_M of the maximum of the dielectric permittivity ε. The cubic-quadratic transition of $BaTiO_3$ is influenced by Cu and other dopings; T_M decreases and transition becomes more diffuse for high rates of doping agents. Transition could disappear for very large quantities of inserted ions, such as Cu, Fe, La and Co.

The measured variations of $\varepsilon^{-1}(T)$ are in agreement with the thermodynamic approach of Devonshire [26] for a first-order transition, with the Curie constants doubling when the system passes from the ferroelectric phase to the paraelectric phase in $BaTiO_3$. These dielectric properties of barium titanate could be affected by several different parameters such as temperature, coating process, grains size, etc. The excellent opto-electrical properties (high-k, and large pyroelectric and non linear coefficients) of barium titanate make this ferroelectric eminently suitable for applications such as capacitors, pyroelectric detectors and nonlinear applications. However, many potential applications for $BaTiO_3$ require a thin-film form rather than a bulk crystal.

Acknowledgements

The authors wish to express their gratitude to Prof. Pierre Saint-Gregoire at the University of Nîmes (France) for his suggestions.

References

1. G. Chanussot, Phys. Stat. Sol. (b) **187** (2), 565 (2006) – published online. doi:10.1002/pssb.2221870240
2. L. H. Yuan, Z. Y. Z. Songyin, and N. Ce-Wen, *Ferromagnetic and ferroelectric behaviors observed in ABO3-based perovskite thin films*, in: MRS International materials research conf.. Symposium F: functional ceramics. Shanghai (2008).
3. P. Mathey, P. Jullien, P. Lompre, and D. Rytz, Applied Physics A **66**, 511 (1998). doi:10.1007/s003390050705
4. B. H. Tsao, S. Heidger, and J. A. Weimer, *Sputtered barium titanate and barium strontium films for capacitor applications*, in: Proc.12th IEEE international symp. on Applications of Ferroelectrics: Honolulu, Hawaii, U.S.A (July 21-August 2, 2000) pp. 837-840.
5. Y. Yamashita, *Piezoelectric materials in the 21st century*, in:Proc.12th IEEE international symp. on Applications of Ferroelectrics: Honolulu, Hawaii, U.S.A (July 21-August 2, 2000) pp. 139-146.
6. A. Khalal, D. Kathib, and B. Jannot, Ann. Ch. Mat. **24** (7) 471. (1999). doi:10.1016/S0151-9107(00)88439-1
7. A. Ouedraogo, Ph. D. Thesis, University of Ouagadougou (2002).
8. J. P. Remeika, J. Am. Chem. Soc. **76**, 940 (1954). doi:10.1021/ja01632a107
9. W. J. Merz, Phys. Rev. **76**, 1221 (1949). doi:10.1103/PhysRev.76.1221
10. U. Knauer, Phys. Stat. Sol. (a) **53** (1) 207 (1979). doi:10.1002/pssa.2210530122
11. A . Ouedraogo, K. Palm, I. Ouedraogo, and G. Chanussot, JZUS A **9**, 429 (2008).
12. M. A. Yaser, A. L. Gentile, and O. M. Stafsudd, J. Appl. Phys. **100**, 104111 (2006). doi:10.1063/1.2356789
13. O. Bidault, M. Maglione, M. Actis, M. Kchikech, and B. Salce, Phys. Rev. B **52** (6), 4191 (1999). doi:10.1103/PhysRevB.52.4191
14. M. Kchikech, Ph. D. Thesis, University of Dijon (1993).
15. A. Khalal, D. Kathib, and B. Jannot, Physica B **27** (1-4), 343. (1999). doi:10.1016/S0921-4526(99)00202-1
16. A. Chen, J. Zhi, and Y. Zhi, J. Phys. Condens. Matter **11** (48), 9703, (1999). doi:10.1088/0953-8984/11/48/327
17. J. Choi, P. A. Dowben, C. N. Borca, S. Adenwalla, A. V. Bune, S. Ducharme, V. M. Fridkin, S. P. Palto, and N. Petukhova, Phys. Rev. B **59** (3), 1819 (1999). doi:10.1103/PhysRevB.59.1819
18. G. Chanussot and A. Ouedraogo, Ferroelectrics **31**, 160, (1981).
19. P. Papon, L. Leblond and P. H. Meiger, Physics of phase transitions (Dunod, Paris, 1999).
20. A. Ouedraogo and G. Chanussot, Ann.Univ. Ouagadougou B **VI**, 259 (1998).
21. V. N.Tsygankov and V. V. Safonov, Inorg. Mater. **38** (4), 297 (2002). doi:10.1023/A:1015170309056
22. N. Bernaben, Ph. D. Thesis, University of Dijon (1996).
23. CIRIMAT, Activities report OVM. Paul Sabatier University, Toulouse (2005).
24. J. Guillan, Ph. D. Thesis, Joseph Fourier University, Grenoble (2005).

25. A. Ouedraogo and P. Saint-Gregoire, J. Soc. Ouest-Afr.Chim. **015**, 115 (2003).
26. A. F. Devonshire, Phil. Mag. **40**, 1040 (1949).