

STRUCTURAL AND DIELECTRICAL PROPERTIES OF
NANO-STRUCTURE BaTiO₃ POWDERS DOPED WITH Eu³⁺ IONS
PREPARED BY SOL-GEL PROCESS

M. BETTINELLI^a, A. SPEGHINI^a, S. I. SELIMAN^b and I. K. BATTISHA^{c,1}

^a*Dipartimento Scientifico e Tecnologico, Università di Verona and INSTM, UDR Verona, Italy*

^b*Ain Shams University, Faculty of Girls, Cairo, Egypt*

^c*National Research Center, Department of Solid State Physics, Guiza, Egypt*

Received 6 July 2003; revised manuscript received 18 November 2004

Accepted 22 November 2004 Online 23 December 2004

Nano-structure BaTiO₃ powders doped with Eu³⁺ ions have been prepared by a sol-gel technique. X-ray diffraction (XRD) results indicate that BaTiO₃ gel powders crystallize into tetragonal symmetry on heat treatment at 750 °C. Particle sizes as small as 3.5 nm were measured for pure BaTiO₃ powders. The XRD data were confirmed by transmission electron microscope. Room-temperature luminescence spectra of BaTiO₃:0.5% Eu³⁺, BaTiO₃:1% Eu³⁺ and BaTiO₃:2% Eu³⁺ powders have been measured. The luminescence spectra of prepared ultrafine powders are dominated by the ⁵D₀ → ⁷F₂ transition in Eu³⁺, suggesting a strong distortion of the Eu³⁺ sites. The foreign ions are mainly accommodated in Ba²⁺ tetragonal sites, which are then distorted by the occurrence of different ionic charge of the two cations Ba²⁺ and Eu³⁺. The dielectric constant, ϵ , of BaTiO₃, BaTiO₃:0.5% Eu³⁺, BaTiO₃:1% Eu³⁺ and BaTiO₃:2% Eu³⁺ powders at frequency 100 Hz was found to be equal to 1000, 1211, 1455 and 1800, respectively. This high dielectric constant is believed to arise from the increase of the crystallite size, when increasing the concentration of Eu³⁺ ions. After annealing in argon at 400 °C for two hours, at 100 Hz, the dielectric constant of the pure sample was 625 and the AC resistivity also decreased. The room temperature (RT) AC resistivity of the samples depends on the concentration of Eu³⁺ ions in BaTiO₃ powders, and was found to decrease as the concentration of Eu³⁺ ions increased.

PACS numbers: 77.84.-s, 42.70.Mp, 77.22.-d UDC 537.226.4, 538.911, 537.226.2

Keywords: Eu³⁺-doped BaTiO₃, powders, nano-crystalline, sol-gel, XRD, TEM, luminescence, dielectric properties

¹Corresponding author, I. K. Battisha, e-mail address: passtkouine55@yahoo.com, Tel: 002/02/5194104, Fax: 002/02/3370931

1. Introduction

Recently, the size effects in ferroelectric (FE) materials have become a subject of increasing interest, since decreasing dimensions in microelectronic devices require the knowledge of material properties below a critical size [1]. Interesting material used for this purpose is nano-structured barium titanate (BaTiO₃), because of its dielectric and electro-optical properties. Considerable investigations have focused on single-crystal, polycrystalline, thin film and powders of BaTiO₃ [2–13], which have found many applications, such as dielectric layers [14–16], ferroelectrics [17], luminescence near infrared to visible up-conversion [18, 19], sensors [20] and waveguides [21]. The interest in the powders has increased recently due to the need for high-dielectric-constant materials. BaTiO₃ powders are commonly used for making a number of electronic devices such as transducers, piezoelectric actuators, thermal switches and passive memory storage devices. In FE materials, the dielectric constant, ϵ , can be varied by applying a DC electric field, allowing the device characteristics to be tuned in real time for particular applications, e.g. resonators and delay lines. Barium titanate in tetragonal form is a displacement type FE material where the origin of ferro-electricity is derived from the displacement of ions relative to each other. The most remarkable property of BaTiO₃ is its high permittivity constant. The room-temperature (RT) dielectric constant of BaTiO₃ ceramics is known to be greater than 2000 [22].

Uniform BaTiO₃ ultra-fine powders and thin films have previously been prepared by different methods such as sputtering and sol-gel technique [5, 13]. Photoluminescence PL of nanocrystalline BaTiO₃ doped with Eu³⁺ ions in powder and thin film forms is described in Refs. [23], [24], [25] and [26]. The photoluminescence (PL) spectra of these materials have typical emission for europium band corresponding to the ⁵D₀ → ⁷F₂ electronic transitions [27].

In the present work, we report on some of structural and electrical properties of nano-structured BaTiO₃ powders doped with different concentrations of Eu³⁺. The effect of heat-treatment temperature ranging from 40 °C up to 200 °C on the dielectric constant was investigated. The resistivity and the relaxation times were determined. The techniques used for the characterization were XRD, TEM and photoluminescence analysis.

2. Experimental

Powders of pure BaTiO₃ and of BaTiO₃ doped with 0.5%, 1%, and 2% Eu³⁺ ions were prepared by a modified sol-gel method. Barium acetate (Ba(Ac)₂), titanium butoxide (Ti(C₄H₉O)₄) and Eu(NO₃)₃ were used as the starting materials, while acetyl acetone (AcAc, C₅H₈O₂), acetic acid (HAc)-H₂O mixtures were adopted as solvents of Ti(C₄H₉O)₄ and Ba(Ac)₂, respectively. Eu(NO₃)₃-H₂O solution was added to the precursor with different concentrations of Eu³⁺ ions ranging from 0.5% up to 2% to obtain transparent yellow sol. Above 2% concentration of europium nitrate, a specific emission luminescence has aggregated europium oxide or

europium nitrate particles. The sol was kept in air at room temperature, yielding transparent solution. The dry gel obtained by baking the gel at 130 °C, was annealed at 750 °C for 30 minutes to form powders of pure BaTiO₃ and BaTiO₃ doped with different concentrations of Eu³⁺ ions.

The X-ray diffraction (XRD) patterns of the powders were recorded with the Philips X-ray diffractometer PW/1710, with monochromatic CuK α radiation (using the with Ni filter) of wavelength 0.15418 nm at 40 KV and 30 mA. The accurate crystallite sizes were determined using the width of the lines and the Scherrers equation $G = l/(D \cos q)$ where G is the grain size, l is the wavelength of X-rays (0.15418 nm), q is the angle of incidence of the X-ray beam and D is the corrected width (in radian) of the peak at half maximum which is equal to $\sqrt{D_s D_q}$, where D_s is the FWHM of the investigated samples and D_q is the FWHM of the quartz sample, where, in order to obtain the values of the instrumental parameters, a scan has been carried out for a strain free quartz sample of crystallite size ranging between 5 and 10 micron with exactly the same conditions as used for the investigated samples. The fine microstructure of the powder materials were confirmed by transmission electron microscope [EM 10 Zeiss].

The 488.0 nm line of a Spectra Physics 2017 Argon laser was used to excite room-temperature luminescence spectra. A fiber optic probe coupled to a Dilor Superhead, equipped with a suitable notch filter, was employed. The scattered signal was analyzed by a Jobin-Yvon HR 460 monochromator and a Spectrum One CCD detector. A 150 line/mm grating was used to collect the laser-excited luminescence spectra, whilst for high-resolution luminescence spectra a 1200 lines/mm grating was employed. Circular disc specimens of 10 mm in diameter and 1.5 mm in thickness were prepared by pressing the prepared powders using a pressure of 10 tonne at room temperature. The disc of the pure BaTiO₃ sample was annealed in argon at 400 °C for two hours. Silver paste was used for contact electrodes to study the dielectric properties. The real and imaginary parts of ε and ε' (the dielectric constant and dielectric constant loss) were determined using the measured value of capacitance (C_s) with a programmable automatic PLC bridge (PM6304 Philips) at operating frequency ranging from 42 Hz up to 5 MHz. The real, ε , and imaginary, ε' , parts of the dielectric constant, were calculated using the relations

$$\varepsilon = LC_s/(A\varepsilon_0), \quad (1)$$

$$\varepsilon' = \varepsilon \tan \delta, \quad (2)$$

where L is the thickness in m, A is the area in m², C_s is the capacity in F, and $\varepsilon_0 = 8.85 \times 10^{-12}$ C²/(Nm²).

The relaxation times were calculated using the relation

$$\tau = 1/\omega_m, \quad (3)$$

where $\omega_m = 2\pi f$, and f is the frequency.

3. Results and discussion

Single phase tetragonal BaTiO₃ was produced for pure and doped samples with three different concentrations of Eu³⁺ ions, 0.5%, 1% and 2%. The crystallized tetragonal BaTiO₃ phase can be obtained in powders by heating at 750 °C for 30 minutes. The relative increases of XRD line intensities in BaTiO₃ doped with increasing concentrations of Eu³⁺ ions may be seen from XRD patterns shown in Fig. 1.

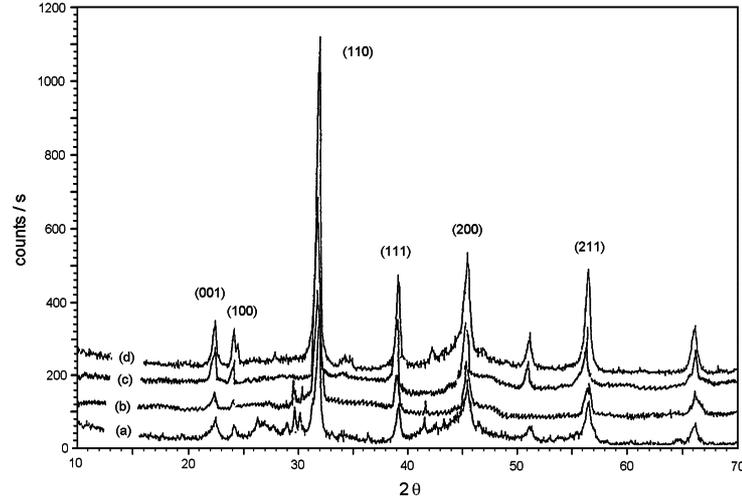


Fig. 1. XRD patterns of (a) pure BaTiO₃ and (b) BaTiO₃ doped with (a) 0.5%, (b) 1% and (c) 2% Eu³⁺ ions, prepared at 750 °C by the sol-gel technique.

The FWHM of BaTiO₃, BaTiO₃:0.5% Eu³⁺, BaTiO₃:1% Eu³⁺ and BaTiO₃:2% Eu³⁺ sol-gel powders were determined from the XRD profiles. Generally, a higher concentration of Eu³⁺ ions imbedded in BaTiO₃ will result in better crystallinity and larger crystallite size than the pure sample. The calculated crystallite size of the pure BaTiO₃ sample was found to be equal to 3.5 nm. By increasing the dopant concentration, the crystallite sizes increase, their values are shown in Table 1. Transmission electron micrographs of surfaces of pure BaTiO₃ and BaTiO₃:2% Eu³⁺ are shown in Figs. 2 and 3. TEM micrographs of the pure BaTiO₃ show differences between the pure powders and BaTiO₃:2% Eu³⁺ sample, where the particles have a well defined

TABLE 1. The RT relaxation time and crystallite size as functions of Eu³⁺ content.

Eu (%)	Cryst. size (nm)	τ (μ s)
0	3.5	0.8
0.5	9	2
1	12	1.3
2	21	4

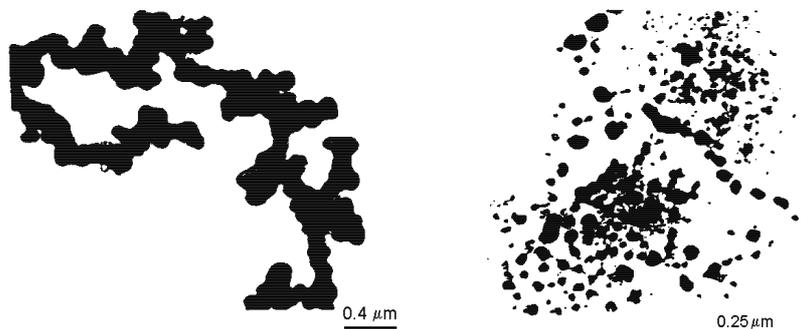


Fig. 2 (left). TEM micrograph of pure BaTiO₃ prepared by the sol-gel technique. Fig. 3. TEM micrograph of BaTiO₃ doped with 2% Eu³⁺, prepared by the sol-gel technique.

spherical shape and become nearer to each other. These spheres might be due to some process of aggregation of particles.

The room-temperature laser-excited luminescence spectrum of the BaTiO₃:1% Eu³⁺ sample prepared by the sol-gel method, measured with an excitation wavelength of 488.0 nm, is shown in Fig. 4. The spectrum consists of $f \rightarrow f$ emission transitions from the ⁵D₀ excited state of the ⁷F_J ($J = 0$ to 4) multiplets of the Eu³⁺ ions. The luminescence spectrum of the barium titanate samples doped with 0.5% and 2% Eu³⁺ are closely similar [27].

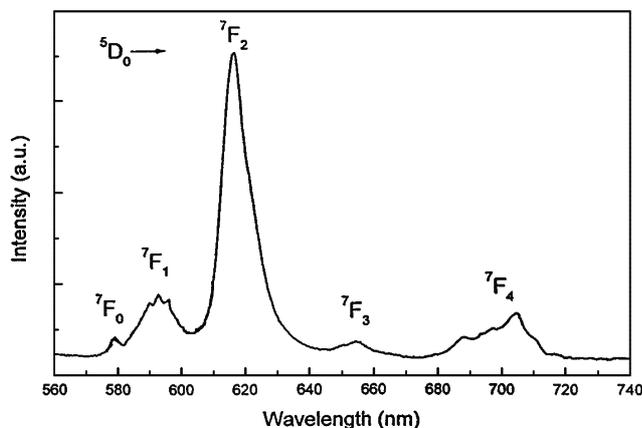


Fig. 4. Room temperature luminescence spectra of BaTiO₃:1% Eu³⁺ prepared by sol-gel, measured with excitation wavelength of 488.0 nm.

The luminescence spectra of the samples under investigation are strongly affected by the broadening due to inhomogeneities. The emission features are much broader than the ones present in the luminescence spectrum of single crystals of the closely related system SrTiO₃:Eu³⁺ [30]. This behaviour is attributed to the presence of disorder caused by the accommodation of Eu³⁺ in the BaTiO₃ lattice which

requires charge compensation. It is worth noting that in the emission spectra of the samples under investigation, the intensity of the hypersensitive ${}^5D_0 \rightarrow {}^7F_2$ transition is strong. Moreover, the formally forbidden ${}^5D_0 \rightarrow {}^7F_0$ transition is clearly detected at about 580 nm. These observations indicate that the sites occupied by the Eu^{3+} dopant are significantly distorted [31]. It is conceivable that the impurity ions are mainly accommodated in the Ba^{2+} tetragonal sites, which are then distorted by the occurrence of nearby defects caused by the different ionic charge on the two cations Ba^{2+} and Eu^{3+} .

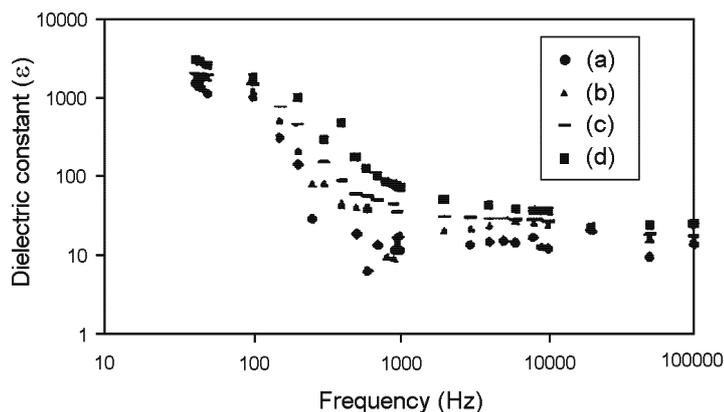


Fig. 5. Room temperature frequency dependence of dielectric constant of (a) pure BaTiO₃, (b) BaTiO₃:0.5% Eu³⁺, (c) BaTiO₃:1% Eu³⁺ and (d) BaTiO₃:2% Eu³⁺ powders.

The effective values of RT dielectric constants, ϵ , of the pure BaTiO₃ and of BaTiO₃ doped with 0.5, 1 and 2% of Eu³⁺ ions are shown in Fig. 5. as functions of frequency. The dielectric constant decreases rapidly at higher frequency due to the easy depolarization of dipoles that exists at the weakly-bonded interfaces and particle boundary regions. In addition, the existence of an interfacial barrier at the electrodes introduces parasitic capacitance and resistance into the system which causes the permittivity to decrease with increasing frequency, as observed in many oxide materials [32,33]. This behaviour is a general trend for the dielectric materials due to the scattering of charge carriers at high frequencies. The fast variation of the electric field accompanied with high frequency leads to random orientation of the dipole moments and, accordingly, decreases the value of ϵ . Another behaviour can be seen in Fig. 5., which is the increase of ϵ when increasing the Eu³⁺ concentration. The dielectric constants were found to be equal to 1000, 1211, 1455 and 1800, for BaTiO₃, BaTiO₃:0.5% Eu³⁺, BaTiO₃:1% Eu³⁺ and BaTiO₃:2% Eu³⁺ powders respectively, at the frequency of 100 Hz, consistent with previously reported values [32,33]. This increase of dielectric constant is believed to be consistent with the increase of both XRD intensity and crystallite size. In other words, the increase of ϵ due to the dopant concentrations can be explained by the findings obtained from the luminescence analysis that the impurity ions are mainly accommodated in Ba^{2+} tetragonal sites, which are then distorted by the occurrence of nearby defects

caused by the different ionic charge on the two cations Ba²⁺ and Eu³⁺. The Eu³⁺ ions may be introduced into the host lattice as trivalent cations, giving rise to more point defects when increasing the dopant concentration. Therefore, the increase of ϵ values when increasing the Eu³⁺ ion concentrations in doped BaTiO₃ samples may be attributed to the lattice defects introduced by the applied dopants. However, the effect of the dopant concentration on the dielectric constant can be summarized by the statement that the higher the lattice defects introduced to the host lattice by the dopant, the higher the value of the dielectric constant.

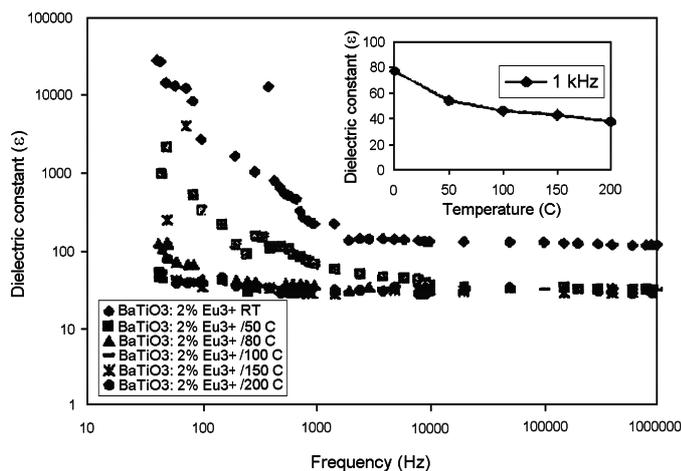


Fig. 6. Dielectric constant of BaTiO₃:2% Eu³⁺ powders, at constant frequency of 1 kHz as a function of heat treatment temperature. The inset refers to pure BaTiO₃ powders.

The values of ϵ of pure and doped samples decrease when increasing the heat-treatment temperature from 50 up to 200 °C. A representative curve of BaTiO₃:2% Eu³⁺ as a function of temperature is shown in Fig. 6, and the inset is for the pure sample, both at a constant frequency of 1 kHz. The heated specimen is an assembly of agglomerated BaTiO₃ particles, separated by particle boundary surfaces. Each agglomerated particle contains a number of randomly oriented nm-sized BaTiO₃ crystallites with weak interfaces. On heating, the particles were consolidated into a dense mass. As a result, a large number of randomly oriented crystallites developed. Due to this randomness in orientation of the crystallites, also the dipole moments were more randomly distributed. Hence, lower ϵ values were obtained at higher temperature. By annealing the pure BaTiO₃ powders at 400 °C in argon for 2 hr, the dielectric constant decreased from 1000 to 625 at the frequency of 100 Hz, as shown in Fig. 7. The results of measurements of AC resistivity for the pure and doped BaTiO₃ powders as function of the Eu³⁺ concentration are shown in Fig. 8. The plots of AC resistivity versus Eu³⁺ concentration display a decrease in the resistivity when increasing the concentration of doping. In general, the resistivity ρ of the samples is inversely proportional to the concentration of free charge carriers and their mobility. At low concentrations of free charge carriers, the electron mobility

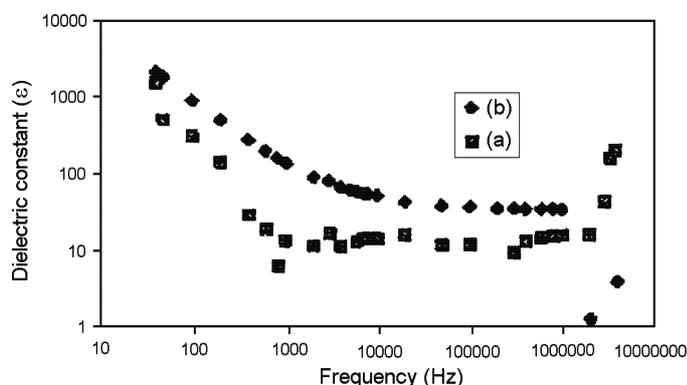


Fig. 7. Dielectric constant of pure BaTiO₃ powders (a) before annealing and (b) after annealing in argon gas for 2 hr at constant temperature 400°C.

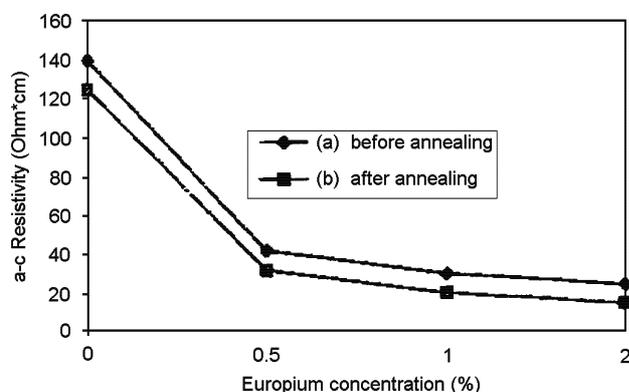


Fig. 8. Room temperature AC resistivity, at the frequency 300 Hz, of BaTiO₃ as a function of Eu³⁺ concentration (a) before annealing and (b) after annealing in argon for 2 hours.

is believed to be constant. Thus, a decrease in the resistivity is due to an increase in the concentration of free charge carriers when increasing the dopant concentration. Another probable cause of the decrease of resistivity may be that the dopant is substituting for Ba³⁺ ions. However, if it is distributed uniformly at the BaTiO₃ particle boundary surfaces, excess holes might have been created within the bulk increasing the conductivity, see Fig. 8a. By annealing the pure BaTiO₃ powders in argon for 2 hr at the temperature of 400°C, Fig. 8b, the pure sample lost oxygen and its resistivity decreased. Figure 9 shows the RT AC resistivity of pure BaTiO₃ and BaTiO₃ doped with different concentrations of Eu³⁺ ions, as functions of temperature. It is observed that by increasing the heat-treatment temperature, the AC resistivity decreases. On heating the samples, mass densification takes place, and excess holes from the bulk migrate into the surface regions and create more electropositive vacancies. Hence, hole conduction develops in the system. Due

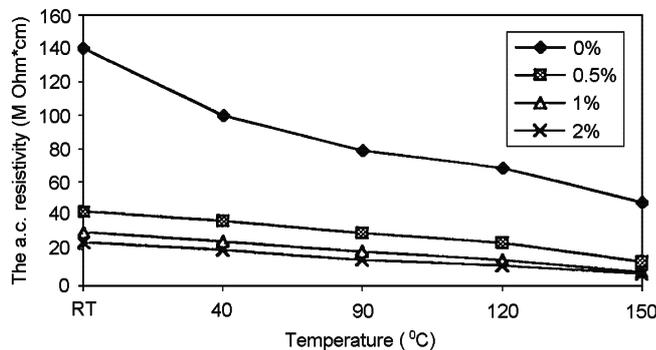


Fig. 9. The AC resistivity of pure barium titanate powders and barium titanate doped with different concentrations of Eu³⁺ ions, as a function of heat treatment temperature.

to the initiation of hole conductivity, the AC conductivity increases, leading to a decrease in the AC resistivity [34]. In general, the increase in conductivity could be related to the increase of the charge carrier density which are localized at ions or vacant sites. Moreover, due to the increase of the drift mobility of the charge carriers and/or due to the lattice vibrations associated with increasing temperature, the ions occasionally come close enough for the transfer of charge carriers and the conduction is induced by lattice vibrations.

The relaxation time, τ , was calculated from the relation (3), for pure BaTiO₃, BaTiO₃:0.5% Eu³⁺, BaTiO₃:1% Eu³⁺ and BaTiO₃:2% Eu³⁺ at room temperature from the Cole-Cole diagram shown in Fig. 10. Their values were found to be equal 0.8, 2, 1.3 and 4 μ s, respectively. The logarithm of the relaxation time τ is plotted

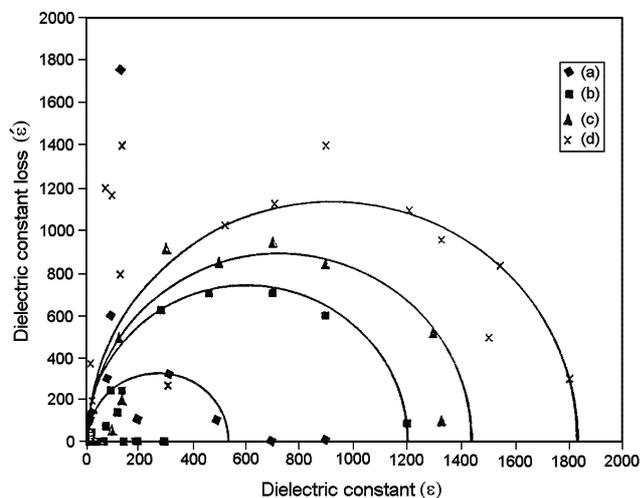


Fig. 10. The Cole-Cole diagrams for (a) pure BaTiO₃, (b) BaTiO₃:0.5% Eu³⁺, (c) BaTiO₃:1% Eu³⁺ and (d) BaTiO₃:2% Eu³⁺ powders.

against the reciprocal temperature to obtain a straight line which is shown in Fig. 11. This straight-line behaviour can be expressed by the following standard relation for the relaxation time

$$\tau = \tau_0 \exp(-E_a/kT) \quad (4)$$

The energy of the dipole relaxation E_a and τ_0 of the dispersion process are given by the slope of the line and y -intercept. The calculated values of E_a and τ_0 are 0.2 eV and 4.5 μ s. respectively.

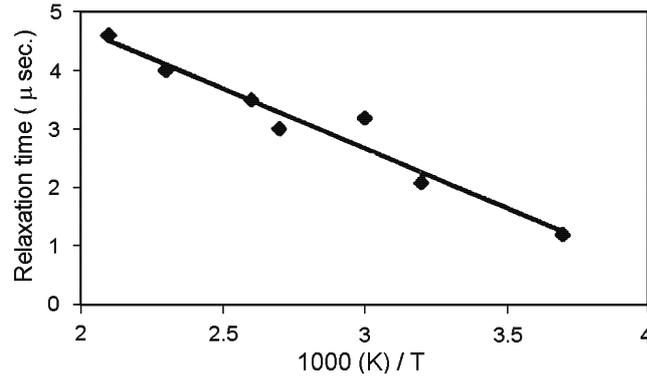


Fig. 11. The dependence of logarithm of τ on reciprocal temperature.

4. Conclusion

Using the sol-gel method, nanocrystalline BaTiO₃ powders doped with Eu³⁺ ions have been successfully prepared. Tetragonal single phase materials have been prepared with particle sizes of 3.5 nm for pure sample. TEM micrograph was used to confirm XRD results.

The luminescence of the dopant ions in BaTiO₃ is strongly influenced by disorder and is affected by an important distortion of the Eu³⁺ sites. The dopant ions are mainly accommodated in Ba²⁺ tetragonal sites, where the defects caused by the different ionic charge on the two cations Ba²⁺ and Eu³⁺ occurred.

The dielectric constant of the BaTiO₃ powders increased when increasing the concentration of Eu³⁺ ion, as a result of the increase of crystallite size, ϵ was found to be equal to 1000, 1211, 1455 and 1800, at 100 Hz for BaTiO₃, BaTiO₃:0.5% Eu³⁺, BaTiO₃:1% Eu³⁺ and BaTiO₃:2% Eu³⁺ powders, respectively. The effect of the dopant concentration on the dielectric constant can be summarized by the statement that the higher the concentration of the lattice defects introduced to the host lattice by the dopant, the higher the value of the dielectric constant. The dielectric constant of the pure BaTiO₃ decreased from 1000 to 625 at 100 Hz by annealing in argon for two hours. After the heat treatment, the dielectric constants decreased, because the samples consolidated. The RT resistivity of the samples depends on the concentration of Eu³⁺ ions in BaTiO₃ powders, and decreased as the concentration of Eu³⁺ ions increased.

Acknowledgements

The authors thank Erica Viviani (Univ. Verona) for expert technical assistance.

References

- [1] J. F. Meng, K. R. Brajesh, S. K. Ram and G. T. Zou, *Phys. Lett. A* **229** (1997) 254.
- [2] J. Zheng, C. Lin, J. Li and K. Li, *Mat. Lett.* **38** (1999) 112.
- [3] H. Shimooka, S. Kohiki, T. Kobayashi and M. Kuwabara, *J. Mat. Chem.* **10** (7) (2000) 1511.
- [4] X. Q. Han, C. H. Kam, S. D. Cheng, Y. Zhou, H. X. Zhang, K. Pita, Y. C. Chan and Y. L. Lam, *Integrated Ferroelectrics*, **1-4** (2001) 221.
- [5] H. X. Zhang, C. H. Kam, Y. Zhou, X. Q. Han, Y. L. Lam, Y. C. Chan and K. Pita, *Mat. Chem. and Phys.* **2** (2000) 174.
- [6] B. Sharma, H. N. K. Sarma and A. Mansingh, *J. Mat. Science* **6** (1999) 1385.
- [7] W. Schwartz, P. G. Clem, J. A. Voigt, E. R. Byhoff, M. Van Stry, T. J. Headley and N. A. Missert, *J. Amer. Ceram. Soc.* **9** (1999) 2359.
- [8] K. Yao, L. Y. Zhang, X. Yao and W. G. Zhu, *J. Mat. Science* **14** (1997) 3659. [8] K. Yao, LY. Zhang, X. Yao and W.G. Zhu, *J of Mat. Sci.* **14** (1997) 3659.
- [9] Ms. Zhang, J. Yu, W. C. Chen and Z. Yin, *Progr. Crystal Growth and Charact. Mat.* **1-4** (2000) 33.
- [10] H. X. Zhang, C. H. Kam, Y. Zhou, X. Q. Han, Q. Xiang, S. Buddhudu, Y. L. Lam and Y. C. Chan, *J. Alloys and Compounds* **134** (2000) 8.
- [11] W. Eiser and H. P. Beck, *Fresenius J. Analyt. Chem.* **5** (1999) 417.
- [12] W. L. Luan, L. Gao and J. K. Guo, *J. Advan. Mat.* **4** (1999) 3.
- [13] H. X. Zhang, C. H. Kan, Y. Zhou, X. Q. Han, S. Buddhudu, Q. Xiang, Y. L. Lam and C. W. Chan, *Appl. Phys. Lett.* **77** (5) (2000) 609.
- [14] W. L. Luan, L. Gao and J. K. Guo, *J. Inorg. Mat.* **2** (1999) 287.
- [15] S. J. Lee, K. Y. Kang and S. K. Han, *Appl. Phys. Lett.* **12** (1999) 1784.
- [16] W. Suchanek, T. Watanabe and M. Yoshimura, *Sol. Stat. Ionics* **109** (1998) 65.
- [17] B. Jiang, J. L. Peng and L. A. Bursill, *Ferroelectrics* **3-4** (1998) 445.
- [18] I. K. Battisha, *J. Sol-Gel Sci. and Tech.* **30** (2004) 163.
- [19] H. X. Zhang, C. H. Kan, Y. Zhou, S. L. Ng, Y. L. Lam and S. Buddhudu, *Spectrochem. Act. A: Molecular and Biomolecular Spectroscopy*, **56** (11) (2000) 2231.
- [20] J. Ray and P. Hing, *J. Appl. Phys.* **88** (2000) 1008.
- [21] D. M. Gill, B. A. Block, C. W. Conrad, B. W. Wessels and S. T. Ho, *Appl. Phys. Lett.* **69** (1996) 2968.
- [22] G. Arlt, D. Hennings and G. de With, *J. Appl. Phys.* **58** (1985) 1619.
- [23] M. S. Zhang, J. Yu, W. C. Chen and Z. Yin, *Prog. Cryst. Growth and Charact. Mat.* **40** (1-4) (2000) 33.
- [24] J. Li, Y. J. Wu, T. Yamamoto and M. Kuwabara, *J. Scie. Techn. Advan. Mat.* **5** (4) (2004) 393.
- [25] J. Li and M. Kuwabara, *J. Scie. Techn. Advan. Mat.* **4** (2) (2003) 143.

- [26] D. Hreniak, W. Strek, J. Amami, Y. Guyot, G. Boulon, C. Goutaudier and R. Pazik, *J. Alloy Comp.* **380** (2004) 348.
- [27] I. K. Battisha, A. Speghini, S. Polizzi, F. Agnoli and M. Bettinelli, *J. Mater. Lett.* **57** (1) (2002) 183.
- [28] S. S. Bhoga and K. Singh, *Sol. Stat. Ionics* **111** (1998) 45.
- [29] M. J. Weber and R. F. Schaufele, *Phys. Rev.* **138** (1965) A1544.
- [30] R. D. Peacock, *Struct. Bonding (Berlin)* **22** (1975) 83.
- [31] R. N. Viswanath and S. Ramasamy, *J. Nanostruct. Mat.* **8** 2 (1997) 155.
- [32] E. H. Nicollian, J. R. Brews, *Metal Oxide Semiconductor Physics and Technology*, Wiley, New York (1982).
- [33] H. B. Sharma and A. Mansighn, *J Mater. Scien.* **33** (1998) 4455.
- [34] R. Thomas, D. C. Dube, M. N. Kamalasanan and S. Chandra, *J. Thin Solid Films* **346** (1999) 212.

STRUKTURNA I DIELEKTRIČNA SVOJSTVA NANOSTRUKTURNIH
PRAHOVA BaTiO₃ PUNJENIH IONIMA Eu³⁺ I PRIPREMLJENIH SOL-GEL
PROCESOM

Pripremali smo sol-gel metodom nanostrukturne prahove BaTiO₃ punjene Eu³⁺ ionima. Difrakcija X-zračenja (DXZ) pokazuje da se gel prahovi BaTiO₃ kristaliziraju u tetragonalnoj simetriji zagrijavanjem na 750 °C. Utvrdili smo veličine zrna od samo 3.5 nm u čistom prahu BaTiO₃. Podatke od DXZ potvrdili smo prolaznom elektronskom mikroskopijom. Mjerali smo fotoluminescentne spektre prahova BaTiO₃:0.5% Eu³⁺, BaTiO₃:1% Eu³⁺ i BaTiO₃:2% Eu³⁺ na sobnoj temperaturi. U luminescentnim spektrima pripremljenih ultrafinih prahova prevladava prijelaz ⁵D₀ → ⁷F₂ u Eu³⁺, što ukazuje na snažna izobličenja na mjestima Eu³⁺ iona. Ugrađeni se ioni Eu³⁺ uglavnom smještaju na tetragonalne položaje Ba²⁺, a velika razlika ionskih naboja dvaju kationa, Ba²⁺ i Eu³⁺, uzrokuje snažne promjene oko tog defekta. Dielektrične konstante, ε, prahova BaTiO₃, BaTiO₃:0.5% Eu³⁺, BaTiO₃:1% Eu³⁺ i BaTiO₃:2% Eu³⁺ na frekvenciji 100 Hz prema našim mjerenjima iznose 1000, 1211, 1455 odn. 1800. Smatramo da su tako velike vrijednosti dielektrične konstante posljedica povećanih veličina kristalita za veća punjenja ionima Eu³⁺. Nakon opuštanja u argonu na 400 °C tijekom dva sata, dielektrična konstanta čistog praha bila je 625, a otpornost se također smanjila. Izmjenična otpornost prahova BaTiO₃ ovisi o punjenju ionima Eu³⁺ i nalazi se da se smanjuje kada se poveća sadržaj iona Eu³⁺.