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Structure, spectroscopy and dielectric properties of $BaTiO_3:Eu^{3+}$ nanocrystallites prepared by the sol–gel method[*]

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Eu^{3+}-doped $BaTiO_3$ nanocrystalline powders have been obtained by sol–gel method. Their morphology, structure and dielectric properties have been investigated as a function of sintering temperature. The powders sintered at the temperatures below 800 °C demonstrate luminescence behaviour characteristic of the inversed symmetry Eu^{3+} sites, where only the $^5D_0 \rightarrow {}^7F_1$ transitions are allowed. Above this temperature the system undergoes a phase transition characterized by lack of inversion symmetry enabling the dipole–electric transitions.

Key words: barium titanate, europium, nanocrystallites, sol–gel processing, luminescence

1. Introduction

Barium titanate ($BaTiO_3$) is a classical example of a ferroelectric crystalline material. The $BaTiO_3$ ceramics are widely applied in electronic devices as high-permittivity capacitors, infrared detectors or transducers. It is well known that ferroelectric and optical properties of ferroelectric ceramics depend on the grain size [1]. Recently, the sol–gel route has been suggested for preparation of transparent, nanostructured $BaTiO_3$ monolithic xerogels [2]. The size-dependence of the ferroelectric phase transition of small $BaTiO_3$ particles has been a subject of many reports [3–10]. The ferroelectric crystal size of about 50 nm has been reported [7] as critical for ferroelectric properties.

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In this paper, we present the preliminary studies of structural, optical and dielectric properties of $BaTiO_3$ nanocrystallites (nc-$BaTiO_3$) doped with Eu^{3+} ions. They were prepared by the modified sol–gel method. It is well known that for crystal structure evaluation of crystalline materials X-ray powder diffraction (XRD) is used quite often. However, in the case of nc-$BaTiO_3$ it is not a sensitive enough technique to unravel subtle structure characteristics existing in the nanoscale range. It has been reported that XRD measurements were used only to probe global structure for $BaTiO_3$ crystallites [8]. However, there exist methods which are more suitable for investigation of local structure and symmetry changes: combination of XRD and Raman scattering [7, 8] or infrared spectroscopies [11], measurements of the second harmonic-generation [8, 12] and photoluminescence studies [13]. We employed the europium(III) ion as an optical probe for structural investigations and detection of phase transitions in the nanocrystalline grains. The fluorescence properties of the europium(III) ion were investigated as a function of the sintering temperature. The basic dielectric properties of Eu^{3+}: $BaTiO_3$ nanocrystalline powders were determined.

2. Experimental

2.1. Preparation

The europium-doped $BaTiO_3$ crystalline powders were prepared by the sol–gel method similar to that described by Tian et al. [14]. Barium acetate $Ba(CH_3COO)_2$ (Aldrich 99%), titanium butoxide $Ti(OC_4H_9)_4$ (Alfa Aesar 99+%) and europium oxide Eu_2O_3 (Koch-Light Laboratories 99.99%) were used as starting materials. Acetyl acetone $C_5H_8O_2$ (Aldrich 99+%) and acetic acid (POCh p.a.) were selected as solvents of titanium butoxide and barium acetate, respectively. Europium chloride $EuCl_3{\cdot}6H_2O$ was obtained by reacting stoichiometric amount of europium oxide with hydrochloride acid of analytical grade (POCh). Dissolved barium acetate was added dropwise to titanium butoxide solution under stirring. The obtained solutions were vigorously stirred at 50 °C for about 2 h. The europium salt was dissolved in small amount of water and added slowly to the obtained transparent, yellow sol with 1 molar percent of Eu vs. $BaTiO_3$. The obtained solution was heated at approximately 100 °C for 24 h to form barium titanate (BT) gel powders. The samples of crushed gels were heated at 750 °C (A), 800 °C (B), 900 °C (C), 1100 °C (D) and 1200 °C (E). Pure, undoped samples of nc-$BaTiO_3$ were obtained in a similar manner.

2.2. Apparatus

Fluorescence spectra were recorded on an Ocean Optics SD 2000 spectrophotometer. Decay curves of luminescence were recorded with a Jobin-Yvon TRW 1000 spectrophotometer equipped with a photomultiplier (Hamamatsu R928). XRD diffractograms were measured using CuKα source radiation on a DRON-3 powder diffractometer. The mean crystallite diameters were estimated applying the Scherrer formula [15] to the X-ray diffraction patterns. Electrical properties were measured using computer-based apparatus for dielectric measurements in the frequency range 100–1 MHz.

3. Results and discussion

3.1. XRD measurements

The x-ray diffraction results of the undoped samples as a function of heating temperatures are shown in Fig. 1. The recorded patterns show that all the samples were well crystallized. The nanocrystalline particle sizes were estimated to be 24–30 nm for the samples A, B, C and about 43 nm for the samples D and E. Sharp peaks in all the recorded XRD patterns could be ascribed to pseudocubic paraelectric phases [16] which (probably) co-exist with the tetragonal ferroelectric $BaTiO_3$ phase [17] in the case of D and E.

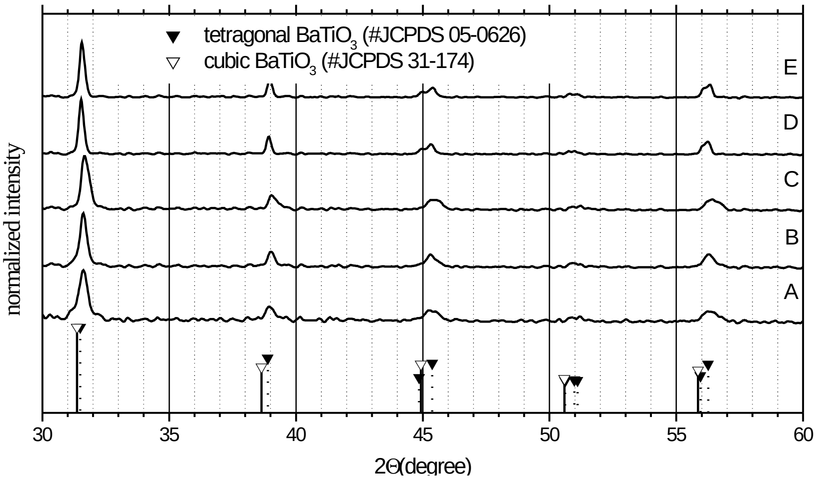

Fig. 1. XRD patterns of $BaTiO_3$ heated at different temperatures

3.2. Luminescence

The emission spectra of $BaTiO_3$:Eu^{3+} nanocrystallites prepared at different temperatures and measured at 300 K and 77 K are shown in Fig. 2. The spectra consist of characteristic bands attributed to the $^5D_0 \rightarrow {}^7F_J$ ($J = 0, 1–4$) transitions. With increasing crystallite sizes the band with the maximum at 616 nm (the hypersensitive electric-dipole $^5D_0 \rightarrow {}^7F_2$ transition) becomes much weaker as compared to the band with the maximum at 595 nm (assigned tentatively to the magnetic-dipole $^5D_0 \rightarrow {}^7F_1$ transition). These changes are probably due to the variations in symmetry of the environment of the Eu^{3+} ions and may be linked to the structural changes possible for the sample processed at temperatures above 1100 °C.

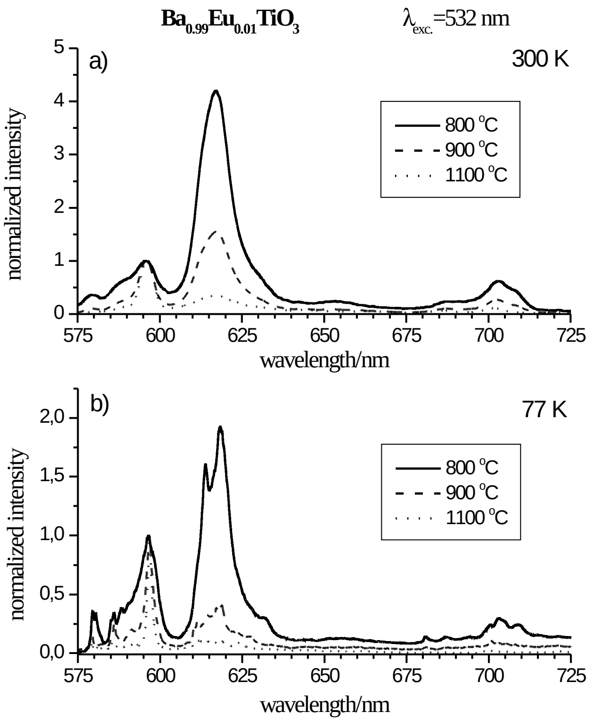

Fig. 2. Emission spectra of Eu^{3+}-doped $BaTiO_3$ powders prepared at different temperatures

Assuming the existence of the areas with the local tetragonal phase (what is in agreement with the XRD data) it can be assumed that the symmetry changes observed in the Eu^{3+} emission spectra are related to phase transitions occurring in those areas. The europium ions are positioned either inside of those spots. Changes in luminescence spectra and stabilization of the tetragonal phase by Y [19] and Pr [20] ions have been reported for cubic ZrO_2. The emission spectra measured at room temperature are poorly resolved while the spectra measured at 77 K demonstrate a complex structure characteristic of the multi-site Eu^{3+} spectra.

3.3. Decay time measurements

We have measured the dependence of the emission decay times of the band attributed to the $^5D_0 \rightarrow {}^7F_1$ transition on the size of the $BaTiO_3$:Eu^{3+} grains. The examples of emission decays measured at 595 nm are shown in Fig. 3. As it can be seen the characteristic decay times increase systematically with increasing temperature. They are shorter for $BaTiO_3$ sintered at lower temperatures and the emission decay profiles demonstrate clearly non-exponential character. The shorter decay times recorded for the samples heated at 800 °C and 900 °C may be due to the presence of small amounts of –OH groups in the crystallites leading to quenching of the Eu^{3+} fluorescence. For the samples sintered at higher temperatures (1100 °C and 1200 °C) the emission decays are perfectly exponential and the estimated emission lifetimes are very long (t = 2.2 ms at 300 K and t = 3.5 ms at 77 K).

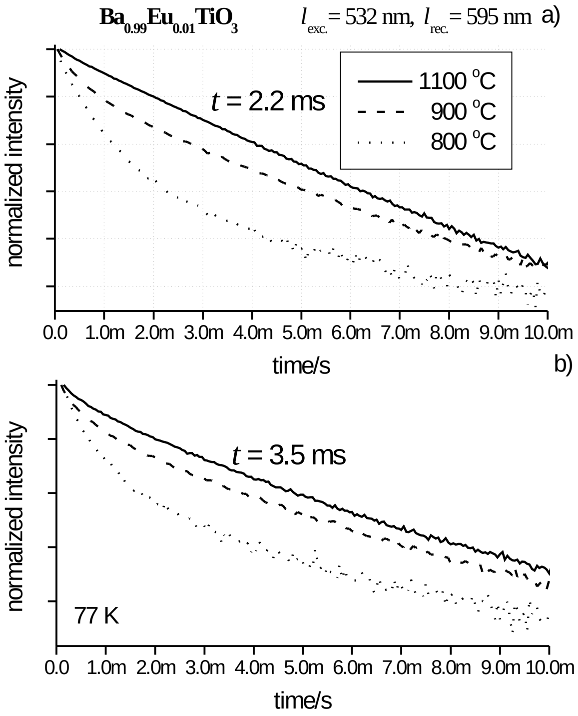

Fig. 3. Emission decay curves of Eu^{3+}–doped $BaTiO_3$ powders prepared at different temperatures. The decays were obtained at 300 K (a) and at 77 K (b)

In our opinion, the characteristic non-exponential decay for samples treated at 800 °C and 900 °C is due to the aggregation of the Eu^{3+} ions, which is more pronounced for smaller grains. Analogous results have been reported for Eu^{3+}-doped Lu_2O_3 nanocrystallites [18].

3.4. Dielectric studies

Dielectric studies have been performed in a wide temperature range. The electric permittivity e_r' and dielectric loss tan$d$ have been measured at different frequencies for the undoped $BaTiO_3$ powders sintered at 800 °C and 1100 °C. During the first cycle of heating we have observed the maximum of e_r' in the range 300–330 K. This maximum has not been observed in the second (Fig. 4) and successive cycles of heating. This effect results most likely from the material dehydration. There has been observed only a slight change of permittivity during further heating. During cooling of the sample we have observed monotonic decrease of permittivity. In this case we have not observed the maximum in the range of 300–330 K and only a weak temperature dependence of dielectric permittivity. Comparison between the room-temperature values of e_r and tan*d* at different frequencies is presented in Table 1.

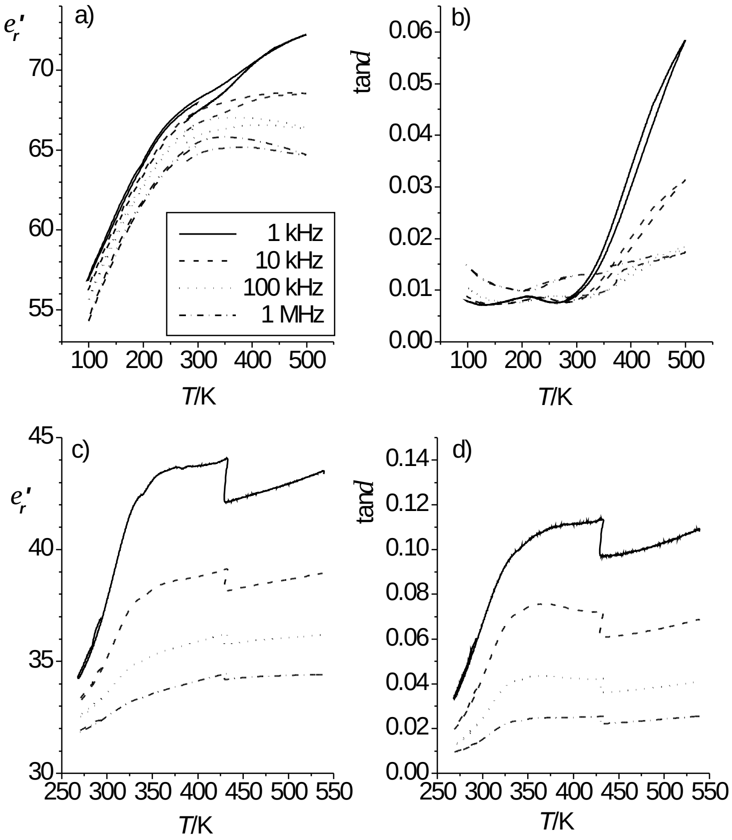

Fig. 4. Temperature-dependency of electric permittivity e_r' and loss tangent tan*d* of europium-doped $BaTiO_3$ prepared at 800 °C (a, b) and at 1000 °C (c, d) measured at different frequencies

These results are distinctly different from those obtained for typical ferroelectric $BaTiO_3$ which exhibits e_r' in the range 10^3–10^4 [1]. Undoped samples demonstrated also the hysteresis loops characteristic of ferroelectric materials (Fig. 5), but the value of spontaneous polarization was estimated to be only $1.0 \cdot 10^{-3}$ C·m^{-2}. It is almost an order of magnitude smaller than that observed for tetragonal ferroelectric phase

$BaTiO_3$ monocrystals ($7.5\cdot10^{-2}$ $C\cdot m^{-2}$) [1]. This fact indicates that the paraelectric phase dominates in undoped samples.

Table 1. Room temperature values of e_r' and tan*d* at different frequencies

Frequency/kHz	Sample B (24 nm)		Sample D (43 nm)	
	e_r'	tan*d*	e_r'	tanδ
1	68	0.009	37	0.065
10	67	0.008	35	0.041
100	66	0.008	33	0.023
1000	65	0.009	32	0.014

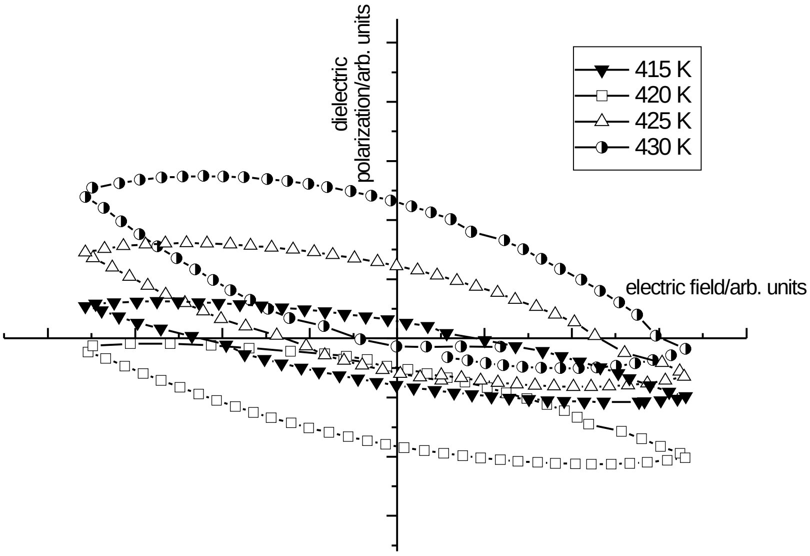

Fig. 5. Ferroelectric hysteresis loops of europium-doped $BaTiO_3$ obtained at 1100 °C measured at different temperatures

4. Conclusions

The nc-$BaTiO_3$ nanocrystals doped with Eu^{3+} ions have been obtained by the sol–gel technique. The structure and morphology of the $BaTiO_3$ grains has been determined. The fluorescence properties of the Eu^{3+} ion were investigated as a function of thermal sintering of the nc-$BaTiO_3$. It was found that with increasing temperature the intensity of the $^5D_0 \rightarrow {}^7F_2$ transition decreased significantly as compared to the $^5D_0 \rightarrow {}^7F_1$ transition. Above 1100 °C the second one dominates the spectrum. This suggests that above this temperature a local phase transition occurs in the material influencing the symmetry of the Eu^{3+} ion sites, being probably rhombohedral at 77 K and tetragonal at 300 K. The synthesized nc-$BaTiO_3$ can well be described as pseudocubic, with some fraction of the particles retaining ferroelectricity.

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References

[1] Nalwa H.S., *Handbook of Low and High Dielectric Constant Materials and Their Applications*, 1999, USA, Academic Press.
[2] Vasiljev V.A., Vorotilov K.A., Yanovskaya M.I., Solovieva L.I., Sigov A.S., J. Sol–Gel Sci. Techn., 1998, 13, 877.
[3] Uchino K., Sadanaga E., Hirose T., J. Am. Ceram. Soc., 1989, 72, 1555.
[4] Saegusa K., Rhine W.E., Bowen H.K., J. Am. Ceram. Soc., 1993, 76, 1505.
[5] Shih W.-H., Lu Q., Ferroelectrics, 1994, 154, 71.
[6] Shih W.Y., Shih W.-H., Aksay I. A., Phys. Rev. B, 1994, 50, 575.
[7] Zhang M.-S., Yu J., Chen W., Yin Z., Progress Cryst. Growth Charact. Mat., 2000, 33.
[8] Frey M.H., Payne D.A., Phys. Rev. B, 1996, 54, 3158.
[9] McNeal M.P., Jang S.-J., Newnham R.E., J. Appl. Phys., 1998, 83, 3288.
[10] Ayyub P., Palkar V.R., Chattopadhyay S., Multani M., Phys. Rev. B, 1995, 51, 6135.
[11] Busca G., Buscaglia V., Leoni M., Nanni P., Chem. Mater., 1994, 6, 955.
[12] Lines M.E., Glass A.M., *Principles and Applications of Ferroelectrics and Related Materials,* 1977, Oxford, Clarendon.
[13] Zhang M.-S., Yu J., Chen W., Zhang W., Yin Z., Solid St. Comm., 2001, 119, 659.
[14] Hu-Yong Tian, Thermochimica Acta, 2000, 360, 57.
[15] Klug P., Alexander L.E., *X-ray Diffraction Procedure*, 1954, New York, Wiley, Chap. 9.
[16] Joint Committee for Powder Diffractions Standards, Card No. 31-174.
[17] Joint Committee for Powder Diffractions Standards, Card No. 05-174.
[18] Zych E., Hreniak D., Stręk W., J. Phys. Chem., accepted for publication.
[19] Paje S.E., Llopis J., J. Phys. Chem. Solids, 1994, 55, 671.
[20] Savoini B., Munoz Santiouse J.E., Gonzales R., Phys. Rev., 1997, B 56, 5856.