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Synthesis and luminescence properties of nanocrystalline $BaTiO_3:Nd^{3+}$ obtained by sol-gel methods

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Neodymium-doped barium titanate ($BaTiO_3$) nanocrystalline powders were prepared by the sol-gel method. Structure and average grain sizes were analysed by X-ray powder diffraction (XRD) measurements. Grain sizes amount from 30 to 60 nm, depending on dopant concentration and sintering temperature. The luminescence properties of $BaTiO_3:Nd^{3+}$ were investigated as a function of the concentration of Nd^{3+} (0.5–2 mol %) and sintering temperature (700–1050 °C). The influence of Nd^{3+} concentration on the grain size and crystal structure of $BaTiO_3$ nanocrystallite powders was found and a weak hot emission from the $^4F_{5/2}$ level was observed for the nanopowders obtained.

Key words: *barium titanate; neodymium; sol-gel; luminescence; size effect*

1. Introduction

Barium titanate ($BaTiO_3$), a classical ferroelectric material belonging to a numerous group of perovskite materials, is characterized by a general formula ABO_3. Depending on the valencies of the metal cations (A and B), perovskite materials are subdivided into two main groups, described by the formulas $A^{2+}B^{4+}O_3$ (e.g. $BaTiO_3$, $PbTiO_3$) and $A^{3+}B^{3+}O_3$ (e.g. $NdAlO_3$, $LaAlO_3$). In both groups the crystal structure is usually depicted in a pseudocubic form. It contains two cation sites in the crystal lattice: (A) large cations located in the corners, (B) small cations occupying the centre of the unit cell, and oxygen ions on the centres of the cell walls. Possible displacement in ion arrangement in the unit cell is directly responsible for characteristic properties of these materials [1, 2].

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Recent developments in nanotechnology create new and interesting challenges for researchers and opens broader fields of practical applications of nanomaterials. One of many methods for obtaining such materials [3–7] is the sol-gel technique [8]. The sol-gel method for obtaining nanocrystalline particles of $BaTiO_3$ is relatively simple and easy to carry out. Furthermore, this method has a few important advantages in comparison to the conventional solid state method (SSM) [9]. The sol-gel route is less expensive (temperatures lower than 1000 °C), enables a high concentration of dopant to be introduced, and assures a better control of reaction conditions such as pH or temperature.

Grain size of the nanocrystalline barium titanate strongly influences its structure and ferroelectric properties. Therefore, size effects in nanoparticles of $BaTiO_3$ have been the subject of many studies [10–17]. A hypothesis on a critical size above 50 nm for the existence of ferroelectric properties has been put forward by Frey and Payne [14]. Moreover, Uchino [15] and Saegusa [16] found the tetragonal phase, responsible for the ferroelectricity, disappear at grain sizes below 100 nm. In our previous studies, the stabilization and enhancement of the tetragonal structure with increasing europium ion concentration in $BaTiO_3$ has been reported. A strong size dependence of the luminescence properties of Eu^{3+} has been shown as well [8, 17].

In this work, we present results of preparation and characterization of Nd^{3+}-doped $BaTiO_3$, obtained via the sol-gel method. The main aim of our work was to investigate luminescence properties (spectra, decay times) of $BaTiO_3$ nanocrystalline powders in terms of the size dependence effect, obtained at sintering temperatures in the range of 700–1200 °C and doped with neodymium ions of various concentrations. We have also studied the influence of grain size on the hot emission from the $^4F_{5/2}$ level and the effect of doping with Nd^{3+} on the crystal structure of $BaTiO_3$ nanopowders.

2. Experimental

Details concerning the preparation of $BaTiO_3$ nanocrystallites have been described by us elsewhere [17]. Barium acetate, titanium butoxide and neodymium oxide were used as starting materials. Acetylacetone and acetic acid were selected as solvents for titanium butoxide and barium acetate, respectively. Neodymium chloride was obtained by reacting stoichiometric amounts of neodymium oxide with hydrochloric acid. Dissolved barium acetate was added dropwise to titanium butoxide solution while stirring. The obtained solutions were vigorously stirred at 50 °C for about 2 h. The neodymium salt was dissolved in a small amount of water and added slowly to the obtained transparent yellow sol with different molar ratios of Nd^{3+} to $BaTiO_3$. The sols obtained were heated at approximately 100 °C for 24 h to form barium titanate gels. The samples of crushed gels were heated above 700 °C to form nanocrystalline $BaTiO_3$ powders doped with Nd^{3+}.

3. Results and discussion

3.1. XRD analysis

Samples of $BaTiO_3$ doped with Nd^{3+} ions of different concentrations and sintered at 700–1100 °C were characterized by X-ray diffraction. The XRD patterns of $BaTiO_3$ powders doped with Nd^{3+} ions of various concentrations are presented in Fig. 1. Peaks shown in the patterns are sharp and well defined, indicating that all samples are well crystallized. The patterns were compared to the reference standard cards for tetragonal and cubic $BaTiO_3$ [18, 19]. The average size of crystallites, estimated from the broadening of diffraction peak using the Scherrer equation [20], varies from 30 to 55 nm depending on sintering temperature and dopant concentration (Fig. 2).

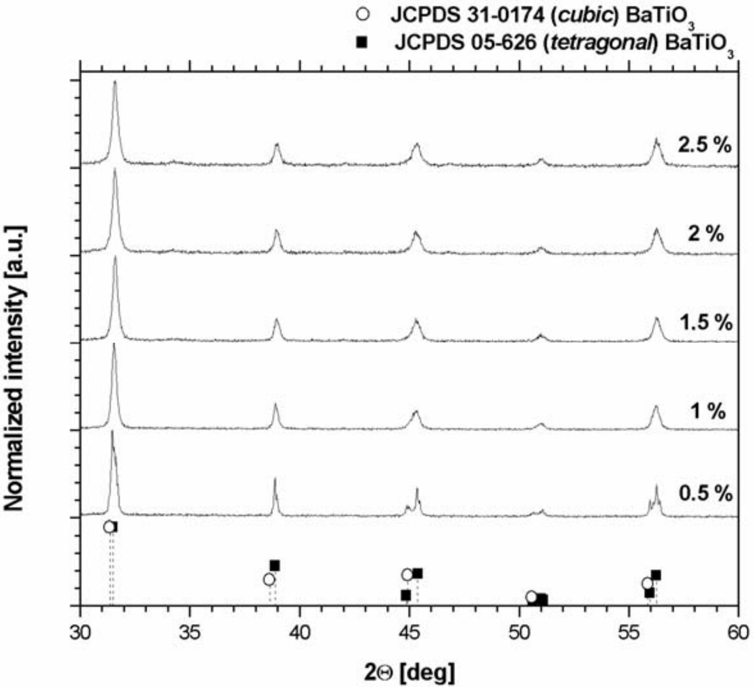

Fig. 1. XRD patterns of the $BaTiO_3$ powder samples doped with $Nd^{3+}$of various concentrations

An analysis of the XRD patterns for samples with different neodymium ion concentrations (0.5–2%) and heated at 1050 °C showed that all samples, except the one with 0.5% Nd, were in the cubic phase characteristic of paraelectric $BaTiO_3$. Furthermore, we observed a dependence of the dopant concentration on the grain size, which has also been reported by Buscaglia [2] and Tsur [21]. It is well known that the dopant ionic radius is a main parameter determining the substitutions in the $BaTiO_3$

crystal lattice. Thus, Nd^{3+} ions (1.08 Å) are mainly placed at Ba^{2+} sites (1.35 Å) and not at Ti^{4+} ones (0.68 Å), due to the size incompatibility. Increasing dopant concentration causes an overall shrinkage of the $BaTiO_3$ unit cell, changing lattice parameters and resulting in a change of the crystal structure.

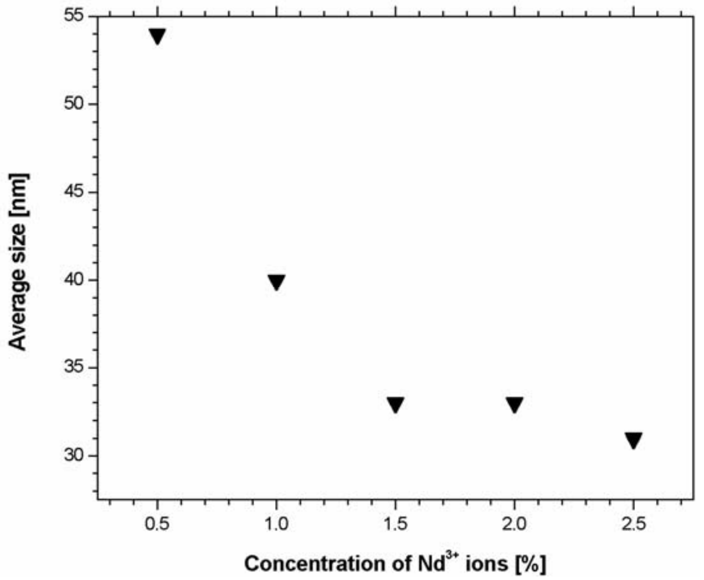

Fig. 2. Effect of dopant concentration
on the average size of $BaTiO_3:Nd^{3+}$ crystallites

In nanosized grains, effects resulting from a progressive decrease of particle size are more pronounced. Many authors, when considering the size effect on the structure and ferroelectric properties of $BaTiO_3$, emphasized importance of grain size, responsible for new phenomena occurring in nanostructured materials in comparison to their equivalents composed of larger crystallites [14, 22, 23]. Thus, increasing concentration of Nd^{3+} ions causes a decrease in grain sizes (from 54 nm for 0.5% of Nd^{3+} to 30 nm for 2.5%) up to a boundary value of dopant concentration (1,5% of Nd^{3+}). Above that value there is no further decrease of the grain size. Moreover, the shrinkage of the unit cell and decrease in a grain size causes additional changes in the crystal structure. An analysis of the diffraction peak around $2\theta \approx 45$ ° for the sample doped with 0.5% of Nd^{3+} showed its splitting into a doublet ascribed to 200 and 002 peaks, characteristic of the tetragonal phase of $BaTiO_3$. Samples with the concentration of Nd^{3+} ions exceeding 1% are characterized by the paraelectric cubic crystal structure. This is quite different form our previous results. We have proved that the incorporation of Eu^{3+} ions into the barium titanate crystal causes a significant increase of the sample tetragonality [8]. Such behaviour is probably caused by the existence of europium of two different valencies in the crystal structure: larger Eu^{2+} ion will be placed at Ba^{2+} sites, whereas smaller Eu^{3+} enters Ti^{4+} or Ba^{2+} sites.

3.2. Emission spectra and discussion

The emission spectra of barium titanate nanocrystallites doped with neodymium ions at various concentrations (0.5–2 mol % vs. BaTiO$_3$) and heat-treated at temperatures in the range 700-1050 °C, were measured at room temperature. They are shown in Fig 3a. All spectra consist of characteristic bands, ascribed to the $^4F_{3/2}\to{}^4I_j$ (J = 11/2, 9/2) electronic transitions of Nd^{3+} ions, according to the established energetic model [24]. The band with a maximum at 876 nm corresponds to the $^4F_{3/2}\to{}^4I_{11/2}$ transition, and the one at 1064 nm to the $^4F_{3/2}\to{}^4I_{9/2}$ transition. Additionally, a weak emission corresponding to the ($^4F_{5/2}$, $^2H_{9/2}$)$\to{}^4I_{9/2}$ transitions (Fig. 3b) was observed. The hot emission from $^4F_{5/2}$ and $^2H_{9/2}$ levels takes place during an excessive self-heating of samples due to the scattering of optical excitation energy in individual nanocrystals. This explains the increase of intensity under increasing excitation power [25]. Thus, higher-lying levels were populated at the cost of desired laser emission from the metastable $^4F_{3/2}$ level.

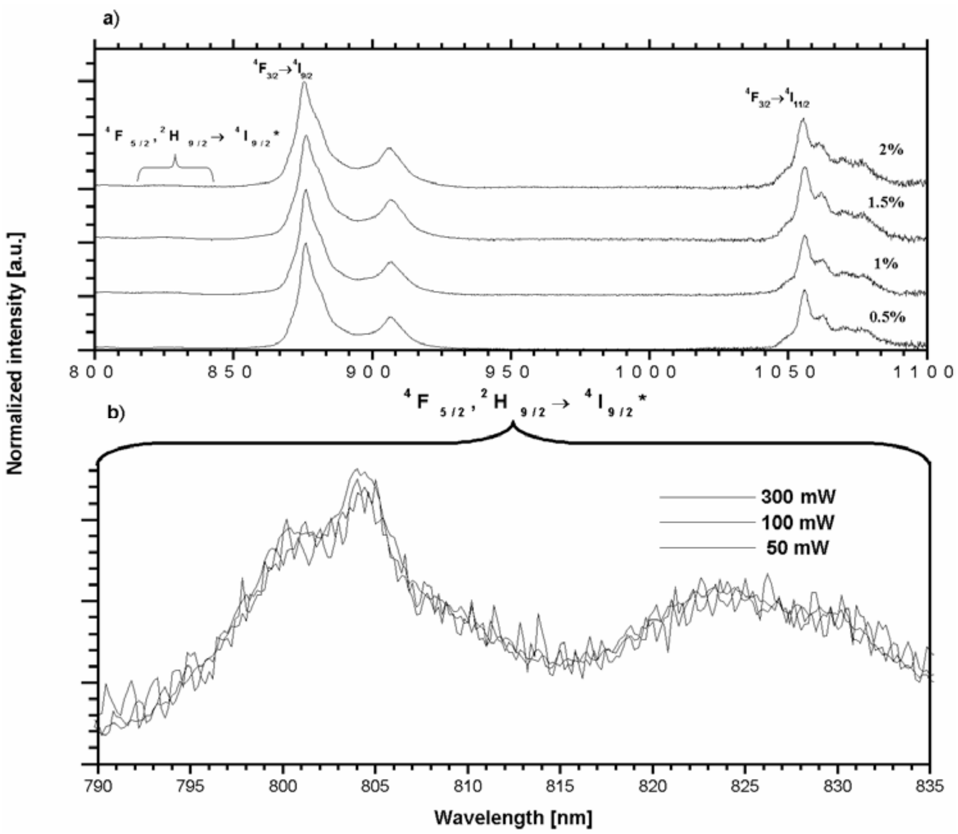

Fig. 3. Emission spectra of BaTiO$_3$:Nd^{3+}: a) with different concentrations of Nd^{3+}, b) hot emission from ($^4F_{5/2}$, $^2H_{9/2}$) to the $^4I_{9/2}$ level

We performed measurements of power-dependent emission as a function of the average size of $BaTiO_3$:Nd^{3+} grains. No increase of the hot-emission intensity with increasing excitation power was observed. This indicates that the particles of nanocrystallite $BaTiO_3$ warmed up only slightly. The aggregation of grains, facilitating escape of the excess heat from the sample, favourable luminescence properties and a weak hot emission make Nd^{3+} doped $BaTiO_3$ a promising material for use in thin layers.

4. Conclusion

$BaTiO_3$ nanocrystals were obtained via the sol-gel route. The structure and average size of $BaTiO_3$ nanocrystallites were determined. The average size ranged between 30 and 60 nm, depending on the dopant concentration and sintering temperature. The influence of dopant concentration on the grain size and crystal structure of $BaTiO_3$ was established. Crystallites in samples with low concentrations of Nd^{3+} ions are larger than those in highly doped samples (over 1% of Nd^{3+}). The former ones have the tetragonal ferroelectric crystal structure in contrast to the latter ones, crystallizing in the cubic paraelectric phase. Moreover, selecting a specific type of dopant enables nanocrystallite powders of $BaTiO_3$ with a desired crystal structure to be obtained. In this way, properties of the final product can be controlled (ferroelectric or paraelectric state). By controlling the dopant concentration, the sizes of nanocrystallites can be minimized. The luminescence properties of Nd^{3+} were investigated as a function of the thermal treatment, concentration and excitation power. Weak emission from the ${}^4F_{5/2} \rightarrow {}^4I_{9/2}$ has been observed due to a slight thermal self-heating of $BaTiO_3$ nanopowders.

References

[1] SCHWARTZ R.W., Chem. Mater, 9 (1997), 2325.
[2] BUSCAGLIA M.T., BUSCAGLIA V., VIVIANI M., NANNI P., HANUSKOVA M., J. Eur. Ceram. Soc., 20 (2000), 1997.
[3] ANURADHA T.V., RANGANATHAN S., MIMANI T., PATIL K.C., Scripta Mater., 44 (2001), 2237.
[4] PECHINI M., US Patent No. 3,330,697 (1967).
[5] HU M. Z.-C., KURIAN V., PAYZANT E.A., RAWN C.J., HUNT R.D., Powder Tech., 110 (2000), 2.
[6] HER Y.-S., LEE S.-H., MATIJEVIF E., J. Mater. Res., 11 (1996), 156.
[7] LI S., EASTMAN J.A., THOMPSON L.J., BJORMANDER C., FOSTER C.M., Mater. Res. Soc. Symp. Proc., 457 (1997), 45.
[8] STRĘK W., HRENIAK D., BOULON G., GUYOT Y., PĄZIK R., Optical Mater., 24 (2003), 15.
[9] PARK Y., KIM C.I., Korean Patent No. 91-11699 (1991).
[10] ZHANG M-S, YU J., CHEN W., YIN Z., Progress Cryst. Growth Charact. Mat., 40 (2000), 33.
[11] SHIH W.-H., LU Q., Ferroelectrics, 154 (1994), 71.
[12] SHIH W.Y., SHIH W.-H., AKSAY I.A., Phys. Rev. B, 50 (1994), 575.
[13] MCNEAL M.P., JANG S.-J.,. NEWNHAM R.E., J. Appl. Phys., 83 (1998), 3288.
[14] FREY M.H, PAYNE D.A., Phys. Rev. B, 54 (1996), 3158.

[15] UCHINO K., SDANAGA F., HIROSE T., J. Am. Ceram. Soc., 72 (1989), 1555.

[16] SAEGUSA K, WENDELL E.R.,. BOWEN H.K, J. Am. Ceram. Soc., 76 (1993), 1505.

[17] HRENIAK D, ŁUKOWIAK E., MARUSZEWSKI K., PĄZIK R., STRĘK W., Mater. Sci., 20 (2002), 43.

[18] *JCPDS Powder Diffraction file Card No. 05-526*, International Center for Diffraction Data, Newtome Square, PA, (1967).

[19] *JCPDS Powder Diffraction file Card No. 31-0174*, International Center for Diffraction Data, Newtome Square, PA, (1967).

[20] KLUG P., ALEXANDER L.E., X-ray Diffraction Procedure, New York, Wiley, 1954 Chap. 9.

[21] TSUR Y., DUNBAR T.D., RANDALL C.A., J. Electroceram., 7 (2000), 25.

[22] TAKEUCHI T., TABUCHI M., ADO K., HONJO K., NAKAMURA O., KAGEYAMA H., SUYAMA Y., OHTORI N., NAGASAWA M., J. Mater. Sci., 32 (1997), 4053.

[23] CHO W.S., J. Phys. Chem. Solids, 59 (1998), 659.

[24] CARNALL W.T., CROSSWHITE H., CROSSWHITE M., *Energy level structure and transition probabilities of the trivalent lanthanides in* LaF_3, Argonne, National Laboratory, Illinois, 1975.

[25] HRENIAK D., STREK W., J. Alloys Comp., 341 (2002), 183.

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