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Influence of Composition and Temperature on Nd Doped $BaTiO_3$ Obtained by Zol-Gel Technology

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Abstract
Materials with high relative permittivity are important for the development of various sectors of industry. Such material is also $BaTiO_3$. Neodymium-doped $BaTiO_3$ was synthesized by the sol-gel method. Barium acetate – $Ba(CH_3COO)_2$, titanium butoxide – $Ti(OBu)_4$ and neodymium oxide – Nd_2O_3 were used as precursors of the preparation of sol. Absolute alcohol 99.9%, water, acetic acid were used as sol vents and stabilizers of the sol. After heating of the stabilized sol, a gel is obtained. Temperatures in the range of 600°C, 800°C, 1000°C and 1100°C were used in order to monitor the effect of heat treatment on the formation of the doped tetragonal $BaTiO_3$. Two compositions were studied: $Ba_{0.95}$ $Nd_{0.05}TiO_3$ and $Ba_{0.97}$ $Nd_{0.03}TiO_3$. It was found that in both cases the tetragonal phase of doped $BaTiO_3$ with Nd became predominant at temperatures of 1000°C and 1100°C. X-ray diffraction and thermal analysis (DTA and TG) were used to characterize the obtained samples.

Keywords: $BaTiO_3$, ceramic materials, sol-gel, doping

1.Introduction

$BaTiO_3$ is known for its wide range of applications: electronics [1-3], optics [4-5], medicine [6-7], photocatalysis [8-9] etc. Of particular interest is the doped $BaTiO_3$. It is used in the manufacture of: semiconductors, piezoelectric devices, supercapacitors, optoelectronics, thermistors, etc. [10-11] Barium titanate can be obtained with high dielectric permittivity and thus itis a particularly attractive material for use in electronics. Sn, Zr, Sr, etc. appear as suitable dopants. [12-14] For now, the most promising dopants are the ions of the transition metals: Nd3+, La +, Ce3+, Y3+, etc. [15-17] Various physicochemical methods have been used in the preparation of above mentioned compounds and materials: conventional solid phase synthesis, co-precipitation, hydrothermal production, sol-gel method, combustion method mechano chemistry, etc. [15, 17-19] The sol-gel method seems very promising. Some of its advantages are: significant lowering of the synthesis temperature, easy mixing of the initial components at the molecular level, precise control of the composition, fine size of the particles and crystallites (frequently nano size). The aim of the present work is to obtain Nd doped $BaTiO_3$ by sol-gel technology. [20-22]

2. Materials and methods

Precursors for the sol synthesis are: Ti $(OBu)_4$, Ba $(CH_3COO)_2$, Nd_2O_3. The required molar percentages of the constituent oxides are calculated in advance according to the formula: $Ba_{0.95}Nd_{0.05}TiO_3$. Initial compounds are dissolved:
(i) Nd_2O_3 in nitric acid,
(ii) Ba $(CH_3COO)_2$ in a mixture of water and acetic acid 5:1 volume ratio,
(iii) Ti $(OBu)_4$ in C_2H_5OH (99.9%) and CH_3COOH in a volume ratio of 1:1.
The barium acetate solution is mixed with the neodymium oxide solution (Solution A).

Finally, solution A is added to Ti (OBu)$_4$. The resulting sol is stirred vigorously and heated at 60°C. The gel is dried at mentioned temperature and after heating at 600°C, 800°C, 1000°C and 1100°C a powder sample is obtained.
Bruker D8 advance automatic X-ray diffractometer with CuK$_\alpha$ radiation equipped with Ni filter and Lynx Eye solid detector was applied in order to characterize the obtained products. The spectrum is recorded in the angular range (2Θ) from 10 up to 80ºC, in a step 0.02 and counting time 17.5sec/step.

3. Results and Discussion

XRD spectra of obtained powder samples are presented in Fig.1. It is seen that the samples calcined at 600ºC and 800ºC revealed the formation of $BaTiO_3$ and concomitant Ba_2TiO_4 phases. $BaTiO_3$ is the desirable tetragonal phase and Ba_2TiO_4 is the orthorhombic polymorph modification. Barium titanate is considerably prevailing at 1000ºC and 1100ºC (Fig.3 and Fig.5). Nd containing phase is not registered due to the low concentration of the dopant (under the susceptibility of XRD analysis).

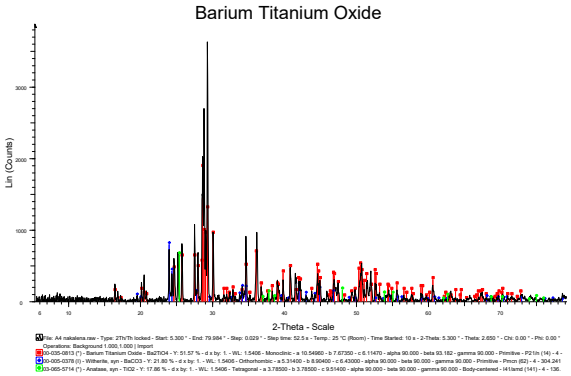

Fig. 1 XRD of the sample A4 of Ba_2TiO_4

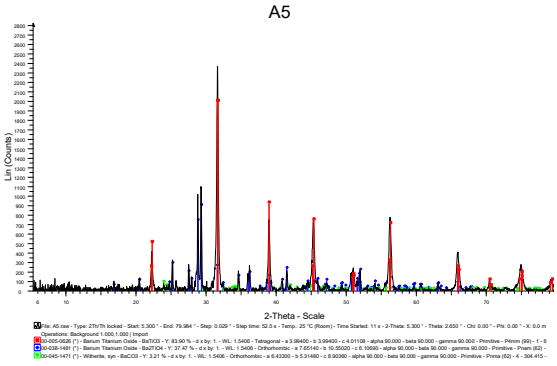

Fig. 2 XRD of the sample A5 of $BaTiO_3$

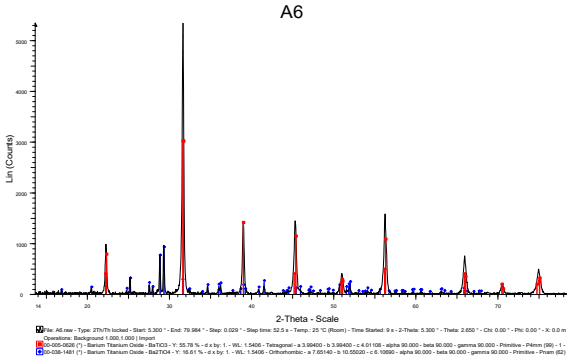

Fig. 3 XRD of the sample A6 of $BaTiO_3$

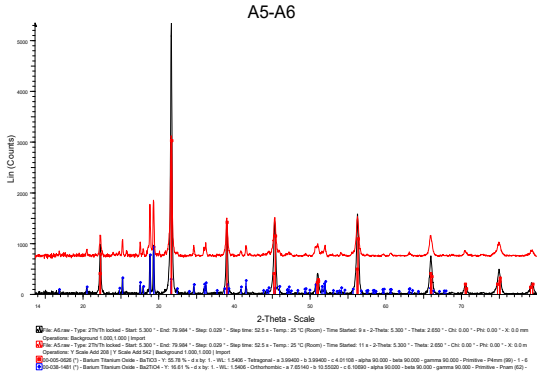

Fig. 4 Comparative diagram of samples A5 and A6

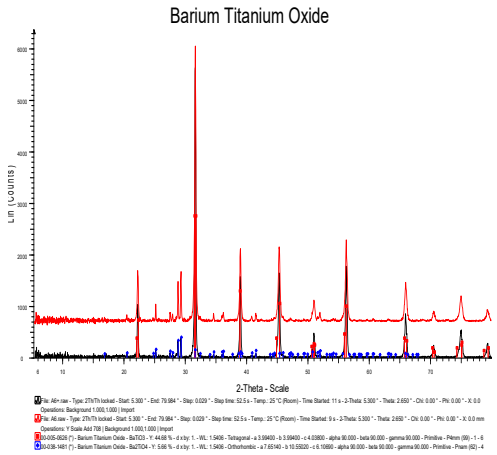

Fig. 5 Comparative diagram of samples A6 and A6+

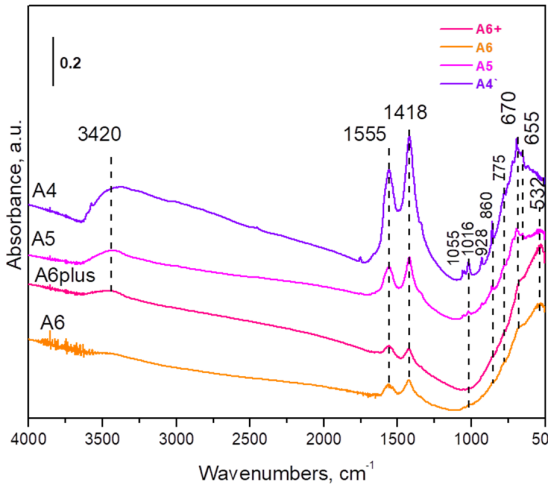

Fig. 6 IR of the samples of A4, A5, A6, A6+ in the range of 500 – 4000 cm^{-1}

In Fig.6 are presented the IR spectra of samples heated at temperatures in the range from 600°C to 1100°C, corresponding to samples denoted by symbols A4, A5, A6+, A6.

The band at 3420 cm^{-1} assigns to OH^- groups, and those at 1555 and 1418 cm^{-1} attribute to the presence of COO^- groups. The band at 775 cm^{-1} corresponds to Ba_2TiO_4, but almost disappears, which is in accordance with the results of XRD (for samples A6 and A6 +).
The band at 532 cm^{-1} is characteristic of Nd^{3+}, i.e. the dopant is embedded in the crystal lattice of $BaTiO_3$.

4. Conclusion

Doped ceramic powders are synthesized by sol-gel method. The tetragonal $BaTiO_3$ is prevailing phase after calcination at 1000ºC and 1100ºC. No other phase except Ba_2TiO_4 is registered. The obtained XRD results show that the chosen approach is correct. The composition of the sol as well as the mode of precursor addition are of resolute importance for preparation of stable Nd doped barium titanate sol. We foresee to proceed the investigation in order to obtain pure tetragonal $BaTiO_3$ aiming at precision of calcination treatment and gel preparation.

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