Investigation of the properties of Ce dopant titanate ceramics prepared by sol-gel method

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Abstract: *The research in this article focuses on the synthesis of Ce donated $BaTiO_3$ needed to make a target for magnetron sputtering. Synthesis is $BaTiO_3$ by sol-gel method with a certain concentration of a modifying additive of Ce. The process of the sol-gel method is considered and the obtained results are characterized. Additional termal treatment of the obtained samples was performed at $T^OC = 900^OC$ in a muffle furnace in Ar / H_2 medium and in a laboratory furnace in air. Physicochemical methods by XRD analysis and Raman spectroscopy were used to characterize the results obtained.*

Keywords: *SOL-GEL, $BaTiO_3$ MODIFY, XRD, RAMAN SPECTROSCOPY*

1. Introduction

Nowadays, the development of materials for electronics is intensifying more and more. Interest in new advanced materials obtained by low-temperature synthesis methods has grown significantly in recent years. New lead-free titanium materials used in electronics have become a desirable product for various branches of industry. [1]

Traditional ceramics and glass-ceramics are materials that are obtained by high-temperature synthesis methods. The obtained samples have a dense structure after the determined temperature treatment. High temperature solid phase synthesis produces materials with controlled particle size.

Low-temperature synthesis methods are one of the methods that contribute to the development of new materials with different applications. [1-3]

The chemical reactivity of metal alkoxides offers a wide range of possibilities for modifying different materials. The process of hydrolysis and condensation can be completely different, leading to new products. An analysis is provided on some of the most common chemical additives used in the sol-gel process. The most important characteristics are the reactivity of the new ligand to hydrolysis, the charge distribution in the new molecular precursor and the coordination numbers of the metal atom.

It is known that very high values of the dielectric permittivity can occur in ferroelectrics [4,5]. Approximation of the ferroelectric phase transition at Tc (Curie temperature), ε(T) (relative dielectric permittivity) increases sharply, usually at Curie temperature and begins to decrease again below Tc. In addition, ferroelectrics have pronounced nonlinear dielectric properties, for example showing characteristic hysteresis circuits of polarization dependent on the electric field [6-18]. Both phenomena are related to the inability to apply in electronic devices. This can be partially overcome by doped and special treatment, thus regulating the microstructure and the internal arrangement of the particles in the cell. Well-known barrier layer ceramic materials use a combination of polarization effects and ferroelectrics such as $BaTiO_3$ to achieve high values of capacity with temperature and voltage that are suitable for different applications [6–15].

Many transition metal oxides show very high ("colossal") dielectric constant values and thus have huge potential for modern microelectronics applications and for the development of new capacity-based energy storage devices. In the present paper, we discuss the mechanisms of sol-gel technology, modification of ceramic materials that can lead to colossal values of dielectric constant. In addition, we offer an overview and discussion of the properties of Ce subsidized $BaTiO_3$, which emerges as a material with colossal dielectric constant.[12-24]

2. Experimental

$Ba0_{.945}Ce_{0.055}TiO_3$ ceramic was synthesized by the sol-gel method. The starting materials used were $C_4H_6BaO_4$ (barium acetate), $C_{16}H_{36}O_4Ti$ titanium butoxide and $Ce(NO_3)_3.6H_2O$ (cerium nitrate) in certain stoichiometric ratios. CH_3COOH was used as a complexing agent. The solutions are mixed and homogenized on a magnetic stirrer model for 3 hours. The resulting sol was stabilized by the addition of DEA (diethanolamine). The solution is gelled at room temperature. The resulting gel was dried in an oven at 100°C. The annealing is performed in an air laboratory furnace and in a muffle furnace in an environment of Ar/5% H_2. The obtained phases are characterized by XRD and Raman spectroscopy, which are explained in the next part of the discussion.

3. Results and Discussion

X-ray phase analysis of the experimental samples was performed using an automatic powder X-ray diffractometer Bruker D8 Advance with Cu K radiation. In laboratory conditions, ceramic samples with desired properties are synthesized by the described technological methodology.

X-ray phase analysis of the obtained experimental samples revealed the presence of a predominant crystalline phase of tetragonal $BaTiO_3$. Figure 1 shows a diffraction pattern with a predominant phase of $Ba_{0.945}Ce_{0.055}TiO_3$. The intensity of the peak is marked in red. The annealing was performed at 900°C in a laboratory furnace. In FIG. 2 shows a monophase of pure $BaTiO_3$ at 900°C in an Ar/H_2 medium. The size of the crystallites was also determined by the Atoms program. The crystallites of the $Ba_{0.945}Ce_{0.055}$ TiO_3 phase are 37 nm in size, while the $BaTiO_3$ monophase shows a size of 19 nm.

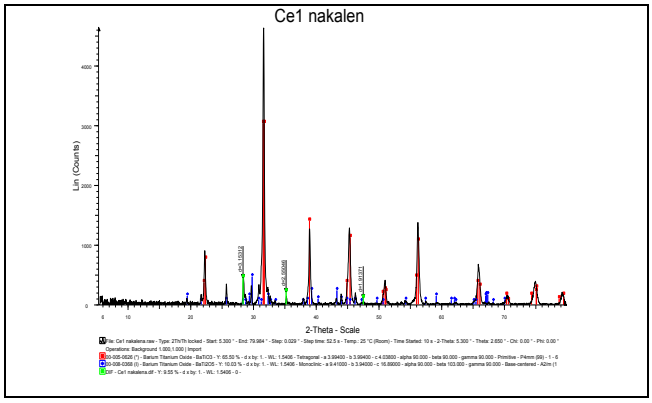

Fig. 1. *XRD of $BaTiO_3$ doped with Ce in air*

The Raman spectra were collected using Lab RAM HR Visible Raman spectrometer. For excitation the 633 nm line of a He-Ne laser was used. As some of the investigated powder samples are dark ones and strongly absorbing, a laser power test was done and the laser power not causing local overheating effects on the sample surface was determined as 30μW. An objective X50 was used both to focus the incident laser light onto a spot with diameter about 4 μm and to collect the scattered light in backscattering geometry. Several spectra

from different arbitrary spots from each sample were collected. The investigated spectral range was 70 cm^{-1} - 1290cm^{1}.

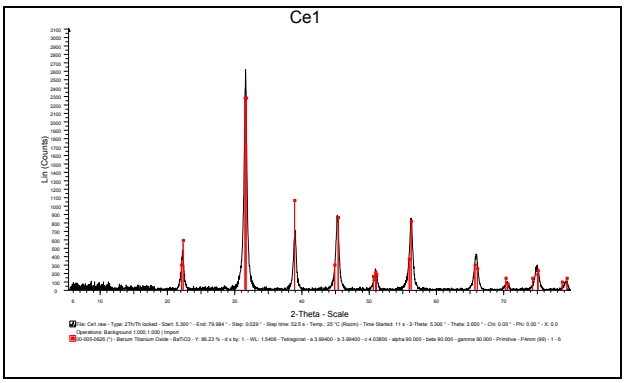

Fig. 2. *XRD of $BaTiO_3$ doped with Ce in Ar/H_2*

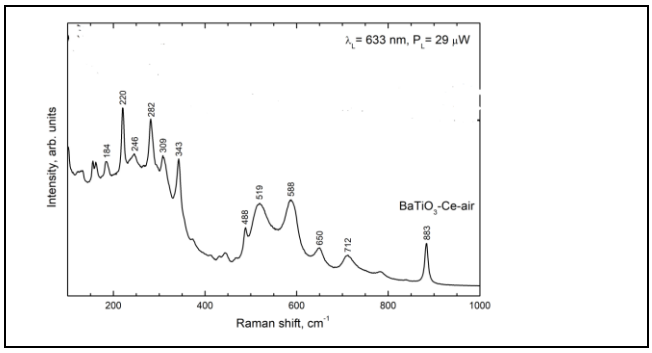

Fig. 3 *Raman spectroscopy of the Ce doped $BaTiO_3$*

The Raman spectra of $BaTiO_3$-Ce-air samples were shown in Fig. 3. The light (transparent) $BaTiO_3$ - Ce-air sample. By this reason its Raman spectrum is about 10 times less intensive. For better comparison this spectrum is multiplied by a number of 10.

The lines observed at 246, 309, 519, and 712 cm^{-1} (in spectrum of $BaTiO_3$-Ce-air) correspond to Raman-active modes in the tetragonal $BaTiO_3$. All other observed lines correspond to impurity phase(s).

4. Conclusions

According to the above results, it can be concluded that a phase of $BaTiO_3$ with Ce modifier has been synthesized. Sol-gel technology was used for the synthesis. The heat treatment was carried out in two ways: by annealing in a laboratory furnace in air and in a stream of Ar / H_2.

X-ray diffraction patterns prove the presence of a monophase of $BaTiO_3$ in an argon and hydrogen medium, and the presence of a $Ba0_{.945}Ce_{0.055}TiO_3$ phase is also proved. Raman spectroscopy proves these results. At 883cm^{-1} we have a characteristic peak for $Ba_{0.945}$ $Ce_{0.055}TiO_3$. The lines at 246, 309, 519, and 712 cm^{-1} determine the presence of tetragonal $BaTiO_3$.

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