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Features high-temperature synthesis of barium zirconium titanate powder by using zirconium dioxide nanopowders

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ABSTRACT

During the synthesis of the $BaCO_3/TiO_2$ and $BaTiO_3$ powders with the ZrO_2 nanopowders the increase of the yield of the $BaZr_{0.25}Ti_{0.75}O_3$ phase has been established. It was obtained by comparing the XRD results for the synthesis of the barium zirconium titanate powders using the ZrO_2 micropowders vs. nanopowders. The effect caused by the high specific surface of the nanoparticles as well as low bonding energy of surface atoms. The changes in the solar absorptance (Δa_s) after electron exposure on the $BaZr_{0.25}Ti_{0.75}O_3$ powder decrease at using ZrO_2 nanopowders.

1. Introduction

Barium titanate is a major chemical compound for the ferroelectric and piezoelectric ceramics, which have the temperature-dependent phase transitions. The partial replacement of the cations of the barium or the titanium by the atoms of other elements leads to the shift of the phase transition from 120 °C to low temperatures. The well-studied [1–4] are the patterns of the titanium cations displacement by the zirconium atoms and the barium cations by the strontium atoms.

The synthesis of the barium titanate ceramic on the basis of the powder mixtures is carried out with the use of the pressure, the high temperatures and the long heat treatment time. These modes give almost 100% yield of the main phase. According with [1], the synthesis of barium zirconium titanate (BZT) ceramic with the compound $BaCO_3/TiO_2/ZrO_2$ is carried out at the temperature from 1390 to 1420 °C and the heating time about10 h.

The dependence of the emissivity (ε) from the phase transitions was registered not only in ceramics but also in powders for the barium titanate with partially substituted cations [4]. This gives the promising prospects for the use of such powders as the pigments for the creating heat regulating coatings (HRC).

These coatings are important for the space application in the spacecraft cause the temperature of them is determined by the ratio of $T \sim (a_s/\varepsilon)^{1/4}$, where a_S—the solar absorptance. During the long flight the solar absorption increases due to the formation of the defects and the absorption centers under the influence of the space radiation, the emissivity of it does not change, or changes within no more than 5%, which lead to the temperature increase of the spacecraft to 60 °C and more, according with the satellite telemetry. This problem can be solved by the proportionally increasing of the emissivity ($\Delta\varepsilon$) with the increasing of the spacecraft temperatures if used as the pigment phase transitions materials.

In other cases the use of the phase transitions materials (PTM) for spacecraft can reduce the incoming solar energy. It is often associated with the set of spacecraft in the shadow of the Earth or in the shadow of his own body during the rotation around its axis. If applied HRC based on the PTM compounds, their emissivity will then be reduced, there by reducing the radiated energy and the rate of temperature drop down.

Therefore, the development of the pigments based on the compounds of the barium titanate with the partially substituted cations is an urgent problem of the space materials. Such pigments are required for the temperature stabilization process in the various industries, to conserve the heat in the homes and the industrial buildings when the temperature of the air in the cold winter and hot summer.

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The powder synthesis under the same values of temperature as well as for ceramics leads to the powder agglomeration. Subsequent grinding sintered powders to produce the desired particle size distribution, and application of pressure during the synthesis gives a greater concentration of dislocations and other lattice defects. These defects are the potential color centers under the action of solar spectrum photons on the ground and the exposure of charged particles in space. The presence of such color centers leads to reduce of the reflectance of the HRC based on the phase transition of the powders which may cause the failure of the temperature stabilization condition.

Since the investigated powders are designed to work under radiation exposure (photons of the solar spectrum in the terrestrial conditions separately and together with the charged particles in space), the actual are comparative studies of the radiation stability of the BZT powders obtained by the heating mixtures in the different modes.

Use of the ZrO_2 nanopowders in the synthesis of BZT compounds may be more effective than for the ZrO_2 micropowder cause the modification of the other pigments by the nanoparticles gives the beneficial effects [5,6].

Thus, urgent problem is synthesis barium zirconium titanate powder at $T \leq 1200$ °C. That will reduce the defects which are potential color centers.

2. Experiment

The research was carried out on the commercial chemically pure $BaCO_3$, $BaTiO_3$ and TiO_2 powders with the average particle size–0.5–1 μm. As a component of introduction have been applied high chemical purity ZrO_2 micropowders (1.5–2.2 μm, 4–5 m^2/g) or nanopowders (30–40 nm, 25–50 m^2/g). The monoclinic phase of ZrO_2 was registered for the micropowders, while the tetragonal and cubic structures were typical for the nanopowder.

Two types of the powder $BaTiO_3/ZrO_2$ and $BaCO_3/TiO_2/ZrO_2$ were prepared. The first type of powder mixture has1 mol $BaTiO_3$ and 2 mol ZrO_2 powders. The second mixture of the powders has three components of the $BaCO_3$, TiO_2 and ZrO_2 powders where in the output obtained 100% of the barium zirconium titanate powder (main phase).

The typical procedure for obtaining the $BaTiO_3/ZrO_2$ and $BaCO_3/TiO_2/ZrO_2$ powder mixtures was dispersed the initial component in the distilled water under the magnetic stirrer. Then the resulting solution is dried at 150 °C for 5 h. Afterward the powders were heat-treated at the temperature of 1000, 1100 and 1200 °C in the ambient for 2 h. Also two consecutive heat-treated of the $BaCO_3/TiO_2/ZrO_2$ powder mixtures with the mode 800 °C during 2 h then 1200 °C during 2 h are performed.

The X-ray diffraction analysis was performed using a Shimadzu XRD-6000 (CuKα = 1.5405) by the full-profile analysis POWDER CELL 2.5.

The radiation stability of the synthesized compounds estimate by the measure *in situ* (in a vacuum and in place of irradiation) spectral reflectance before ($\rho_{\lambda 0}$) and after the irradiation ($\rho_{\lambda f}$) in the range of 350–2000 nm under electron exposure (E = 30 keV, $\varphi = 1 \times 10^{12}$ cm^{-2} s^{-1}, $F = 3 \times 10^{16}$ cm^{-2}, T = 300 K, $P = 5 \times 10^{-7}$ Torr) [7].

The value of solar integrated absorption coefficient of the samples was calculated in accordance with the ASTM (E490 and E903-00a-96) for the powders by the formula:

$$a_S = 1 - \rho_S = 1 - \frac{\int_{\lambda_1}^{\lambda_2} \rho_\lambda I_\lambda d\lambda}{\int_{\lambda_1}^{\lambda_2} I_\lambda d\lambda} \quad (1)$$

The ρ_λ is defined as an average of two experimental points.

3. Results and discussion

The synthesis of the $BaTiO_3$ and ZrO_2 powders at 1000, 1100 and 1200 °C for 2 h leads to the formation of the $BaZr_{0.25}Ti_{0.75}O_3$. In addition to the main phase formed barium zirconate (Figs. 1 and 2, Table 1). With the increase of the heating temperature the lattice parameters of the $BaZr_{0.25}Ti_{0.75}O_3$ powders don't changed. The concentration of the main phase is increased by the use of the ZrO_2 nanopowder (nano-ZrO_2) instead of the ZrO_2 micropowder (micro-ZrO_2). Its largest value reaches at T = 1200 °C and $BaZr_{0.25}Ti_{0.75}O_3$ phase yield equal to 6.6% for micro-ZrO_2 and 10.3% for nano-ZrO_2. The concentration of $BaZrO_3$ vs. the total composition decreases with the increasing temperature from 1000 to 1100 thereafter 1200° C: 4.5 → 3.3 → 3.1% of the compounds for micro-ZrO_2 and 5.9 → 5.4 → 5.0% of the compounds for nano-ZrO_2. The concentration of unreacted ZrO_2 phase is 28–34%.

These results indicate that the $BaZr_{0.25}Ti_{0.75}O_3$ concentration for all conditions of the synthesis is more in the powder mixtures with the nanopowders instead of the micropowders. It is due to the higher concentration of the unsaturated bonds and the higher concentrations of the zirconium atoms on the surface of particles belong to nanoparticles. So it reacts more intensity with the molecules of $BaTiO_3$ compared with the microparticle.

The concentration of the unreacted barium titanate solid solution is determined not only by the ratio of the specific surface area, but also by the energy of the surface atoms in the grains of the micro- and nanoparticles. Therefore, one should expect a smaller number of the unreacted barium titanate molecules provided that the reaction with the zirconium oxide nanopowders.

The synthesis of the $BaTiO_3/ZrO_2$ powders mixtures, as well as the mixtures of $BaCO_3/TiO_2/ZrO_2$ synthesis gives higher yield of the main phase ($BaZr_{0.25}Ti_{0.75}O_3$) if use the nano-ZrO_2 instead of the micro-ZrO_2. The $BaZr_{0.25}Ti_{0.75}O_3$compound almost not formed at the temperature of 1000 °C. At 1100 and 1200 °C it is formed by the using of the ZrO_2 micro- and nanopowders. Moreover, it generates more using the nano-ZrO_2 (Figs. 3 and 4, Table 2). The heat-treated of the powder mixtures in the sequential mode is result in a significant increase in the $BaZr_{0.25}Ti_{0.75}O_3$ yield phase compared with the heat-treatment at single mode. The $BaZr_{0.25}Ti_{0.75}O_3$ phase output reaches 90.1% at using of micro-ZrO_2 powder, for nano-ZrO_2 it is 96.0% (Fig. 5).

In addition to the main phase formed $BaTiO_3$ and $BaZrO_3$. The processes of the formation $BaZr_xTi_{1-x}O_3$ solid solution apparently have two steps. The first step is the formation of $BaTiO_3$ and $BaZrO_3$in direct solid reactions:

$$BaCO_3 + TiO_2 = BaTiO_3 + CO_2. \quad (2)$$

$$BaCO_3 + ZrO_2 = BaZrO_3 + CO_2. \quad (3)$$

The $BaTiO_3$ concentration is more than the $BaZrO_3$ concentration for any synthesis temperature (Table 2). The difference in the concentration can be determined by the difference in the activation energy of these compounds, which is 34.3 kcal/mol for the $BaTiO_3$ and 48.4 kcal/mol for $BaZrO_3$ [8], as well as the larger Zr^{4+} cation ionic radius (0.68 Å) compared with the Ti^{4+} cation ionic radius (0.42 Å).

In the second step is formation of the $BaZr_xTi_{1-x}O_3$ solid solution results of diffusion of Zr into the in BaTiO3 lattice, the activation energy of this stage is 116 kcal/mol (489 kJ/mol) [9]. Therefore, $BaZr_xTi_{1-x}O_3$ solid solution is not yet formed at 1000 °C temperature, but at 1100 °C formed in a small amount.

The concentration of the total composition of $BaZr_{0.25}Ti_{0.75}O_3$ at temperature of 1100 °C is 5.2% using micro-ZrO_2 and 8.5% for nano-ZrO_2. The increase of the synthesis temperature to 1200 °C results