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Modified Composite Thermal Control Coatings Irradiated with High−Energy Particles

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Abstract. The main trends in modern space instrumentation are an increase in the active life of spacecraft, the tightness of their structure, and the widespread use of new polymer composite materials. Composite thermoregulatory coatings are designed to maintain the required thermal regime of objects by establishing a balance between the energy absorbed from the outside and the energy emitted into the environment. The aim of this work is to study the structure of new composite thermoregulatory materials (coatings) irradiated with high−energy particles − an electron with an energy of 3.5 MeV and a proton with an energy of 18 MeV, using X−ray diffraction analysis, optical photoluminescence doped with cerium, as well as other coatings, a new composition of thermoregulatory coatings (TRC) was developed by the method of hydrothermal microwave synthesis. According to the results of studies of modified TRCs, it was found that the samples synthesized by the microwave method have a crystalline structure after heat treatment. It is shown that the mechanisms of the effect of radiation spectra on the material medium are completely different and are determined by the atomic−molecular structure of matter. Irradiation with highly energetic particles gives rise to color defect centers of two types.

1. Introduction

Insufficient radiation resistance of spacecraft structural materials is one of the main obstacles for the development of modern astronomy. Minimizing the impact of cosmic radiation (CR) or increasing the durability of structural materials is one of the most important challenges for state of the art science. The CR can affect not only astronomers, but also cosmic stations, artificial satellites and equipment therein. If in case of astronauts the exposure of CR can be minimized by limiting their working period in the space, in case of space stations, this problem is much deeper, as the equipment are continuously operating at space conditions for decades. Most sensitive to radiation damages are semiconductor and polymer materials, which are an indispensable part of the spacecrafts [1]. Considerable effort is being invested in identifying new materials with even better performance than the current industry standards. Silicate solution based powders (Zn_2SiO_4, $ZrSiO_4$, Na_2SiO_4, Y_2SiO_5), pyrochlore oxides ($La_2Zr_2O_7$), perovskites, aluminates as well as yttria stabilized zirconia (YSZ) obtained by plasma spraying (PS), electron beam physical vapor deposition (EB–PVD), sol−gel or laser chemical vapor deposition [2, 3] are among the most known materials used as a TBC [4−9]. They are fire−proof, are resistant to high temperatures and radiation, can be used as heat protection at thermal and nuclear plants, electrostatic safety systems, etc... Temperature extremes, vacuum, radiation (of both charged particles and energetic photons), atomic oxygen (AO) are the main factors that should be considered when designing future space crafts. The destructive influence of such factors had been demonstrated in Low Earth Orbit (LEO) flights. Thermal barrier coatings that may be proposed for exterior surfaces of spacecraft must be able to withstand all of the effects of the space environment. From the other hand such coating is a crucial thermal insulation technology that enables the underlying substrate to operate near or above its melting temperature. They find application in turbine engines in aircrafts and in ceramic coated diesel engines. Improvement of such coatings will allow to increase the power and efficiency of gas turbine engines through increasing the turbine inlet temperature. Another application of TBC is the possible reduction of cooling loads in military vehicles. As a result, the total weight of the vehicle can be significantly reduced. To that end TBCs are being studied for their potential as insulators, particularly for military engines space- and aero crafts.

The purpose of this work is to investigate the radiation resistance and optical properties of zinc and zirconium silicate doped with cerium by X-ray diffraction analysis methods and optical spectroscopy (photoluminescence).

2. Materials and techniques

The synthesis of hydrosilicate zirconium was carried out in a microwave oven brand "CE1073AR" of "Samsung" company, in an open glass flask equipped with a reflux condenser and stirrer. Microwave frequency was 2.45 GHz, and microwave power was 600 Watts during synthesis. Concentrations of initial aqueous solutions of $ZrSO_4$ and $Na_2O{\cdot}SiO_2$ were 0.5 mol/l. The synthesis was carried out by reaction of zirconium sulfate and sodium silicate solutions, maintaining the pH of the medium at 7.0 [10]. Aqueous solutions of zinc chloride (ZnCl2, 99.5%) and Na_2SiO_3 with the concentration of 1.0 mol/l were mixed and irradiated in a MS−6 "VOLTA" microwave oven (2.45 GHz frequency) for 1.5−3.5 hours. The maximum temperature during the synthesis was ∼240 ^{0}C. Cerium (III) nitrate hexahydrate ($CeH_{12}N_3O_{15}$) (99.0%) was added to solutions for cooking 5% wt. pigments Ce–Zn_2SiO_4. This concentration was chosen to ensure alloying of the material, and not to form the second phase. After microwave irradiation, the precipitates were filtered and washed with warm deionized water to remove NaCl by−products and then was dried at 110 ^{0}C [11]. Irradiation of samples was carried out at A. Alikhanyan National Laboratory using a linear electron accelerator with energy of 4 MeV, and irradiation dose 10^{16} el/cm^2. The temperature of the samples during irradiation did not exceed 25 ^{0}C. For complete removal of bound water, the samples of zinc orthosilicate Ce/Zn_2SiO_4 (1050^{0}C) and zirconium Ce/$ZrSiO_4$ (1200^{0}C) were heat treated. The X-ray phase analysis of the samples was carried out by the powder method. X-ray powder diffraction (XRD) is a rapid analytical technique primarily used for phase identification of a crystalline material and can provide information on unit cell dimensions. The analyzed material is finely ground, homogenized, and the average bulk composition is determined. For optical studies, spectroscopic methods were used, which are based on the interaction of electromagnetic radiation with a material. The LUMEN experimental facility is designed for spectral measurements with a high spectral resolution, wide temperature range. A 1kW DKSEL 1000−5 xenon ultra-high-pressure lamp was used as a light source. The registration system made it possible to measure luminescence spectra at various spectral points with selective photoexcitation up to ~ 5eV.

3. Results and discussions

As it is known, under the high−energy radiation, radiation defects and electronic excitations arise in the TBC [10–14]. The parameters for irradiating thermoregulatory silicate minerals with electrons, for example, were chosen with the potential of them being in the Earth's radiation belt for more than ten years in mind. Because silicate compounds have such a complicated structure, proving the system of flaws responsible for the creation of certain radiation color centers is not always attainable. During exposure to ionizing radiation, traps present in the material and responsible for the formation of color centers filled with electrons and holes, which leads to an increase in the optical density of silicate materials.

The mechanism of action of different parts of the radiation spectrum on the material environment is completely different, which is determined by the atomic−molecular structure of the substance. When powders are irradiated with TBC, two types of color centers are formed:

- radiation defects caused by nonstoichiometry of the crystal structure and on intrinsic point defects of the surface;
- defects formed during irradiation in the volume of the crystal lattice.

The concentration of defects of the first type largely depends on the specific surface area and grain size of the powders. As the specific surface area increases, the concentration of defects usually increases or changes along a curve with a maximum.

When light quanta and ionizing radiation act on powders (defects of the second type), electron−hole pairs are formed, after which their separation is possible. The holes formed move to the surface, where they interact with the adsorbed O_2, H_2O molecules and impurities. Free electrons can increase electrical conductivity and reduce surface potential barriers between coating grains. It follows that decompositions are characteristic both under the action of light quanta or radiation with energies greater than the energy gap of the powder, and under the action of electrons with an energy lower than the forbidden gap of the powder (not sufficient for the formation of Frenkel pairs).

It is known that the luminescence spectra of some simple oxides (BeO, Al_2O_3), may contain several bands of intrinsic luminescence, but in complex crystals, such as TBC, there can be several sublattices and structural fragments of different types respectively and defects formed as a result of heat treatment, radiation and the presence of impurity ions [15]. Doping with cerium helps to obtain highly crystalline nanoscale structure as shown in our previous work [11]. It also stabilizes crystalline structure, due to the difference between the electric field of the Ce^{3+} /Ce^{4+} and Zn^{2+}, Zr^{2+} cations. This difference can lead to a decrease in the total energy of the lattice, which will make it more stable under irradiation with high−energy electrons [11].

The phase composition of the TBC was investigated using X-ray diffraction analysis (XRD) which follows that the samples obtained have a crystalline structure. Fig. 1 shows the X−ray diffraction patterns of the Ce−$ZrSiO_4$ and Ce−Zn_2SiO_4 samples. The Ce−$ZrSiO_4$ sample has diffraction peaks of a tetragonal structure with lattice parameters a = b = 0.65989 nm, c=0.59857 nm. The average grain size is 19.1 nm (from the Scherrer equation) (Fig. 1a).

The Ce−Zn_2SiO_4 sample exhibits broad diffraction peaks of the rhombohedral structure of αZn_2SiO_4 with the space group R–3 and the cell constant a=b=1.395 nm, c=0.9312 nm. The average grain size is 20.2 nm (Fig. 1b).

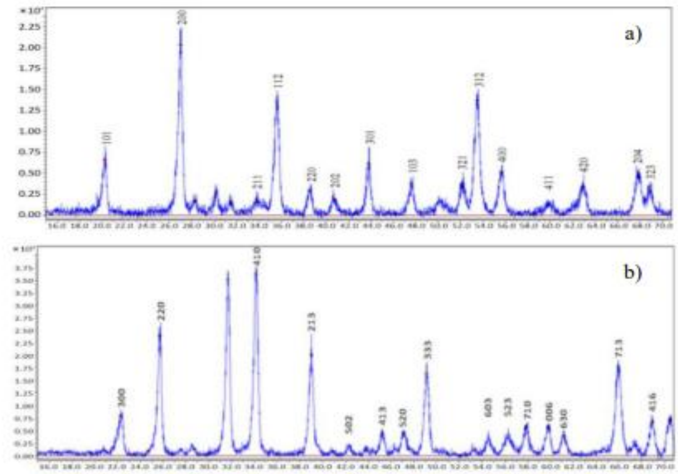

Fig. 1. X−ray diffraction patterns of Ce−$ZrSiO_4$ (a) and Ce–Zn_2SiO_4 (b) synthesized by microwave-assisted.

To evaluate in more detail the TBC radiation resistance, some optical properties of the samples were investigated before and after electron irradiation. Irradiation point defects serve as traps for electrons and holes and become color centers. Electrons and holes fill these centers, which leads to an increase in the optical density of silicates. Optical density depends on the radiation dose rate, as well as on the isothermal rate of annealing of color centers. Fig. 2 shows the photoluminescence spectra of the samples before and after irradiation with electrons with energy of 4 MeV and a dose of 10^{16} e/cm^2.

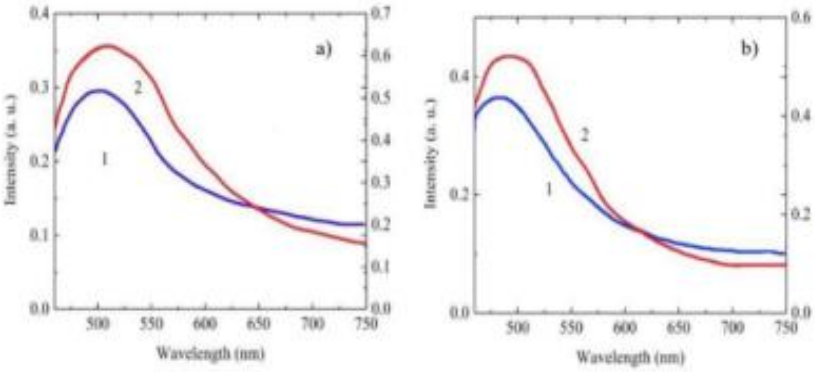

Fig. 2. Photoluminescence spectra of samples a) $ZrSiO_4$ (Ce_2O_3−5%), b) Zn_2SiO_4 (Ce_2O_3−5%), T=300K, E_{exc} = 3.06eV (1−before irradiation, 2−after irradiation with electrons with an energy of 4 MeV and a dose of 10^{16} el/cm^2).

The bands at 480 nm (2.6 eV) observed in the PL spectra of the samples under study (Fig. 2); 500 nm (2.5 eV) characteristic of the luminescence of many silicates are usually associated with radiation, for example, defective centers $[SiO_4]^{4-}$ caused by local distortions of silicon−oxygen tetrahedra [15]. Zirconium (zinc) ions can be in a tetrahedral environment in the form of (OH)−Zr−$(OSi)_3$ or Zr−$(OSi)_4$ groups and appear when the symmetry of the silicon−oxygen tetrahedron is broken due to a closely located defect. Luminescence bands can also be associated with the creation of complex radiation defects: zinc, zirconium, oxygen vacancies, respectively, with the formation of anionic vacancies such as F, F^+ as emission centers. The observed bands are possibly due to the intermediate stage of the formation of exciton−defect complexes or short−lived defects in the form of V_{Zr}^-, V_{Zn}^- vacancies and interstitial Zr^+, Zn^+ ions formed upon bond breaking [3, 4]. Thus, it can be assumed that upon irradiation with electrons with energy of 4 MeV, the observed maxima in the PL spectra are due to the formation of point defects−anion vacancies. TBCs subjected to heat treatment at 220^0C have an amorphous phase, which follows from the spectra of X-ray diffraction patterns. Therefore, the work presents TBC, which had a crystalline structure after heat treatment at 1050^0C and 1200^0C.

4. Conclusions

Examining the materials' radiative−optical properties, we may conclude that the samples obtained by the hydrothermal microwave method at high temperatures have a crystalline structure, based on the results of X−ray diffraction research. The spectra of fluorescence show that after electron irradiation, there is a modest rise in luminescence, indicating the formation of new radiation centers. The results lead us to believe that Ce–Zn_2SiO_4 and Ce–$ZrSiO_4$ coatings are ideal choices for space vehicles.

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