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Optical Properties and Radiation Resistance of Zirconium Silicate Obtained by Microwave Method

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Abstract. A microwave (MW) method of hydrothermal synthesis of zirconium silicate is developed. At low temperature (240°C), nuclei of crystalline phase of zirconium silicate (zircon) are obtained. Some optical characteristics of the synthesized product are determined. The dependence of the diffuse reflectance on radiation is studied at low temperatures (90 K) and pressures (10^{-5} - 10^{-6} Pa). Based on gravimetric, X-ray and thermographic studies is revealed that the synthesis of zirconium silicate from water-soluble salts of initial components in microwave ovens promotes the formation of zircon at lower temperatures. MW synthesis of zirconium silicate ensures obtaining of nanosized zircon powder after heat treatment at 1200°C.

Keywords: hydrothermal-microwave treatment, zirconium silicate, zircon, thermoregulating coatings, diffusion reflection.

1. Introduction

Zirconium silicate, due to the very low reactivity, high strength and hardness, low coefficient of thermal expansion, stability of technological properties, high resistance to chemical and thermal influences, as well as its optical luminescent properties is a promising material for manufacturing high-quality surfaces. Zirconium silicate coatings are corrosion-proof, heat- and radiation resistant, and can be also used as thermoregulating coatings (TRC) to maintain thermal behavior of space vehicles [1], nuclear power plants, electrostatic safety systems, etc. Thermal coatings are used in space vehicles (SV) in order to maintain their thermal behavior. The stability of the SV thermal behavior is one of the main factors that determine the reliability and durability of SV. Analysis of the existing TRC suggests that they cannot provide an increase in their active lifetime up to 15 years, especially for those SV operated in high elliptical and geostationary orbits, because spectroscopic characteristics of SV coatings are changed under the effect of space flight factors at long-term orbital missions. This fact leads to violations of stable operation of electronic equipment and thus reduces the SV active lifetime. Therefore, the development of TRC with both stable thermoradiation characteristics during long-term orbital flight and low gas release is one of the important tasks of the XXI century astronautics. The development of such coatings in order to reduce deviations from the specified thermal regime, as well as failures in operation of highly sensitive optical and electronic equipment, should ensure an opportunity to increase the terms of SV active lifetime up to 15 years and more.

At present, powders of oxides, ZnO, ZrO_2, TiO_2, Zn_2TiO_4, are used as pigments for TRC [2-10]. The use of silicate pigments for the SV TRC is limited due to the sophisticated technology of their manufacturing. Since the process of producing high-purity silicate is multistage and of long

duration, as well as carried out at high temperatures, the development of new methods of synthesis of the silicates is an urgent task. In recent years, the unique capabilities of microwave (MW) chemistry have been used to obtain various materials [11-15]. We have developed a MW method of liquid-phase synthesis of zirconium silicate. Synthesis of zirconium silicate by reacting aqueous solutions of zirconium salts and sodium silicate is easy to operate and economical, however, the chemical reactions occurring under MW heating are much effective. The obtaining of silicates by hydrothermal microwave (HTMW) method is an effective way to produce nanocrystalline silicates compared with the solid-phase reactions methods. The developed method allows the use of silica-containing rocks as raw materials. We have also developed a new and efficient HTMW method for obtaining sodium and potassium silicate solutions from rocks and a method for cleaning of the obtained silicate solutions [16-21], as well as a low-temperature (200-250°C) method of synthesis of nanocrystalline silicates doped with different components. According to the developed HTMW method of processing of silica-containing rocks (perlite, diatomite, quartzite, silica sand), at 95-200°C alkali silicate solutions ($Na_2O{\cdot}nSiO_2$ or $K_2O{\cdot}nSiO_2$, n=l-4.0) are obtained. HTMW processing of silica-containing rocks accelerates the process of obtaining silicate solutions by a factor of 3-5 compared with hydrothermal treatment. Further, silicates are precipitated from the solutions of alkali silicates and water-soluble salts of various metals. Microwave chemistry combined with hydrothermal treatment is an effective way to produce inorganic materials due to uniform and rapid heating and high purity process conditions.

The aim of this work is to develop a HTMW method for synthesis of zirconium silicate, zircon, with high reflectivity (ε), low coefficient of integral absorption of solar radiation (a_s) and high radiation resistance.

2. Materials and technique

Obtaining of sodium silicate from rocks and its cleaning from coloring impurities. As raw materials for the production of sodium silicate solutions, diatomite of Dzhradzor deposits, perlite of Aragats deposit and quartzite of Shahnazar deposit of the Republic of Armenia were used.

HTMW processing of perlite, diatomite and quartzite was carried out in teflon autoclaves of VOLTA MC-6 multimode microwave oven. The parameters of HTMW processing of rocks using sodium hydroxide were as follows: temperatures of 95-200°C, microwave frequency of 2.45 GHz and a power of 50-100 W [16-20]. The cleaning of silicate solutions from iron was performed using an electromagnetic unit and subsequent introducing to the solution freshly prepared lime milk as a collector-precipitator of iron compounds at MW heating [21].

Obtaining of zirconium silicate. Synthesis of zirconium silicate was performed again in teflon autoclaves of VOLTA MC-6 microwave oven. Synthesis conditions were as follows: temperature of 240°C, pressure of 33 bars, duration 30-240 minutes. The temperature and pressure were automatically controlled using the temperature and pressure monitoring devices. Synthesis was carried out by interaction of zirconium oxychloride and sodium silicate solutions when maintaining pH of the medium was ~ 7.0. The concentrations of the initial $ZrOCl_2$ and $Na_2O{\cdot}SiO_2$ aqueous solutions were 0.5 mol/ l. The amounts of the initial reagents were calculated according to the following reaction:

$$ZrOCl_2 + Na_2O{\cdot}SiO_2 \rightarrow ZrSiO_4 + 2NaCl$$

After holding at 240°C in MW oven, the mixture was filtered. Zirconium silicate precipitate was washed with distilled water (70-80°C) to remove Na^+ and Cl^- ions. The obtained zirconium hydrosilicate was dried in SAMSUNG CE1073AR microwave oven. The heat treatment of the zirconium silicate samples was carried out in NABERTHERM LHT 08/17 electric furnace.

The compositions of the initial and final products were determined by physical and chemical analyses (weight, spectroscopic, photocalorimetrical, flame photocalorimetrical methods). X-ray diffraction analysis of the samples was performed by the powder method using URD 63 diffractometer (CuKa radiation), and differential thermal and thermogravimetric analysis at up to 1500°C using MOM derivatograph (Hungary). Diffuse reflectance of the irradiated and non-irradiated Zn_2SiO_4 samples was determined using SPECORD-M-40-UV VIS spectrophotometer. Irradiation of the samples was performed using ELU-5 linear electron accelerator at the low pressure (10^{-5} - 10^{-6} Pa) and temperature (90K) mode with 5 MeV electrons at a dose of 10^{16} electrons/cm^2.

3. Results and discussion

By HTMW processing of diatomite, perlite and quartzite, sodium silicate solutions of a predetermined composition were obtained, which after filtration and cleaning represented transparent liquids containing $Fe_2O_3 < 0.0001\%$.

Zirconium silicate. The synthesized zirconium silicate represented a white fine-grained powder. Chemical analysis showed that the composition of the final product corresponds to $ZrSiO_4 \cdot nH_2O$ zirconium silicate formula; its humidity was 48-50% and 5% after drying.

Figure 1 presents the results of thermal analysis of the dried $ZrSiO_4$ samples. Endothermic effects are due to gradual removal of water. Wide temperature range of water removal indicates that water in the synthesized hydrosilicates is located at the structurally nonequivalent positions. It is seen from the presented thermogramm that in the mode of continuously raising temperature, the sample at first loses the adsorbed water. The analysis of weight loss curves shows that the structurally bound water is removed at higher temperatures. The weight loss of samples due to removal of OH groups occurs at the temperatures below 1200°C. At higher temperatures, the exothermic effects related to solid phase transformations, crystallization of the samples is observed.

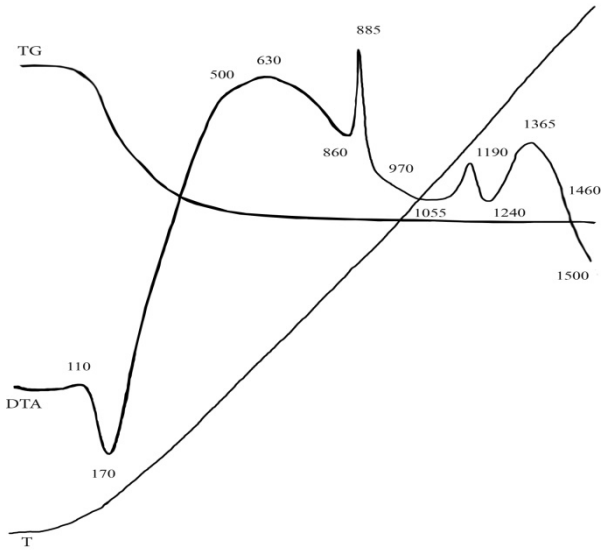

Fig.1. DTA of zirconium hydrosilicate

Analysis of X-ray patterns of the samples heat-treated at various temperatures, allows to monitor the formation of crystalline phases and phase transformations when heating the synthesized zirconium silicate [22].

The comparison of the results of DTA and X-ray phase analysis shows that the exothermic effects at 885˚C correspond to the decomposition of amorphous zirconium metasilicate with the formation of the crystalline phase of tetragonal zirconium oxide. Within the temperature interval of 1055-1240˚C, a crystalline phase of zircon with a maximum at 1190˚C is formed, as evidenced by X-ray phase analysis (Fig. 2). The state diagram of waterless ZrO_2-SiO_2 system contains (within the studied composition range) only one binary compound formed at the temperatures above 1300˚C, and its composition corresponds to $ZrSiO_4$ formula [23, 24]. The absence of new reflexes in the X-ray pictures that would confirm the formation of a new crystalline phase, allows to assume that the exothermic effect at 1240-1640˚C with a maximum at 1365˚C is related to the compaction and stabilization of the structure of the previously formed $ZrSiO_4$ and to the decrease in the internal energy of the system [24]. XRD of the products has shown that after heat treatment of the synthesized hydrosilicates at the temperatures above 1100˚C, the main crystalline phase becomes $ZrSiO_4$ which decomposes at 1650˚C with the formation of monoclinic ZrO_2 and vitreous SiO_2 [22].

Based on XRD, it is determined that because of heat treatment at 1200˚C, a crystalline phase of zircon is formed, which nuclei appear already at 240˚C during the MW synthesis (Fig. 3).

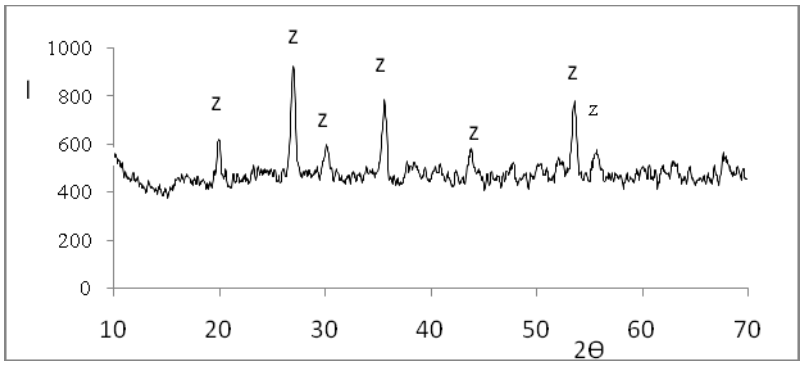

Fig. 2. X-ray diffraction pattern of $ZrSiO_4$ samples heat-treated at 1200°C (Z-zircon)

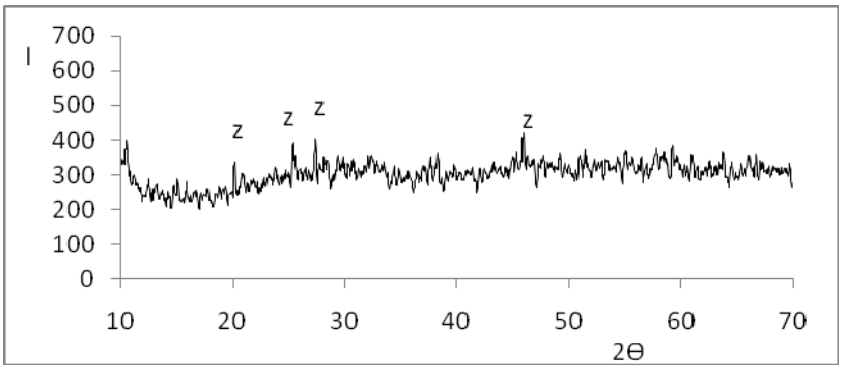

Fig. 3. X-ray diffraction pattern of $ZrSiO_4 \cdot nH_2O$, samples synthesized by MW heating at 240°C (P = 33 atm)

Diffusion reflection of $ZrSiO_4$: Diffuse reflectance of zircon ($ZrSiO_4$) samples within the region of 350-950 nm was measured. Figure 4 shows the results. The impact of radiation on the optical properties of $ZrSiO_4$ was studied. The reflection coefficients of both the zircon samples and the TRC based on them were measured. To prepare TRC, the synthesized zircon was stirred with the potassium silicate solution (mass ratio 1: 1) in a planetary agate mill with agate balls for 45-60 minutes to obtain a homogeneous mass, and the mixture was applied to a metal surface. In addition, radiation resistance of the coatings after irradiation at a dose greater than that corresponding to 10 years of exposure to cosmic radiation, was determined (5 MeV fast electrons at a dose of 10^{16} electrons/cm^2), see Figure 5.

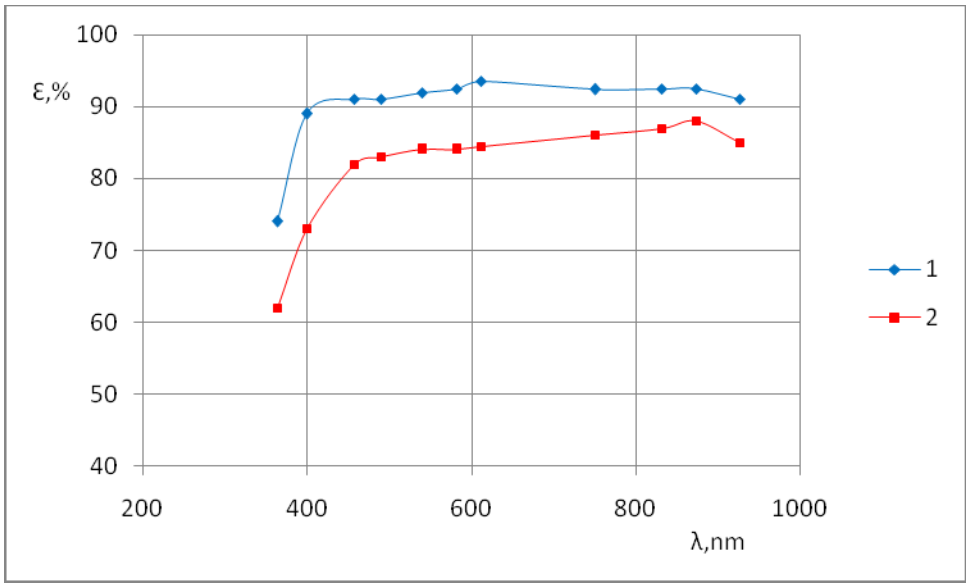

Fig. 4. Diffuse reflectance of $ZrSiO_4$ samples (MW synthesis at 240°C, heat-treatment at 1200°C, 2 hrs). 1: before irradiation, 2: after irradiation.

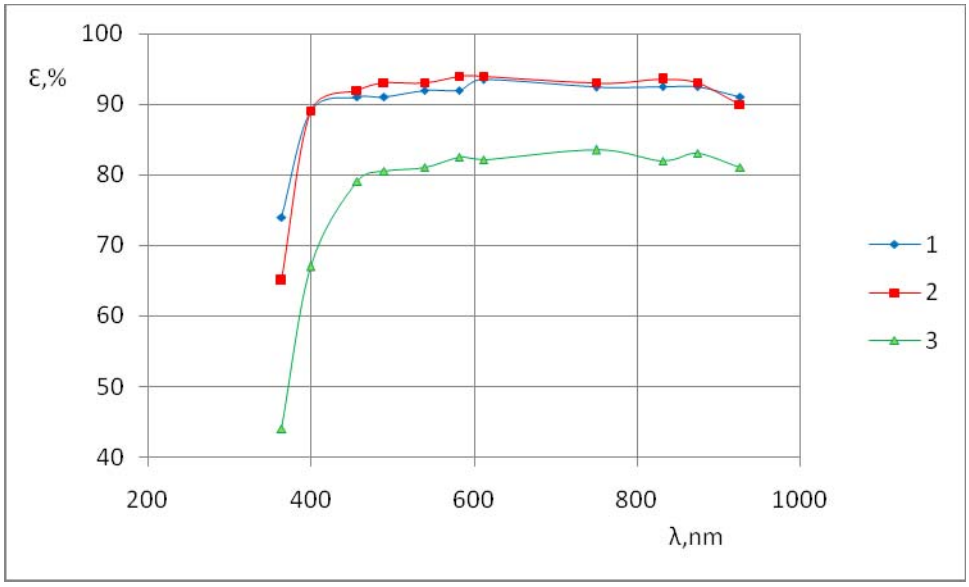

Fig. 5. Diffuse reflectance of $ZrSiO_4$ samples and TRC. 1: Zn_2SiO_4 (MW synthesis at 240°C, heat-treatment at 1200°C, 2 hrs), 2: TRP, 3: TRC after irradiation

In addition, the optical absorption spectra of the synthesized zirconium silicate were studied in the near-IR region zircon for non-irradiated and irradiated samples (Figure 6). The measurements were performed under identical conditions for all the samples within the wavelength range of 1 - 2.2 microns. Figure 6 presents the absorption spectra. It can be seen from the spectra that due to radiation, the absorption intensity of color centers responsible for 1.32 micron and 1.54 micron

bands is reduced. This fact testifies that the change in intensity is related to the formation of radiation damages in the sample structure after irradiation.

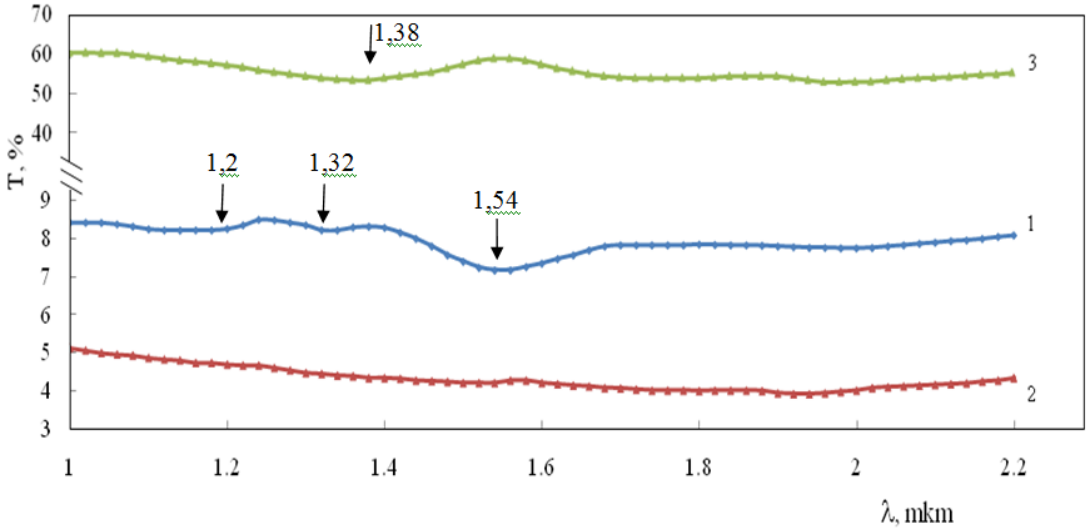

Fig.6. Optical absorption spectra of $ZrSiO_4$ heat-treated at 1200°C for 2 hours.
1: non-irradiated, 2: irradiated, 3: induced absorption induced absorption: the absorption difference between irradiated and non-irradiated samples.

Thus, the observed change in the absorption spectra of the studied samples after the heat treatment and electron irradiation, confirms the fact of changing the charge states of zircon and forming radiation structural defects in the form of point defects with various charge states.
The radiation leads to a redistribution of the intensities responsible for defect formation in the crystal lattice and, thus, promotes an increase in the materials resistance to radiation.
The diffuse reflectance of the synthesized samples of zircon and TRC on their base is above 92%. The results indicate that the TRC reflection coefficient is higher than that of the pigment, zircon. This is due to the formation of new defects in the structure and the change of the coating surface owing to the interaction between the pigment and binding agent.

After irradiation, diffuse reflectance of the samples is slightly reduced. TRC reflection factor decreases by no more than 12-15%. The decrease in the diffuse reflectance of the existing TRP after radiation is about 20%. Obviously, our zircon synthesized by MW method has a high reflection factor and is resistant to radiation.

4. Conclusions

For the first time, a systematic study of the possibility of using microwave energy to produce silicates based on silica-containing rocks is carried out. Zircon is synthesized under low temperature (1200°C). The synthesized zircon has a high reflection coefficient and high radiation resistance. Performed research reveals very high effectiveness of the microwave synthesis of zircon with high reflection coefficient and radiation resistance.

MW heating is especially effective for the reactions carried out at elevated pressures, since noncontact energy supply to the reacting liquids, high power density and short heating times lead to acceleration of the reactions. Pressure allows to generate much higher microwave power for liquids than it is possible under atmospheric pressure, since the dielectric breakdown voltage is increased and electric discharge is easily avoided. On the other hand, microwaves allow to deliver

high power to liquids under high pressure without contacting heating elements or electrodes, which can cause contamination or formation of a temperature gradient. The proposed reaction lasts for several minutes instead of hours.

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