The effect of high-temperature nanoparticle-based modification on the structure of zinc oxide powders

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Abstract. The authors have studied the effect of solid-state nanoparticle-based modification on the structure of zinc oxide powders. To carry out the experiment, seven types of nanoparticles of various oxides were applied. The modification was performed by heating the powder mixtures in the air at 650°C for 2 hours. The concentration of nanopowders was 10 wt.%, the average grain size of nanoparticles varied from 10 to 80 nm. It was established that high-temperature nanoparticle-based modification does not lead to significant structural changes and cannot affect the properties of zinc oxide powder. While modifying zinc oxide powders, an increase in photo- and radiation stability can occur primarily because of mechanisms associated with the deposition of nanoparticles on the surface of the micropowder. Due to structural changes, certain types of nanoparticles (e.g., alumina in the sample under investigation) can make a rather insignificant contribution to the stability of optical properties when exposed to radiation.

1. Introduction
Zinc oxide powders are widely applied in various fields of science and technology. One of their main applications is manufacturing of pigments for paints and coatings. Zinc oxide powders are frequently used as a base for thermal control coatings of spacecraft [1-3]. This area of application implies exposure to various types of radiation, which results in the degradation of the optical properties of zinc oxide-based coatings. To improve photo- and radiation stability and to increase the durability of coatings, their components are modified with nanoparticles of various oxide compounds [4,5]. During solid-state modification, high-temperature affects a mixture of zinc oxide powders with nanoparticles. This can lead to structural changes that might influence the properties of the powders. In this work, the authors studied the phase composition and structure of zinc oxide micropowders in the initial state and after high-temperature modification with nanoparticles of various oxides.

2. Materials and methods
The object of the study was micron-sized ZnO powder of the purity grade 14-2 (average particle size 1.3 μm). As modifiers, oxide nanopowders with various grain sizes were used, nm: Al₂O₃ - 40, CeO₂ - 20-30, MgO - 70, SiO₂ - 10-12, TiO₂ - 80, ZnO - 50, ZrO₂ - 40. The components were mixed with 10wt.% nanoparticles, dissolved in distilled water, treated with the application of ultrasonic waves, and stirred for 2 hours in a magnetic stirrer. The mixture was dried at 150°C. Then it was ground in an agate mortar and heated in the air for 2 hours at 650°C (the optimal modification temperature for ZnO powders). Heating ZnO powder at a temperature above 650°C changes its color causing yellowing and decreases its reflectance. This effect was previously studied [6], and it was found that it is caused by the
presence of a high concentration of interstitial Zn$^+$ ions in the ZnO crystal lattice. The energy level of such ions is 0.12 eV below the conduction band bottom [7]. Heating at $T \geq (650 \div 700) ^\circ C$ leads to 1) a thermal ionization of Zn$^+$ ions with the formation of Zn$^{2+}$ ions; 2) a decrease in the reflectance coefficient; 3) powder yellowing. Therefore, the temperature for solid-state modification of ZnO powders should not exceed $(650 \div 700) ^\circ C$. The rate of temperature increase was 50°C/min, and the rate of cooling was 9°C/min.

X-ray diffraction spectra were recorded using an XRD-6100 X-ray diffractometer (Shimadzu, Japan). The analysis of the obtained spectra was carried out using the QualX2 application [8].

3. Experimental results and discussion

9 samples were investigated, that is, the initial ZnO powder, the ZnO powder heated at 650°C, and the same powder modified with 7 types of different nanopowders. The results of X-ray diffraction analysis are shown in Figure 1.

All presented XRD spectra contain 8 high-intensity reflections. They belong to the main compound – ZnO with hexagonal symmetry – and coincide with the record 9004180 from the COD database [9,10]. Certain samples demonstrate low-intensity reflections, which are related to the nanopowders introduced for modification. Because the modification temperature is rather high, such solid-state modification could form solid solution compounds such as Al$_2$ZnO$_4$, ZnZrO$_2$, Zn$_2$TiO$_4$, etc. However, the authors did not observe a significant change in the intensity of the main compound peaks, nor did they record the appearance of additional peaks belonging to the new compounds.
For all the samples obtained, the parameters of the crystal lattice were calculated whose values are presented in Table 1 and in Figure 2. The table data demonstrate that the most notable changes in the lattice constants occur immediately after heating. For the modified samples, the changes are insignificant in comparison with the heated powder. The most notable changes compared to the initial zinc oxide powder can be traced in the sample modified with nanoparticles of alumina. The least significant changes occur in samples modified with nanoparticles of magnesia and zirconia. In general, the changes can be considered insignificant.

**Table 1.** Calculated lattice parameters for the initial ZnO powder, the ZnO powder heated at 650°C, and the one modified with nanoparticles of various oxide compounds at 650°C.

| Lattice parameter | Sample type | initial | 650°C | +Al₂O₃ | +CeO₂ | +MgO | +SiO₂ | +TiO₂ | +ZnO | +ZrO₂ |
|-------------------|-------------|---------|-------|--------|-------|------|-------|-------|------|-------|
| a                 |             | 3.2620  | 3.2437| 3.2407 | 3.2433| 3.251 | 3.2466| 3.2479| 3.2532| 3.2432|
|                   |             | 9       | 1     | 4      | 8     | 2    | 7     | 5     | 9    | 8     |
| b                 |             | 3.2620  | 3.2437| 3.2407 | 3.2433| 3.251 | 3.2466| 3.2479| 3.2532| 3.2432|
|                   |             | 9       | 1     | 4      | 8     | 2    | 7     | 5     | 9    | 8     |
| c                 |             | 5.2259  | 5.1960| 5.1903 | 5.1932| 5.208 | 5.2008| 5.2028| 5.2123| 5.1961|
|                   |             | 7       | 4     | 8      | 6     | 4    | 5     | 2     | 2    | 9     |

In Figure 2, the samples are arranged in the order of increasing grain sizes of nanoparticles. When the average grain size is exceeded by 40 nm, the effect of high-temperature heating on the lattice parameters decreases. Thus, when choosing a nanoparticle size of 40 nm or smaller, the density of the resulting modified powder can be slightly increased where necessary. When choosing particle sizes larger than 50 nm, the effect of high-temperature heating on the properties of the main compound can be prevented.

**Figure 2.** Calculated lattice parameters for the initial ZnO powder, the ZnO powder heated at 650°C, and the one modified with nanoparticles of various oxide compounds at 650°C.

The calculated density for the initial zinc oxide powder is 5.6118 g / cm³, which correlates with the reference value. The density obtained for the ZnO powder modified with alumina nanoparticles is 5.725
g / cm³ because of a decrease in the lattice parameters. The difference between the density values of the initial and modified powders is only 2% for the most significant changes in $a$ and $c$ parameters. This difference can insignificantly affect the path of charged particles in modified powders. As for the photo- and radiation stability of the powders under modification, it depends on the relaxation of primary defects formed during irradiation. In turn, these processes will be pre-determined by certain factors the main ones among them being the number and quality of deposited layers of nanoparticles on the surface of zinc oxide powder grains. Therefore, it is impossible to predict the effect of high-temperature nanoparticle-based modification on the photo- and radiation stability of zinc oxide powders without further studies despite the fact that this modification does not result in significant structural changes and / or in the formation of new compounds that would affect the characteristics of the samples obtained.

4. Conclusion

It can be concluded that high-temperature nanoparticle-based modification of zinc oxide powder does not lead to significant structural changes and cannot affect the properties of this powder. Thus, the resulting increase in photo- and radiation stability during modification is primarily caused by the mechanisms associated with the deposition of nanoparticles on the surface of the zinc oxide micropowder. Certain types of nanoparticles (e.g., alumina in the sample under investigation) can make a rather insignificant contribution to the stability of optical properties when exposed to radiation.

Acknowledgments

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References

[1] Heydari V and Bahreini Z 2018 J Coat Technol Res 15 223
[2] Stanley T Peters 1967 J Spacecraft Rockets 4 10 1390
[3] Wang X D, He S Y and Yang D Z 2003 Mater Chem Phys 78 1 38
[4] Mikhailov M M, Lapin A N, Sokolovskiy A N and Yuryev S A 2021 Opt Mater 115 111038
[5] Mikhailov M M, Sokolovskiy A N, Yuryev S A and Karanskiy V V 2020 Adv Space Res 66 11 2703
[6] Djurisic A B, Ng A M C and Chen X Y 2010 Prog Quant Electron 34 191
[7] Altomare A, Corriero N, Cuocci C, Falicchio A, Moliterni A and Rizzi R 2015 J Appl Cryst 48 598
[8] Vaitkus A, Merkys A and Gražulis S 2021 J Appl Cryst 54 2 661
[9] Gražulis S, Daškevič A, Merkys A, Chatelaigner D, Lutterotti L, Quirós M, Serebryanaya N R, Moeck P, Downs R T and LeBail A 2012 Nucleic Acids Res 40 420