A facile synthetic route to synthesize the nanocrystalline zirconia particles via preparing polyzirconoxane with zirconium tetraalkoxide is reported, and the luminescent properties of the so-obtained ZrO₂:Ti nanophosphors are systematically investigated in this paper. The bluish-white photoluminescence and phosphorescence originating from the recombination of electrons trapped by anion vacancies and the holes created in the valence band, and the Ti³⁺ ion substituting for Zr⁴⁺ is assumed to be the luminescent center. The long afterglow from ZrO₂:Ti is attributed to the oxygen vacancies caused by the addition of Ti³⁺ ions into ZrO₂ host.

Compared with the bulk ZrO₂:Ti, the nanosized phosphors exhibit a longer persistent time because of the increased surface traps due to the large surface-to-volume ratio in the nanoparticles. This long persistent process can be elucidated by a simple possible mechanism.

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tetragonal phase of ZrO2 are observed in the 900°C sintered sample, which disappeared when sintered at 1100°C. Raman lines sharpen with increasing heat-treatment temperature, as expected for the growth of crystallinity. Our data are in agreement with Raman spectra reported previously for ZrO2.16,17

The SEM images of the ZrO2:Ti calcined at different sintered temperatures are depicted in Fig. 3. The powder consists of well-crystallized grain with a mean size of 40 nm when sintered at 700°C. The particle size increased with increasing temperatures and reached 100 nm at 1100°C. The crystals with uniform sizes are structurally perfect. High crystallinity can be obtained at a relatively low temperature (700°C); this is important for phosphor, because high crystallinity generally means less defect and stronger luminescence.18

Photoluminescence properties.— The bluish-white light (chromaticity coordinates x = 0.22 and y = 0.33) from the nanocrystalline ZrO2:Ti sample was detected under excitation of 280 nm UV light, and the afterglow emissions were also observed after removing the excitation. The PL, PLE, and afterglow-emission spectra of nanocrystalline ZrO2:Ti sintered at 1100°C are presented in Fig. 4. The broad excitation bands centered at 280 nm are originated from electron transitions from the valence band to the localized midgap states, which are singly occupied anion vacancies.19,20

The emission spectra with the excitation at 280 nm show a broad band centered at 471 nm. The Ti3+ ions substituting for Zr4+ are assumed to be the luminescent centers. When the samples are sintered in a sealed crucible, mixture valence states of Ti (Ti4+, Ti3+) ions should coexist in the samples with different ratios. The Ti3+ ionic radius of 0.76 Å is closer to that of Zr4+ (0.79 Å) than that of Ti4+ (0.68 Å),21 so the titanium ions tend to substitute for Zr4+ in the trivalent state rather than in the tetravalent state. Two Ti3+ ions substituting a Zr4+ ion produce one oxygen vacancy for charge compensation, and these anion vacancies are effective and deep traps for electrons generated in the conduction band during excitation. A trapping center is formed between the Ti/Zr ion and an oxygen vacancy. The irradiation creates the electron–hole pairs. It is believed that the electrons are trapped by oxygen vacancies. In order to check whether the electron traps are related to the presence of the abundant oxygen vacancies in ZrO2, we also prepared the sample of ZrO2:Ti sintered in weak reducing atmosphere (CO gas is produced by krypton in high temperatures). The reduced sample presents much higher luminescence intensity than the sample sintered in air. This phenomenon confirms that the concentration of oxygen vacancies indeed affects the intensity of the sample.

In addition, the emission intensity increases as the quality of crystallinity improves, which is consistent with the order as shown in the XRD pattern in Fig. 1. It was found that at doping concentrations of 0.1% Ti3+ in nanosized ZrO2, there was maximum emission intensity.22 This quenching concentration was higher than the 0.05% doping concentration for bulk ZrO2:Ti. A higher doping concentration without concentration quenching in nanoparticles, would lead to a higher PL intensity.

The fluorescence lifetimes of nanosized ZrO2:Ti and bulk ZrO2:Ti are also measured. Figure 5 represents the lifetime-decay...
The lifetime of nanocrystal ZrO₂:Ti is defined as the luminescent lifetime. These fitting results revealed that the lifetime of the nanocrystal ZrO₂:Ti sample is about 15 min longer persistence time detected by eyes than the bulk phosphor. The observed emission from the same radiating centers, as shown in Fig. 4. Compared with the PL peak (471 nm), the afterglow emission peak of the sample shows a slight blueshift. The behavior can be explained by the perturbing effect of neighboring defects due to the change in the crystal field near the Ti³⁺ ion. The afterglow-decay curves of the nano and bulk ZrO₂:Ti samples when monitoring 471 nm emission. The nanosized phosphor has about 15 min longer persistence time detected by eyes than the bulk phosphor. The observed enhancement of afterglow intensity and lengthening of decay time in the nanosized sample can be attributed to the existence of a large amount of surface traps in the nanoparticles. The decay curves can be fitted well by the following hyperbolic curve, as shown in Fig. 6, suggesting that the afterglow process is a second-order mechanism.

\[ I(t) = I_0/(1 + Yt)^p \]

where \( I(t) \) and \( I_0 \) are the phosphorescence intensities at time \( t \) and 0, and \( Y \) is the mean decay rate. From the fit of the decay curves, the mean decay rates were estimated to be 0.03 and 0.06 s⁻¹ for the nano and bulk samples, respectively. The smaller mean decay rate in the nanoparticles is a reflection of more trapping centers.

Long-lasting phosphorescence. — Afterglow is also observed after removing the UV irradiation, and the broad phosphorescent peak is centered at around 460 nm, indicating that the emission still came from the same radiating centers, as shown in Fig. 4. Compared with the PL peak (471 nm), the afterglow emission peak of the sample shows a slight blueshift. The behavior can be explained by the perturbing effect of neighboring defects due to the change in the crystal field near the Ti³⁺ ion. The afterglow-decay curves of the nano and bulk ZrO₂:Ti samples when monitoring 471 nm emission. The nanosized phosphor has about 15 min longer persistence time detected by eyes than the bulk phosphor. The observed enhancement of afterglow intensity and lengthening of decay time in the nanosized sample can be attributed to the existence of a large amount of surface traps in the nanoparticles. The decay curves can be fitted well by the following hyperbolic curve, as shown in Fig. 6, suggesting that the afterglow process is a second-order mechanism.

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Defect (trap) properties of ZrO₂:Ti nanophosphor. — Traps play an essential role in the LLP phosphors. In the following section, we try to study the nature of the traps created under UV radiation and the influence of the traps on the origin of the afterglow of the ZrO₂:Ti nanophosphors by performing TL measurements.

Figure 7 represents the TL spectra of 0.1 mol % Ti-doped ZrO₂ and pure ZrO₂ samples. As is shown in Fig. 7, it is safe to say that there are at least two types of traps present in the ZrO₂ phosphor for at least two peaks in the TL spectra, located at 34 and 130°C, respectively. The TL peak position remains consistent except for higher TL intensity in 0.1 mol % Ti-doped ZrO₂. That is to say, the chemical nature of defects related to these two peaks is not changed. Introduction of Ti in the ZrO₂ lattice leads to an increase of the TL intensity. (One must bear in mind that in fact all “pure” ZrO₂ contains traces of Ti.)

As mentioned above, the same TL position indicates the presence of the same defects in both samples. When Zr⁴⁺ is replaced by Ti³⁺, negative defects and V⁴⁺ positive defects were created. These suitable defects (traps) make an important contribution to the LLP phenomenon in this phosphor. Based on the LLP mechanism discussed above, the LLP phenomenon is assumed to be due to the thermistimulated holes and electrons which are trapped by defect.
centers. The VO positive defects may serve as the electron traps, and the TiO negative defects may be the hole-trapping centers. We conclude that the peak at 34°C is caused by VO", and the peak located at 130°C originates from the TiO defects because the sample sintered in reduction atmosphere showed higher 34°C TL peak intensity.

To confirm whether oxygen vacancies play a role in trapping, ZrO2:Ti codoped with additional Mg2+ phosphor is synthesized and its TL properties are investigated. The oxygen-ion vacancies can be generated via doping other metal cations within the ZrO2 lattice as a result of charge balance. As shown in Fig. 8, the introduction of excess 0.5 mol % Mg2+ ions greatly enhances the 34°C TL peak, indicating that additional Mg2+ ions may induce some intrinsic defects, such as oxygen vacancies, resulting in a higher TL peak intensity at 34°C.

Conclusion

In summary, nanocrystalline ZrO2:Ti that displays a long after-glow has been successfully synthesized by a facile reaction using PZO as starting material. The Ti3+ ions substituting for Zr4+ are assumed to be the luminescent centers of the 471 nm PL. Longer phosphorescence is observed compared with bulk ZrO2:Ti after removing the UV irradiation. This can be interpreted by relatively increased surface traps in the nanosized particles due to the high surface-to-volume ratio.

Acknowledgments

The authors gratefully thank the financial support of One Hundred Talents Project from the Chinese Academy of Sciences and the National Natural Science Foundation of China (grant no. 20571071 and 10574128).

Chinese Academy of Sciences assisted in meeting the publication costs of this article.

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