

PHOTOLUMINESCENCE OF HAFNIUM AND ZIRCONIUM GERMANATES

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Nowadays, oxide-based ceramics and glasses are widely used as scintillators, illuminators, lenses and laser media. Among oxide-based materials, zirconium and hafnium dioxides are of special interest because of their high hardness, transparency, chemical and high thermal stability. These properties make ZrO_2 and HfO_2 the excellent optical materials, for example, as scintillators with high stopping power for gammas and X-rays, waveguides, thermal luminescence emitters, and solar absorbers. Scheelite-like germanates HfGeO_4 and ZrGeO_4 were practically not considered in terms of their optical properties. Nevertheless, there is a rationale for consideration these compounds as the promising high-temperature phosphors. Furthermore, these compounds can be obtained in a thin-film state, which can expand the field of their application. It is widely known that the many functional properties of oxide-based materials including luminescence properties are directly connected with morphology, texture, and phase composition that, in its turn, depend on the method and parameters of preparation.

This work was focused on the comparative study of the ultraviolet/photoluminescence (UV/PL) conversion properties of hafnium and zirconium germanates derived by different chemical routes.

Hafnium and zirconium germanates (HfGeO_4 and ZrGeO_4) were synthesized by two different techniques, namely, so-called ceramic route and co-precipitation ones. Ceramic route involved thorough mixing of the corresponding quantities of ZrO_2 (or HfO_2) and germanium oxides with the agate mortar following by the heat-treatment of mixture at 1200°C (1300°C) in air. Additionally, preliminary mechanical treatment of ZrO_2 (or HfO_2) and GeO_2 powders was applied (planetary ball mill) at a constant speed with time ranging between 5 and 60 min following by the heating to 1200°C or 1300°C in air.

The second approach involved dissolution of the appropriate amounts of ZrOCl_2 or HfOCl_2 in de-ionized water to form 0.1 M solutions. GeO_2 was mixed with de-ionized water with following drop-by-drop addition of concentrated ammonia under stirring to obtain 0.1 M solution. The appropriate volumes of as-prepared solutions were mixed under continuous stirring to obtain MGeO_4 precursors. The obtained precipitates were dried in air and was heated on air/in vacuum at 1000°C for 2 h.

The corrected photoluminescence spectra (PL) of the initial oxides and products were recorded on Fluorog 3 (Horiba Jobin Yvon) spectrometer equipped with a cooled PC177CE-010 photon registration module with photomultiplier P2658. Samples were irradiated with monochrome ultraviolet source with a wavelength of 250 nm. The analysis of spectra was performed with Fityk 0.9.08 software. Voigt profiles were applied to the peak-fitted determination.

For the first time the photoluminescence spectra of hafnium and zirconium germanates optical spectra were obtained (Fig. 1). The alleged defects are revealed, the main differences in the nature of the sample irradiation depending on the conditions for their production are shown.

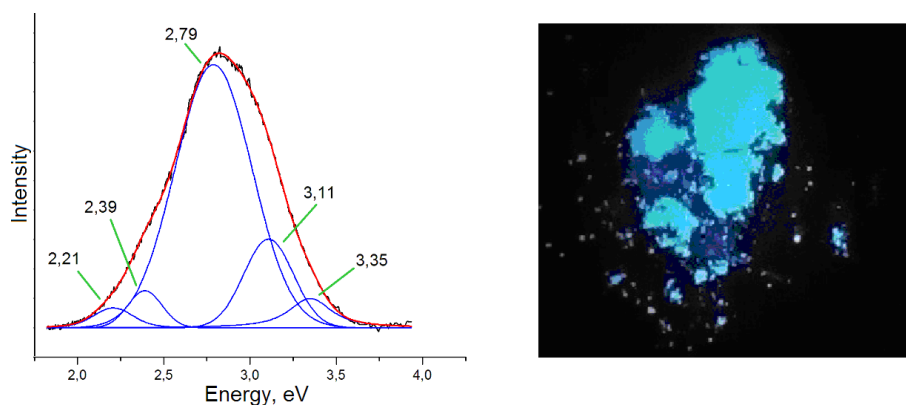


Fig. 1. The photoluminescence spectra of ZrGeO_4 obtained by ceramic route at 1300°C (left) and its optical image upon excitation with 5.17 eV illumination (right)