The effect of TiO_2 crystalline form on microstructure and optical features of Zn_2TiO_4 doped with Mn

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Zinc orthotitanate, Zn_2TiO_4, is a wide band gap semiconductor, which is thermally stable, safe for human health and can be easily synthesized by a conventional solid-state reaction of ZnO and TiO_2 at relatively low temperatures. Doping of Zn_2TiO_4 with transition metal ions is used for managing its structural, optical and electrical properties. In particular, doping of Zn_2TiO_4 with Mn produces its coloration and causes photoluminescence (PL) in the red spectral range due to optical transitions of Mn^{4+} ion substituted Ti^{4+} cites making this material attractive as the low-cost red phosphor. The form of used TiO_2 is known to affect crystal phase formation in ZnO-TiO_2 system. In this work, the influence of rutile and anatase crystalline form of TiO_2 on microstructure and optical properties of Zn_2TiO_4 doped with Mn have been investigated by X ray diffraction (XRD), Scanning electron microscopy (SEM), as well as by optical and electron paramagnetic resonance (EPR) methods.

The Zn_2TiO_4:Mn samples were produced by sintering in the air at 900–1200°C for 3h of the pellets formed by pressing the ZnO and TiO_2 (either rutile or anatase) powder mixture with addition of an aqueous solution of $MnSO_4$.

XRD patterns of the ceramics revealed formation of cubic Zn_2TiO_4 (~98 wt%) and hexagonal ZnO (~2 wt%) crystal phases. The samples produced using rutile had random grain orientations, whereas those made of anatase showed preferred grain orientation in dependence on sintering temperature. The SEM images demonstrated grain growth with the sintering temperature, which was stronger in the phosphors produced using anatase. The Zn_2TiO_4:Mn ceramics showed absorption band in 400-600 nm spectral range and Mn^{4+}-related red PL. The absorption intensity increased with the increase of annealing temperature being larger for the ceramics produced using anatase, while the intensity of Mn^{4+}-related PL was about twice larger in the ceramics produced using rutile. The PL intensity decreased in several times as the annealing temperature increased up to 1100 ºC for the samples produced using anatase and 1200 ºC for those produced using rutile. In these samples, larger residual deformations (dislocation density) were evaluated from XRD data. The PL showed decay time of about 150 μs, which decreased slightly when the an nealing temperature increased. In the EPR profiles, the signals ascribed to Mn^{2+} in the Zn_2TiO_4 and ZnO crystal phases were identified. The intensity of EPR signal due to Mn^{2+} in the Zn_2TiO_4 was larger in the ceramics produced using anatase and increased with the increase of annealing temperature.

It is proposed that Mn incorporates into Zn_2TiO_4 as both Mn^{4+} and Mn^{2+}, but at lower temperatures (≤1100°C) as Mn^{4+} and at higher temperatures as Mn^{2+} in the main. The change of Mn charge state correlates with evaluated microstructure variations in ceramics. The rutile is supposed to be more preferred to generate Mn^{4+} centers in the Zn_2TiO_4.