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Fabrication of potassium salts doped zinc tungstates prepared with nitrate, sulfate, chloride and their photoluminescence properties

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ABSTRACT

In this work, we found the significant improvement of photoluminescence of zinc tungstate doped with potassium salts. The samples were prepared by solid-state reaction using ZnO, WO_3, KNO_3, K_2SO_4, and KCl as starting powders. The powders were mixed with the molar ratios of ZnO: WO_3: potassium salts = 1: 1: x and sintered at 800 °C for 3 h in air. The emission peak of photoluminescence excited at 275 nm was observed at 465 nm. With increasing potassium salts content, the intensity increased reached its maximum at x = 0.02 and decreased. The tendency of the luminescence intensity for KCl doping was almost the same as KNO_3 doping, whereas, for K_2SO_4 doping, the tendency of the decrease was less steep than other doping. The order of each maximum intensity was KNO_3 > K_2SO_4 > KCl. It was considered that K replacing Zn in the crystal lattice enhanced the intrinsic luminescence in the blue wavelength region. Moreover, different anions doping had the different effect of the enhancement of the luminescence.

1. Introduction

Zinc tungstate ($ZnWO_4$) has been studied as promising materials for the photonic field such as scintillators [1,2], optical fiber [3], laser host [4], photocatalyst [5], and optical recording [6]. It is the wolframite lattice compounds having the intrinsic blue emission wavelength between 460 and 490 nm [7]. The studies of optical properties including light yield, emission wavelength, and the afterglow of $ZnWO_4$ have been reported [1,8]. In scintillation applications, zinc tungstate crystals are very interesting and important detectors in fundamental physics: they are used in such principal investigations as searches for neutrinoless double beta decay [9,10] and searches for dark matter [11] where the anisotropic properties of $ZnWO_4$ crystals are used. The advantages of $ZnWO_4$ are less hygroscopic, less toxic and cheaper than other materials such as CsI(Tl) and $CdWO_4$, a widely used scintillation crystals [7]. Single-crystal $ZnWO_4$ is usually grown by Czochralski technique [12], whereas its powder is synthesized by solid state reaction method [13].

Doping of $ZnWO_4$ can improve the photoluminescence activities. Many materials have been doped and investigated for their photoluminescence activities. Wen et al. [14] has reported that $ZnWO_4$ crystals doped with Eu^{3+} show a significant energy transfer from WO_4^{2-} structure to Eu^{3+} ions. Dafinova et al. [15] has reported that the addition of SO_4^{2-}, F^-, and Cl^- ions from ammonium salts to the matrix leads to a substantial increase in the intensity of the self-activated blue emission in $ZnWO_4$. Kraus et al. [16] reported that Ca-doped $ZnWO_4$ could increase the scintillation light yield of samples. For alkali metal doping, it was reported that co-doping of Li_2CO_3, Sm, and B improved the extrinsic photoluminescence properties. And for Sodium salts such as NaCl, Na_2SO_4 doping, the destruction of the WO_6 structures occurs, which decreases the emission.

However, there have not been many studies of other alkali metals. In this research, we investigated the doping material which improved photoluminescence activities of $ZnWO_4$ and found that potassium salts affected to improve the intrinsic photoluminescence of zinc tungstate.

2. Experimental

$ZnWO_4$ powders were synthesized by solid-state reaction technique using starting powders of ZnO (99.99%, Furuuchi Chemical Co., Ltd.),

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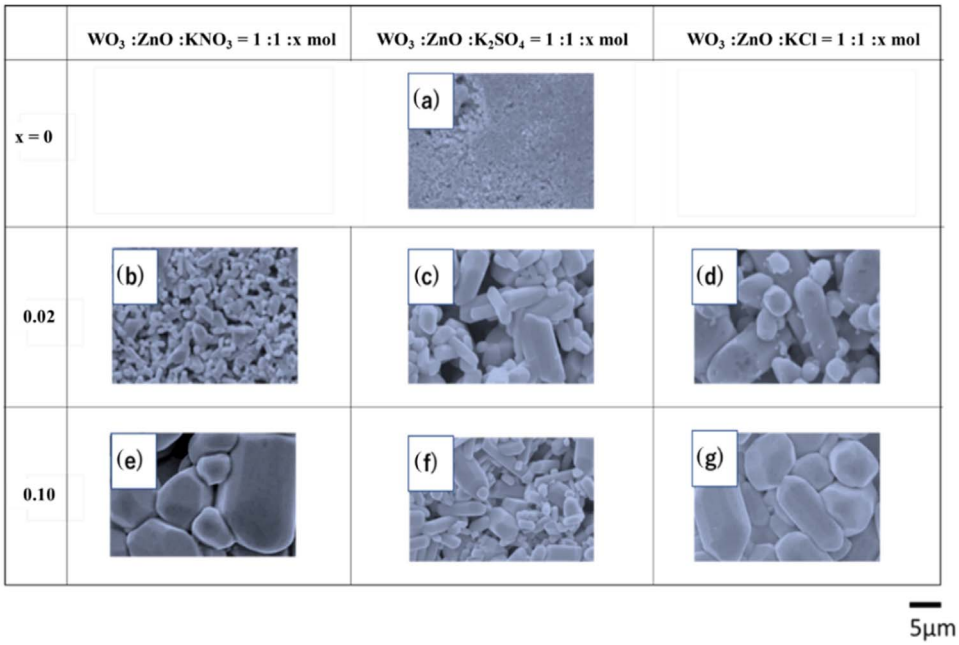

Fig. 1. SEM of samples obtained under different doping conditions: (a) Undoped $ZnWO_4$; (b) doping with 0.02 mol KNO_3; (c) doping with 0.02 mol K_2SO_4; (d) doping with 0.02 mol KCl; (e) doping with 0.10 mol KNO_3; (f) doping with 0.10 mol K_2SO_4; (g) doping with 0.10 mol KCl, respectively.

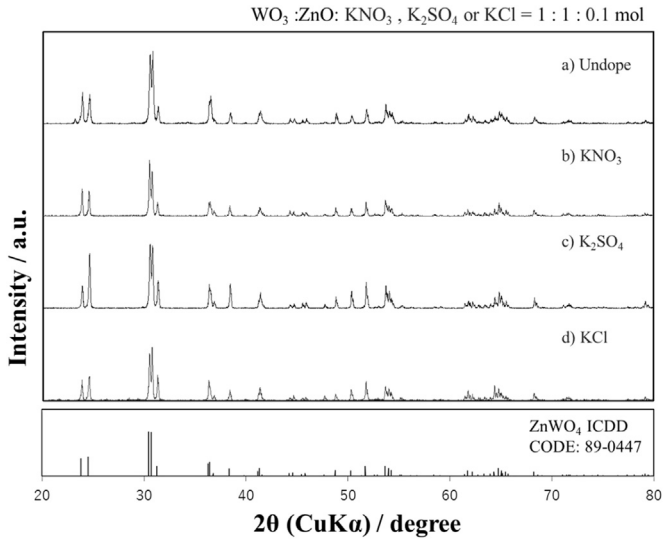

Fig. 2. XRD patterns of samples obtained under different doping conditions: (a) undoped; (b) doped with KNO_3; (c) doped with K_2SO_4; (d) doped with KCl, respectively.

WO_3 (99.99%, Kojundo Chemical Lab.), KNO_3, K_2SO_4 and KCl (> 99.00%, Junsei Chemical Co., Ltd.). The powders were mixed with the molar ratios of ZnO: WO_3: potassium salts = 1: 1: x, where x is from 0 to 0.1. At first, the powder mixtures were ground in distilled water to dissolve salts for 20 min. After that, powders were mixed in 2-propanol for 2 h. After drying, the mixtures were pressed into pellet (diameter 10 mm) under 100 MPa. The pellets were sintered at 800 °C for 3 h in air and ground into powders. The powders were compacted in 2 × 2 cm glass holders for testing. The crystalline phase was measured by X-ray diffractometer (XRD, RIGAKU Multiflex) using Cu Kα radiation (Kα = 1.5418 Å). The morphologies of the samples were observed using scanning electron microscope (SEM, JEOL JSM-5510). The luminescence of the samples was measured around 5–7 times using fluorescence spectrophotometer (Hitachi F-7000). After that, the normalized emission intensity of each sample and experimental error was calculated.

3. Results and discussion

Fig. 1 shows the SEM micrographs of undoped and doped samples after sintering at 800 °C. Undoped sample showed the formation of small crystals. The grain size of the doped potassium salt increased with increasing salt contents. The grain size of samples depended on the type of anions. The melting points of KNO_3, K_2SO_4, KCl are 334, 1069 and 770 °C, respectively. In general, the grain growth is accelerated by the presence of liquid phase. For KNO_3 doping, some portion of KNO_3 would vaporize during sintering because melting point is lower than sintering temperature. Therefore, the grain size of 0.02 mol KNO_3 doping was smaller than K_2SO_4 and KCl doping. But for 0.1 mol KNO_3 doping, the large amount of dopant was supposed to increase the grain size of samples rapidly. The melting point of KCl is slightly lower than the sintering temperature, and the melting point of K_2SO_4 is higher than the sintering temperature. As a result, the crystallite size of KCl was larger than K_2SO_4.

The XRD patterns for all sample powders prepared with different potassium salt are shown in Fig. 2. All the peaks in the patterns were indexed on the basis of the crystallographic data of $ZnWO_4$ (ICDD code 89-0774). In the XRD pattern of the $ZnWO_4$ powders, the peak was slightly shifted in 2θ depending on salt doping. Their lattice constants and unit cell volume were determined using XRD peaks and Bragg's law and shown in Fig. 3. From the data, with increasing content of potassium salts, the lattice constant a decreased whereas b and c increased. Jenkins, et al. [17] reported that the ionic radii of Zn^{2+}, W^{6+}, K^+, N^{3-}, S^{2-}, Cl^- and O^{2-} were 0.074, 0.042, 0.138, 0.171, 0.184, 0.184 and 0.140 nm, respectively. It was considered that the potassium ion, which is the cation, could be highly possible to substitute for Zn^{2+} of $ZnWO_4$ rather than W^{6+} because the ionic radius for K^+ are larger than Zn^{2+} and much larger than W^{6+}, moreover and there is a huge charge