Photoluminescence properties of a hollandite compound K$_2$Ga$_2$Sn$_6$O$_{16}$

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Abstract

A hollandite compound K$_2$Ga$_2$Sn$_6$O$_{16}$ (KGSO) has photocatalytic activity, although little is known about the optical properties of the compound. To design a higher quality photocatalyst, studies on its optical properties are required. In this study, a KGSO powder and a SnO$_2$ (rutile structure) powder were prepared by the sol–gel method. Photoluminescence (PL) and PL excitation spectra of the two powders were measured. To our knowledge, this is the first report of PL from a hollandite compound. It was found that the band gap energy of the KGSO powder is 3.6 eV, the value of which is identical with that of the band gap energy of SnO$_2$. This was confirmed by the result of the photoacoustic spectrum of the KGSO. The shapes of the PL excitation spectra of the two powders agreed. Moreover, the PL spectra of the two powders have one broad band around 600 nm. From these results, one can conclude that the mechanism of PL of KGSO is the same as that of SnO$_2$. In air with ethanol, however, the time-course of the KGSO powder was different from that of the SnO$_2$ powder. By adding ethanol vapor in air, the PL intensity of the SnO$_2$ powder increased, whereas the PL intensity of the KGSO powder remained unchanged. By comparing the PL time-courses of the two powders with those of a commercial rutile TiO$_2$ powder, it was concluded that the photodesorption of O$_2$ in air with ethanol occurs on the SnO$_2$ powder, not on the KGSO powder. This was supported by the results of the inorganic carbon concentrations on the two powders. These results indicate that the behavior of O$_2$ on the KGSO surface during a photocatalytic oxidation is different from that on the SnO$_2$ surface during the oxidation.

Keywords: Hollandite; Tin oxide; Photoluminescence; Band gap energy; Oxygen adsorption

1. Introduction

The hollandite compounds are represented by the general chemical formula A$_x$M$_y$N$_{8-2y}$O$_{16}$ ($x < 3$, $y < 3$), where A = alkali or alkaline earth ions, M = divalent or trivalent cations, and N = tetravalent cations [1]. The hollandite structure consists of a framework of edge- and corner-sharing octahedra forming tunnels of a square cross section along the c-axis. The alkali or alkaline earth ions are situated in these tunnels [2]. Our group has recently found that a hollandite compound K$_2$Ga$_2$Sn$_6$O$_{16}$ (KGSO) has photocatalytic activity for oxidative decompositions of organic chloride compounds [3,4]. To design a higher quality photocatalyst, studies on its optical properties are required. One of the properties is photoluminescence (PL) because it is reported that there is a relation between the PL intensity of a photocatalyst and its photocatalytic activity [5,6]. Anpo and Che [7] have reviewed applications of PL techniques in relation to photocatalysis. PL spectroscopy is a useful method for characterization of semiconductor oxides because their PL properties reflect their crystal structures, band gap energies, and surface conditions [8–10]. So far, however, there are no experimental data on the PL properties of hollandite compounds. In this study, we have measured the PL and the time-courses of the PL intensities of the SnO$_2$ powder and the KGSO powder and have measured the amounts of inorganic carbons on the two powders. From these results, we have determined the band gap energies of the two powders and have considered the mechanism of PL of KGSO and the surface conditions on the two powders.
2. Experimental

The KGSO powder and the SnO$_2$ powder were prepared by the sol–gel method. For KGSO, metal alkoxides such as potassium $n$-propanoxide, gallium $n$-butoxide, and tin $t$-butoxide were used as the starting materials. These materials were mixed at the stoichiometric molar ratio of KGSO in methoxyethanol and hydrolyzed with a mixed solution of water and ethanol. For SnO$_2$, tin $t$-butoxide was used as the starting material, which was mixed in methoxyethanol and hydrolyzed with a mixed solution of water and ethanol. The wet gels were dried to remove the solvent and calcined at 973 K for 3 h after being ground. The products were identified by X-ray diffraction (XRD). A commercial rutile TiO$_2$ powder (99.99%, Aldrich) was used as received.

The PL excitation and emission spectra of the sample powders were obtained using a Spex Fluorolog-3 spectrofluorometer with front-face sample orientation. In the measurements of the excitation spectra, the emission intensities were detected at 550 nm. In the measurements of the emission spectra, the excitation wavelength was 260 nm. All spectra were measured in air at room temperature. The time-courses of the PL intensities of the sample powders were obtained using a Hitachi F-4500 spectrofluorometer at room temperature. Before the time-course measurement in air with ethanol, the sample powder was exposed to ethanol vapor in the dark for 0.5 h. The band gap energies of the KGSO powder and the SnO$_2$ powder were estimated by assuming that the PL intensity of the excitation spectrum is proportional to the photoabsorption coefficient and that the inter-band transitions of the two powders are the direct-type and by using the graph of the square of PL intensity times photon energy against photon energy [11].

To confirm the value of the band gap energy, the photoacoustic spectrum of the sample powder was measured, because photoacoustic spectroscopy provides the optical absorption characteristics rather than the diffuse reflectance spectroscopy [11]. A brief experimental procedure of the photoacoustic spectroscopy is as follows: a light beam from a 300 W xenon arc lamp was modulated at a frequency of 77 Hz. The light absorbed by the sample is converted into heat, which results in a pressure fluctuation. The pressure fluctuation was detected with a sensitive microphone and the electrical signal from the sound was amplified. The detailed procedure is described elsewhere [11].

The concentrations of inorganic carbon on the KGSO powder and on the SnO$_2$ powder were measured with a Shimadzu TOC-5000A. The supernatant fraction of an aqueous suspension of the sample powder after centrifuging was used in the measurement of the concentration. Water used was purified to a resistivity of $> 18 \, \text{M} \Omega \, \text{cm}$ by filtration through a Milli-Q reagent water system.

3. Results and discussion

Fig. 1 shows XRD patterns of the SnO$_2$ powder and the KGSO powder. Fig. 1(a) and (b) indicate that the SnO$_2$ powder has a single rutile phase and the KGSO powder has a single hollandite phase.

Fig. 2 shows the excitation spectra of the SnO$_2$ powder and the KGSO powder. The shapes of the two spectra agree. From the results of these excitation spectra, Fig. 3 was plotted to estimate the band gap energies of the two powders. Their band gap energies were estimated to be 3.6 eV. This value is identical with that of the band gap of SnO$_2$ reported previously [12]. Moreover, from the photoacoustic spectrum, the band gap energy of the KGSO powder was estimated to be 3.5 eV (Fig. 4). This value agrees very closely with the above values estimated from the PL excitation spectra. Hence, we found that the band gap energy of the KGSO powder (3.6 eV) can be determined by the PL method and that the value of the band gap energy is the same as that of SnO$_2$. 

![Fig. 1. XRD patterns of the rutile SnO$_2$ powder (a) and the hollandite KGSO powder (b).](image)
Fig. 5 shows the PL spectra of the KGSO powder and the SnO\textsubscript{2} powder. The two spectra have one broad band around 600 nm. Both the bands agree with the band of the SnO\textsubscript{2} spectrum reported previously [13,14]. From this result and the results in the previous paragraph, one can conclude that the mechanism of PL of KGSO is the same as that of SnO\textsubscript{2}. The emission bands shown in Fig. 5 would be attributed to surface defect states at 1.4 eV above the top of the valence band [14–16]. That is, the transitions of the photo-induced electrons from the conduction band to the surface defect states would be responsible for the PL spectra. The maximal intensity of the KGSO spectrum is about four times that of the SnO\textsubscript{2} spectrum. From this result and the above conclusion, it seems that the difference between the PL intensities of the two powders is caused by the difference between their surface conditions, not by the difference between their structures. It is reported that some adsorbates on TiO\textsubscript{2} powder significantly alter the PL intensity of the TiO\textsubscript{2} powder; adsorbed O\textsubscript{2} on TiO\textsubscript{2} powder
decreases the PL intensity, while adsorbed alcohol on TiO$_2$ powder increases the PL intensity [8,9]. As shown in Fig. 6, the PL intensity of the rutile TiO$_2$ powder in air increased by adding the ethanol vapor. This result is explained by the band bending model [8,9,17,18] as follows: adsorbed O$_2$ on the rutile TiO$_2$ powder is photo-desorbed by the illumination for the PL measurement. Instead, ethanol adsorbs dissociatively and inhibits O$_2$ from re-adsorbing on the powder. This substitution decreases the surface band bending, which enhances the recombination efficiency of the photo-generated electrons and holes, resulting in an increase in the PL. The same phenomenon is expected to occur on the rutile SnO$_2$ powder.

By adding ethanol vapor in air, the PL intensity of the SnO$_2$ powder increased (Fig. 7), whereas the PL intensity of the KGSO powder remained unchanged (Fig. 8). The increase in PL intensity of the SnO$_2$ powder can be explained in the same way as the increase in PL intensity of the TiO$_2$ powder was explained in the previous paragraph. This explanation is consistent with the fact that the photodesorption of O$_2$ occurs on the SnO$_2$ surface [19]. In contrast, the time-courses of the PL intensities of the KGSO powder (Fig. 8) suggest that no photodesorption of O$_2$ occurred on the KGSO surface or that there was no adsorbed O$_2$ on the KGSO surface.

One of the differences between the surface conditions of the KGSO power and the SnO$_2$ powder is that there is potassium on the KGSO surface, not on the SnO$_2$ surface. Hence, the KGSO surface is expected to be covered by carbonates such as K$_2$CO$_3$. Actually, there was approximately 4 wt% of inorganic carbon converted to CO$_3$ on the KGSO powder. This result suggests that the KGSO surface is covered by carbonates, which prevent O$_2$ from adsorbing on the KGSO surface. On the other hand, there was approximately 0.1 wt% of inorganic carbon converted to CO$_3$ on the SnO$_2$ powder. This concentration was equivalent to that in the background. These results are consistent with the consideration on the time-courses of the PL intensities in the previous paragraph. These results indicate that the behavior of O$_2$ on the KGSO surface during a photocatalytic oxidation is different from that on the SnO$_2$ surface during the oxidation; the adsorbed O$_2$ on the SnO$_2$ surface would be active, whereas that on the KGSO surface would be inactive or the amount of the adsorbed O$_2$ on the KGSO surface would be much less than that on the SnO$_2$ surface.

4. Conclusions

We have measured the PL spectra of the SnO$_2$ powder and the KGSO powder and found that the band gap energy of the KGSO powder is 3.6 eV, the value of which is identical with that of the band gap energy of SnO$_2$. The shapes of the excitation spectra of the two powders agreed. Moreover, the emission spectra of the two powders have one broad band around 600 nm. From these results, one can conclude that the mechanism of PL
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