Near-Infrared Raman Spectroscopy as a Unique Tool for Characterization of Visible Luminescent ZnS Phosphor

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近赤外ラマン分光法による可視発光硫化亜鉛系蛍光体の評価

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Near-infrared (NIR) Raman spectroscopy has shown its unique advantages for characterization of ZnS:Cu, Al materials, emitting a strong luminescence in the visible region. We demonstrate that, because of a rapid decrease of luminescence in the NIR region, Raman spectra with 752.5-nm excitation are free from the visible luminescence, which usually masks Raman signals with visible excitations. By comparing the spectra of ZnS:Cu, Al samples with different luminescence efficiencies, we also find that crystal imperfections, including coexistence of hexagonal domains, can lead to a reduction of luminescence properties.

[Received November 28, 2001; Accepted March 25, 2002]

Key-words: Near-infrared Raman spectroscopy, Visible luminescent phosphor, Zinc sulfide, Phase characterization, Luminescence property

1. Introduction

Zinc sulfide (ZnS) is a very important material for visible luminescent devices, since this compound can yield excellent luminescence in almost the whole visible range with suitable dopants.¹⁾ ZnS doped with Cu and Al (ZnS:Cu,Al)²⁾ has introduced as an attractive green phosphor for field emission displays, and its luminescence properties have generated large research efforts.^{2)–4)}

Luminescence properties of ZnS were found closely correlated with its structure and crystallinity.⁴⁾ However, the real structure of ZnS is complicated due to a variety of polymorphic modifications. Although the principal structure of ZnS:Cu,Al is cubic zincblende, crystals encountered in practice are usually non-ideal and contain defects or imperfections, including vacancies, stacking faults, surface inhomogeneities.^{5),6)} Consequently, there is a great interest in these microstructures, the understanding of which can help improve the material and device quality.

Raman scattering is an important tool for characterization of materials properties as it provides useful information on impurity, grain size, crystal symmetry. However, one factor that limits the application of Raman spectroscopy in the study of these visible luminescent materials is interference with their luminescence.⁷⁾ When excited with standard visible lasers such as 488- and 514.5-nm lines, a strong luminescence often obscures Raman signals. Thus, the need for the use of near-infrared (NIR) excitation arises because the smaller photon energy of NIR lasers may not be excited to the electronic state from which the luminescence occurs.

In this study we utilize NIR Raman spectroscopy for characterization of visible luminescent ZnS:Cu, Al phosphor. We show that the selection of the NIR laser allows identification of phonon features of ZnS:Cu, Al. Moreover, by comparing spectra of samples with different luminescence efficiencies, we found that even a small amount of crystal imperfection, including coexistence of hexagonal domains, can lead to a reduction of luminescence intensity.

2. Materials and methods

ZnS:Cu,Al samples were prepared by a chemical precipitation method. Cu concentration was ~150 ppm (mol/mol ZnS) with the Cu/Al ratio fixed at 1. The crystal structure was examined by X-ray diffraction (XRD). Cathode luminescence spectra of these samples exhibited a strong green luminescence with a maximum at ~530 nm [as is also seen from Raman spectra in Fig. 1(a)]. Raman data were obtained from four samples with different luminescence efficiencies. The luminescence efficiencies are 110, 103, 46 and 39 for samples A, B, C and D, respectively. The details of the preparation and characterization are described elsewhere.⁸⁾

Raman spectra were measured at room temperature and excited in a backscattering geometry. The excitation source was an Ar/Kr mixed gas laser operating at 752.5 nm with a power of ~3 mW. For comparison, we also acquired several spectra using 488-, 514.5- and 647.1-nm lines from the same laser. The collection system (Atago Bussan R64000-COE) consisted of a single-spectrograph equipped with a holographic notch filter, microprobe optics, and a liquid-nitrogen-cooled CCD detector. The frequency resolution was set to 2–3 cm⁻¹.

3. Results and discussion

Figure 1 shows the Raman spectra of a ZnS:Cu,Al sample (Sample A) measured with 488-, 514.5-, 647.1- and 752.5-nm excitations. Figures 1(a) and 1(b) are plotted as a function of wavelength and Stokes-Raman shift, respectively. Each figure displays raw spectra with no offset; any background is therefore due to luminescence of the sample. With the 488- and 514.5-nm excitations the spectra contain a strong luminescence as a dominant feature, while phonon features are not clear. With the 647.1- and 752.5-nm excitations, on the contrary, we observed clear phonon features. This is because these excitations shift the wavelengths of Raman scattering away from the luminescence peak to higher wavelength position [as it is illustrated in Fig. 1(a)].

Fig. 1. Raman spectra of ZnS:Cu, Al sample (Sample A) measured with 488-, 514.5-, 647.1- and 752.5-nm excitations. The spectra are plotted as a function of wavelength (a) and Stokes-Raman shift (b). Each figure displays raw spectra with no offset.

In Fig. 1(b) the observed features are in accordance with that of cubic zincblende, and the central Raman mode at 350 cm^{-1} is attributed to the LO mode.⁹⁾ Additional weak features at $\sim 220\text{ cm}^{-1}$ probably arise from two-phonon process.⁹⁾ We note, however, that with the 647.1-nm excitation, the luminescence background still contributes to spectral features. This is in contrast to the spectrum with the 752.5-nm excitation where the luminescence background is no longer evident. As is also seen from Fig. 2(a), the spectrum with the 752.5-nm excitation shows the weak features at $400\text{--}500\text{ cm}^{-1}$ which are attributed to local modes associated with Al-related complexes as was argued by the IR studies.¹⁰⁾ These observations clearly indicate that the selection of the NIR laser allows identification of the phonon features of ZnS:Cu, Al.

We should now remind that Raman spectrum with the NIR excitation is much weaker compared to those using visible or red excitations. This is due to the fact that the Raman intensity is proportional to the fourth power of the laser frequency as well as the sensitivity of the CCD detector is much lower in the NIR region. Nevertheless, in the present case, the requirement of suppressing luminescence clearly outweighs these drawbacks of the NIR Raman spectroscopy. We thus suggest that the NIR Raman spectroscopy provides a satisfactory tool for characterization of ZnS:Cu, Al free from its luminescence.

Fig. 2. NIR Raman spectra of ZnS:Cu, Al samples with different luminescence efficiencies. The inset presents the luminescence efficiency as a function of the LO mode intensity. The dashed line is a guide for eye.

We now turn to the applicability of the NIR Raman spectroscopy for characterization of ZnS:Cu, Al. Figure 2 compares the results of four samples with different luminescence efficiencies. Prior to Raman measurements, the structural properties were characterized by XRD, and all the samples exhibited the cubic zincblende structure. Even in the low luminescence samples (Samples C and D), we did not find any traces of the hexagonal wurtzite structure [e.g., strong diffraction lines of the wurtzite (100), (002) and (101) peaks (at 27.00° , 28.63° and 30.63°) were not visible next to the zincblende (111) peak at 28.50°]. Although the slight broadening of the zincblende (111) peak possibly indicates a faint suggestion of the wurtzite (100), (002) and (101) peaks, it is rather difficult to identify the phases present in the low luminescence samples solely by the XRD technique.

In contrast to the XRD data, the Raman spectra of the low luminescence samples are clearly distinct from the high luminescence ones. The spectra for high luminescence samples (Samples A and B) clearly reveal one strong LO mode at 350 cm^{-1} , reflecting high crystalline phase with cubic symmetry. Although XRD measurements showed the low luminescence sample (Samples C and D) to be predominantly of cubic symmetry, the observed phonon features become much broad and less intense, most notably for the LO mode at 340 cm^{-1} . More interestingly, there seems to be a clear trend between the LO mode intensity and the luminescence efficiency. As shown in Fig. 2 inset the luminescence efficiency almost linearly scales with the LO mode intensity. This trend indicates a close relationship between the local structure and the luminescence efficiency. Another interesting features of the low luminescence samples are the appearance of 300 cm^{-1} mode as well as the evolution of two broad features at $100\text{--}220$ and $350\text{--}400\text{ cm}^{-1}$. These

observed changes for the low luminescence samples imply that some kind of disordering is present in the crystal structure.

The most plausible interpretation of the observed changes for the low luminescence samples is the local symmetry breaking due to defect structures associated with intergrowths of hexagonal domains. An indication comes from the appearance of the E_2 mode at 300 cm^{-1} , which has no counterpart in the cubic phase and is uniquely related to the hexagonal phase. We notice that the atomic arrangements between the zincblende and wurtzite structures are quite similar, and that the only difference in coordination is the substitution of anti-prism in zincblende for a trigonal prism in wurtzite.⁵⁾ Then, the zincblende and wurtzite structures can be viewed as the stacking interleaved closed-packed double layers of Zn and S atoms. In such a picture, hexagonal forms would coexist as a stacking fault in the cubic zincblende structure. Another possibility of the defect structures may come from surface vacancies, as was argued in many nanometer-sized semiconductors.⁵⁾ In any case, these defect structures should alter local symmetry and thereby reduce the intensity of the LO mode. Hence, the evolution of two broad features at $100\text{--}220$ and $350\text{--}400\text{ cm}^{-1}$ can be understood in terms of an increase of disorder-induced scattering.

Here we stress the characteristics and sensitivity of Raman spectroscopy. In contrast to XRD with a coherence length of ≥ 20 unit cells, Raman spectroscopy is sensitive to a short-range order (of the order of approximately ≥ 5 unit cells),¹¹⁾ which allows the detection of polymorphic modifications such as those in the present case. Moreover, small particles and nanometer-sized powder give rise to line broadening of the XRD, which further deteriorates the ability of the XRD technique to detect such polymorphic modifications. From Fig. 2, however, such defect structures may have strong influence on luminescence properties in the actual devices. Since the visible luminescence of ZnS:Cu,Al is originated from transitions involving localized in-gap states, we expect that these defect structures can participate in impurity states and thereby act as luminescence killers. We believe that in conjunction with NIR lasers, Raman spectroscopy can offer a convenient and sensitive means for

characterizing these crystal imperfections of ZnS:Cu, Al.

4. Conclusion

We utilized NIR Raman spectroscopy for characterization of visible luminescent ZnS:Cu, Al phosphor. We showed that the selection of the NIR laser allows identification of phonon features of ZnS:Cu,Al. Moreover, by comparing spectra of samples with different luminescence efficiencies, we found that even a small amount of crystal imperfection, including coexistence of hexagonal domains, can lead to a reduction of luminescence properties.

Acknowledgements The authors thank Ryouzuke Shimizu and Kazutoshi Kainuma (Photon Design Inc.) for the technical supports of the Resonant Raman spectrometer. M.O. acknowledges the financial support of JSPS (No. 11200) and Kanagawa Academy of Science and Technology (No. 0011004). This work is supported by Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science, and Technology of Japan.

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