

Excitonic luminescence properties from new layered mixed-anion compounds with natural superlattice

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INTRODUCTION

Compounds which exhibit excitonic emission are important for optical applications such as new type of phosphor materials and very fast scintillators. Artificial superlattice was developed to achieve large oscillator strength for higher quantum confinement effect to enhance exciton binding energy and stable excitonic luminescence at room temperature. Such low-dimensional structures are usually fabricated using thin-film technology, however, it is difficult to fabricate structures of micrometer size or larger using these techniques. On the other hand, another class of wide band-gap semiconductor with such superlattice can be achieved by the stacking of different kinds of layers. In some layered compounds, excitonic luminescence is observed because their layered structure works as a quantum well, and increases the exciton binding energy through the quantum confinement effect. Such luminescence was reported in several chalcogenide oxide such as LaCuSO₃[1]. Previously we have investigated optical properties of other compounds, Sr₃Sc₂Cu₂Se₂O₅[2] and Sr₂ScCuSO₃[3]. These compounds composed by semiconducting CuS layer and perovskite-related SrScO layers. In both samples sharp emission lines are observed near the band edge. The merit of these group of compounds are their chemical and structural flexibilities. In previous report, we have investigated luminescence properties of Ba₃RE₂Ag₂Se₂O₅ (RE = Y, Lu)[4]. These compounds also shows excitonic luminescence with wavelength region from 400 ~ 600 nm. The emission wavelength of the compounds are different from those of CuS compounds because of narrower band gap of AgSe compounds.

Last year we succeeded to synthesize their relative compounds Sr₃Sc₂Cu₂Se₂O₅ and Sr₂ScCuSeO₃. These oxyselenides have similar crystal structure with those of oxysulfides, while the constituent element in the semiconducting layer is different. The band gap of these compounds are smaller than those of oxysulfides.

In this year, we investigated detailed luminescence properties of these newly found oxyselenides. Luminescence properties, decay kinetics of the excitonic

luminescence and their temperature dependence was investigated.

EXPERIMENTAL

Sintered bulk samples with nominal compositions of Sr₂ScCuSeO₃ and Sr₃Sc₂Cu₂Se₂O₅ were synthesized by solid state reactions starting from stoichiometric amounts of Cu, Se, Sc₂O₃, Sr, and SrO. As the starting reagents are moisture sensitive, the synthesis was carried out in a glove box under argon atmosphere. Powder mixtures were pelletized, sealed in evacuated quartz ampoules, and heated at 650–900 °C for 24–100 hours, followed by slow cooling to room temperature. Phase identification was performed using powder X-ray diffraction (XRD) with a Rigaku Ultima-IV. The XRD intensity data were collected in the 2 θ range of 5–80 degree in steps of 0.02 degree using Cu-Kα radiation. Silicon powder was used as an internal standard. Diffuse reflectivity measurements were performed using a Shimadzu UV-2600 spectrophotometer equipped with an ISR-2600Plus integration sphere. The luminescence were measured with fiber spectrometer (StellarNet Inc., Blue-Wave). The luminescence spectra and decay times for each sample were measured using a spectrograph (groove density 600 gr/mm) with a focal length coupled to a streak camera unit (Hamamatsu C1587) and a charge-coupled device camera. The samples were excited by the third-harmonic generation (THG) of a Ti:sapphire laser operating at 290 nm. The luminescence spectra were collected at temperatures between 6.5 and 300 K.

RESULTS AND DISCUSSIONS

Figure 1 shows the emission-decay time maps measured by a streak camera. The sharp luminescence with short decay time of several tens ps were observed at 3.07 eV (405 nm) in both materials at 6.5 K. The decay time, τ_1 and τ_2 , were evaluated by following equation.

$$I(t) = A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_2}\right)$$

where A_1 and A_2 are constant, τ_1 and τ_2 are decay constant ($\tau_1 < \tau_2$). The decay constant of τ_1 was ~20 ps and τ_2 was over 100 ps. Because A_1 was over 10 times

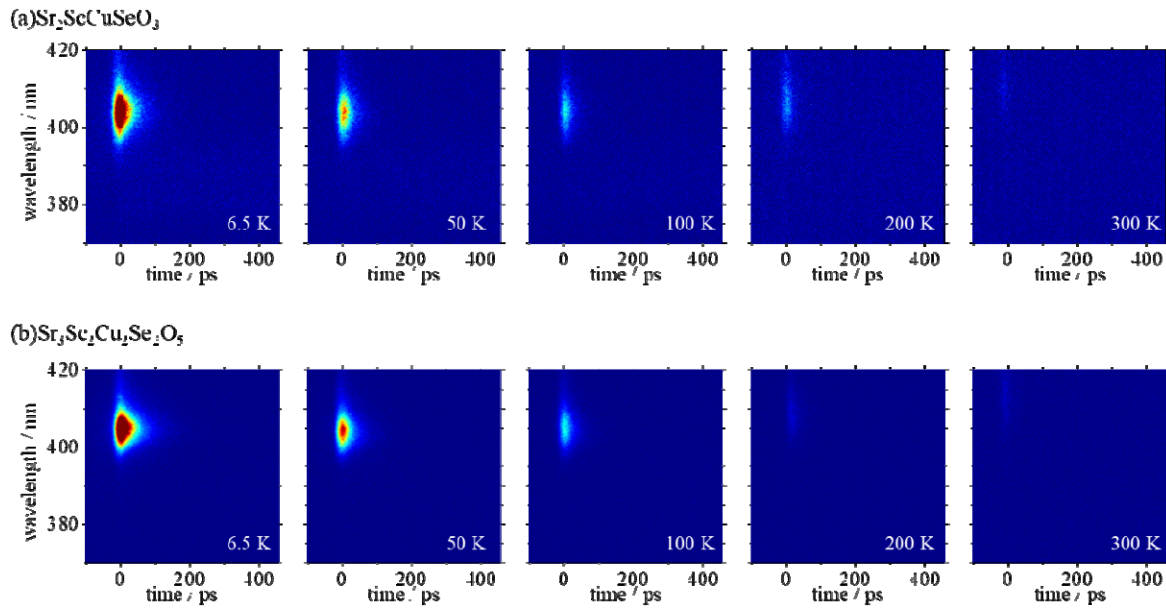


Fig. 1 The emission decay time maps at 370 nm—420 nm of (a) $\text{Sr}_2\text{ScCuSeO}_3$ and (b) $\text{Sr}_3\text{Sc}_2\text{Cu}_2\text{Se}_2\text{O}_5$.

larger than A_2 at all temperature, τ_1 is the main components of the luminescence. The decay constants, τ_1 , were evaluated as 25–30 ps at 6.5 K. The decay constants of both compounds were decreased with increasing the temperature, however, due to the time resolution of instrument the constants above 50 K were not possible to obtain. These decay properties are similar to that of $\text{Sr}_2\text{ScCuSO}_3$ and $\text{Sr}_3\text{Sc}_2\text{Cu}_2\text{S}_2\text{O}_5$. These very fast decay have advantage to several applications such as fast scintillators.

Figure 2 shows the temperature dependence of the peak energy of $\text{Sr}_2\text{ScCuSeO}_3$ and $\text{Sr}_3\text{Sc}_2\text{Cu}_2\text{Se}_2\text{O}_5$. The peak energy of luminescence were shifted to lower energy with increasing the temperature as well as similar materials[10][14]. The peak energy at room temperature were 3.01 eV for $\text{Sr}_2\text{ScCuSeO}_3$ and 2.98 eV for $\text{Sr}_3\text{Sc}_2\text{Cu}_2\text{Se}_2\text{O}_5$. These emission energy were corresponding to the absorption peak at 3.1 eV in figure 3. The peak energy of $\text{Sr}_2\text{ScCuSeO}_3$ shows also smaller temperature dependence than that of $\text{Sr}_3\text{Sc}_2\text{Cu}_2\text{Se}_2\text{O}_5$.

The optical properties of the compounds in this study were almost similar to those of $\text{Sr}_2\text{ScCuSO}_3$ and $\text{Sr}_3\text{Sc}_2\text{Cu}_2\text{S}_2\text{O}_5$ except for emission energy. According to these results, the fast excitonic luminescence can be controlled its emission energy by selecting composition of the material. This makes us flexible to design an application like scintillator.

CONCLUSIONS

New layered mixed-anion compounds, $\text{Sr}_2\text{ScCuSeO}_3$ and $\text{Sr}_3\text{Sc}_2\text{Cu}_2\text{Se}_2\text{O}_5$, were successfully synthesized and their luminescence properties were investigated. The excitonic luminescence were observed at even room temperature. The decay time of luminescence were 30 ps at 4.5 K and decreased with increasing temperature. The $\text{Sr}_2\text{ScCuSeO}_3$, which have longer distance between semiconductor-layer than $\text{Sr}_3\text{Sc}_2\text{Cu}_2\text{Se}_2\text{O}_5$, shows smaller temperature dependence. These fast excitonic luminescence can be controlled its

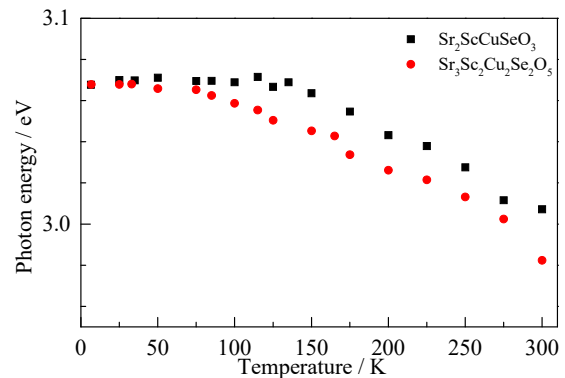


Figure 2 The temperature dependence of the peak energy of the emission.

emission energy by selecting composition of the material.

ACKNOWLEDGEMENT(S)

This work was supported by many collaborators. We thank to J. Ueda and S. Tanabe at Kyoto University for their assistance and fruitful discussions. This work was supported by JSPS Grant-in-Aid for Scientific Research on Innovative Areas “Mixed Anion” (Grant Number JP16H6439).

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