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 phophor 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 LaCuSO[1]. Previously we have investigated optical properties of other compounds, $Sr_3Sc_2Cu_2S_2O_5$[2] and $Sr_2ScCuSO_3$[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 $Ba_3RE_2Ag_2Se_2O_5$(*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 characterized luminescence properties of new compounds $Sr_3Sc_2Cu_2Se_2O_5$ and $Sr_2ScCuSeO_3$.[5] 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 explored this system, and found new material $Sr_3Sc_2Ag_2Se_2O_5$ its structural parameters are refined by Rietveld analysis.

EXPERIMENTAL

Sintered bulk samples with nominal compositions of $Sr_3Sc_2Ag_2Se_2O_5$ were synthesized by solid state reactions starting from stoichiometric amounts of Cu, Se, Sc_2O_3, 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 800-900 °C for 24 hours. Phase identification was performed using powder X-ray diffraction (XRD) with a Rigaku Ultima-IV. The XRD intensity data were collected in the 2 h 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.

RESULTS AND DISCUSSIONS

Bulk samples of a new compound $Sr_3Sc_2Ag_2Se_2O_5$ were successfully synthesized by solid-state reaction

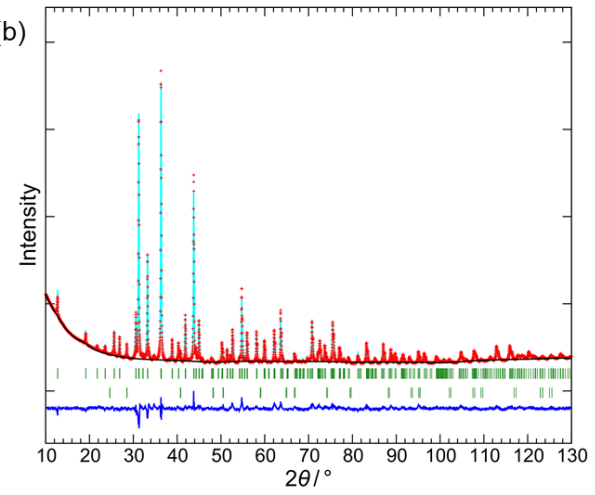

Figure 1. Results of the Rietveld analysis of $Sr_3Sc_2Ag_2Se_2O_5$. Red points represent the experimental patterns, cyan line the calculated patterns, and blue line the difference of these patterns.

method. Because the structural parameters of $Sr_3Sc_2Ag_2Se_2O_5$ have not yet been reported, their crystal structures were refined by Rietveld analysis.

We carried out the Rietveld analysis with a constant occupancy of 1.0 and atomic displacement parameter of 0.0127(6). Fig.1 and Table 1 show the results of the Rietveld analysis of $Sr_3Sc_2Ag_2Se_2O_5$. The compound is almost single phase except for small amounts of SrSe impurities, and their space group is *I4/mmm* isostructural to $Sr_3Sc_2Cu_2S_2O_5$[17]. The lattice parameters are a = 4.13402(5) Å and c = 27.8080(5) Å for $Sr_3Sc_2Ag_2Se_2O_5$, which are slightly larger than those of $Sr_3Sc_2Cu_2S_2O_5$.

The length of Ag-Se in $Sr_3Sc_2Ag_2Se_2O_5$ is 2.76 Å, while Cu-S and Cu-Se lengths in $Sr_3Sc_2Cu_2S_2O_5$ and $Sr_3Sc_2Cu_2Se_2O_5$ are 2.49 Å and 2.52 Å, respectively. The Ag-Se length is longer due to the larger ionic radii of Ag and Se.

Table 1. Refined parameters of $Sr_3Sc_2Ag_2Se_2O_5$

atom	*Occ.*	*x*	*y*	*z*	*U*
Sc	1.0	0	0	0.07124(12)	0.0127
Ag	1.0	0.5	0	0.25	0.0127
Sr1	1.0	0.5	0.5	0	0.0127
Sr2	1.0	0.5	0.5	0.13298(8)	0.0127
Se	1.0	0	0	0.18431(7)	0.0127
O1	1.0	0.5	0	0.0793(2)	0.0127
O2	1.0	0	0	0	0.0127

a = 4.13402(5) Å, c = 27.8080(5) Å

R_{wp} = 3.127 %, R_p = 2.235 %, S = 0.4592, R_B = 9.716%,

R_F = 7.509%

Fig.2 shows the Tauc plots of the $Sr_3Sc_2Ag_2Se_2O_5$ together with related compounds $Sr_3Sc_2Cu_2S_2O_5$ and $Sr_3Sc_2Cu_2Se_2O_5$ calculated from the diffuse reflectance spectra at room temperature. The band gap energy was estimated by using Kubelka-Munk equation.

By linear extrapolation through fitting the absorption edge as shown by the dashed lines, the band gap values were determined to be 3.3 eV, 2.9 eV, and 2.4 eV for $Sr_3Sc_2Cu_2S_2O_5$, $Sr_3Sc_2Cu_2Se_2O_5$, and $Sr_3Sc_2Ag_2Se_2O_5$, respectively. The order of the band gap values for these compounds is consistent with that of the expected band gap energies from DFT calculations, although the absolute values are different. These band gap energies are significantly larger than those of bulk semiconductors such as Cu_2S (1.21 eV)[18], Cu_2Se (1.1 eV)[19], and Ag_2Se (~ 0.2 eV)[20], showing evidence of the quantum confinement effect in low-dimensional structures.

CONCLUSIONS

New layered mixed-anion compound $Sr_3Sc_2Cu_2Ag_2O_5$ was successfully synthesized and the crystal structure was refined by Rietveld analysis. Band gap of the compound is narrower compared to related compounds $Sr_3Sc_2Cu_2S_2O_5$, $Sr_3Sc_2Cu_2Se_2O_5$ due to Ag substitution.

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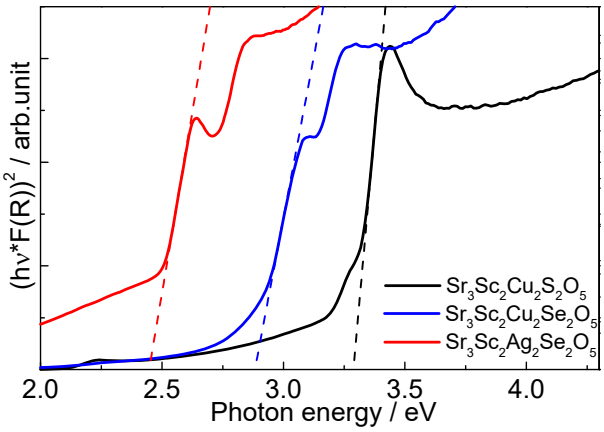

Figure 2. Tauc plots of the $Sr_3Sc_2Ag_2Se_2O_5$ together with related compounds $Sr_3Sc_2Cu_2S_2O_5$, $Sr_3Sc_2Cu_2Se_2O_5$ at room temperature. The dashed lines show the extrapolation of the linear portion at band edges.