Search for new novel ultraviolet luminescent materials based on layered mixed anion compounds

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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 LaCuSO[1], Sr3Sc2Cu2S2O5[2], and Sr2ScCuSO3[3]. Previously we have investigated optical properties of these compounds, and 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. Owing to the discovery of iron-based superconductors[4], layered compounds composed by the stacking of anti-fluorite FeAs layers and perovskite-like oxide layers have been extensively developed[5,6]. In previous report, we have investigated luminescence properties of Ba3RE2Ag2Se2O5(RE = Y, Lu)[7]. The compound has stacking structure with semiconducting Ag2Se2 and perovskite-like Ba3RE2O5 layers. In Kubelka–Munk converted diffuse reflectivity, two sharp peaks are observed near band edge indicating excitonic absorption of these compounds. In this year we have extended search of compounds to CuTe system, and found new layered material Ba3Lu2Cu2Te2O5.

EXPERIMENTAL PROCEDURE

Sintered bulk samples with nominal compositions of Ba3Lu2Cu2Te2O5 was synthesized by solid state reactions starting from stoichiometric amounts of Cu(3N), Te(2N), Lu2O3(3N), Ba(2N), and BaO(2N). 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°C for 24h followed by slow cooling.

Phase identification was performed using powder X-ray diffraction (XRD) with RIGAKU Ultima-IV. The XRD intensity data were collected in the 2θ range of 5–80° in steps of 0.02° using Cu-Kα radiation. Silicon powder was used as an internal standard. Diffuse reflectivity measurements were performed by Shimadzu UV-2600 spectrophotometer equipped with ISR-2600Plus. The luminescence spectra and decay times for each sample were measured using a spectrograph (groove density 600 gr/mm) with a 25-cm 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 4.3 and 295 K.

RESULTS AND DISCUSSIONS

Figure 1 shows the crystal structure and powder XRD pattern of a polycrystalline Ba3Lu2Cu2Te2O5. Single
phase was obtained by the reaction at 800°C for 24 h. The space group of Ba$_3$Lu$_2$Cu$_2$Te$_2$O$_5$ is $I4/mmm$ and its lattice constants are $a = 4.38$ Å and $c = 28.69$ Å, respectively. The lattice constants are slightly longer than those of Ba$_3$Lu$_2$Ag$_2$Se$_2$O$_5$.

The optical band-gap ($E_g$) at room temperature was estimated from the measurement of diffuse reflectance ($R$) of the polycrystalline samples of Ba$_3$Lu$_2$Cu$_2$Te$_2$O$_5$(Fig.2) together with Sr$_2$ScCuSO$_3$ and Ba$_3$Lu$_2$Ag$_2$Se$_2$O$_5$. In contrast to the compounds which we developed previously, Ba$_3$Lu$_2$Cu$_2$Te$_2$O$_5$ did not show absorption peak at measured range. One possible reason is the band gap of this compound is smaller than 1.5 eV, and another possibility is electronic structure of the compound is different with those of Sr$_2$ScCuSO$_3$ and Ba$_3$Lu$_2$Ag$_2$Se$_2$O$_5$, which are similar to type-I artificial superlattice.

We have also measured luminescence spectra of Ba$_3$Lu$_2$Cu$_2$Te$_2$O$_5$. From the temperature range from 5 K to 300 K, we couldn’t observe clear luminescence except for weak broad peaks around 410 and 480 nm at 5 K. This result also indicate two possibilities; their electronic structure is different with similar compounds or the bandgap is shorter than measured range.

In summary, we have developed new compound Ba$_3$Lu$_2$Cu$_2$Te$_2$O$_5$, and investigated its optical properties. In contrast to previous compounds which we developed, sharp absorption peak at the band edge nor luminescence peak was not observed. It is needed to measure its optical properties with shorter wavelength region.

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REFERENCE(S)