

Title

Single crystal growth of LaCuOS by flux method

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Abstract

Preparation of single crystals of LaCuOS, that is a transparent p-type semiconductor exhibiting violet-light emission, was demonstrated by flux method using NaCl+KCl(1:1) as flux. The crystals were grown in an alumina tube inserted in an evacuated silica glass tube using the starting materials of La₂O₂S and Cu₂S, as well as the flux and a small amount of K₂S that reduces the coloration of crystals. Transparent colorless laminate crystals were obtained under the optimized crystal growth conditions; growth temperature of 850 °C, growth time of 72h and cooling rate of 10 °C /h. The size of the largest colorless crystal was 3.0×2.8×0.049 mm³. The crystal showed transmission as high as 60 % and p-type electrical conductivity of 7.1×10⁻⁴ Scm⁻¹ at room temperature.

Keywords:

single crystal, flux method, oxysulfide, LaCuOS, transparent semiconductor

Introduction

The layered oxysulfide LaCuOS is known as a wide gap (3.1eV) transparent p-type semiconductor that shows band gap emission at room temperature.[1] The crystal structure of LaCuOS was composed of a $(\text{La}_2\text{O}_2)^{2+}$ oxide layer and $(\text{Cu}_2\text{S}_2)^{2-}$ sulfide layer stacked alternately along the c-axis.[2] This particular layered structure is considered to bring about the unique electrical and optical properties.[3] Several materials that have similar crystal structure are known and they consist of some combination of two compound layers; for instance, oxychalcogenides, fluorochalcogenides, oxypnictides, fluoropnictides.[4-7] These materials also show various properties due to the layered structure and recently superconductivity was found in some oxypnictides.[8,9] Since LaCuOS is a prototype of these layered materials, preparation of its single crystal is important to understand the unique electrical and optical properties in detail.

In the previous study, synthesis of LaCuOS single crystals was attempted by chemical transport reaction using the starting material of LaCuOS powder and the vapor of iodine.[10] The size of the largest crystal was $100 \times 100 \times 5 \mu\text{m}^3$, therefore, the obtained crystals are too small to handle in some conventional analyses such as optical transmission and electrical conductivity. In this study, preparation of larger LaCuOS single crystals was undertaken by the flux method. Because mm-sized crystals were successfully obtained, the choice of the starting materials and several growth conditions are reported along with preliminary characterization of the crystals.

Experimental

Single crystals of LaCuOS were grown in an evacuated silica glass tube by the flux method. Two types of starting materials were used in the crystal growth; one is La_2O_3 , La_2S_3 and Cu_2S and the other is $\text{La}_2\text{O}_2\text{S}$ and Cu_2S . The starting materials, mixture of NaCl+KCl (1:1) as flux and K_2S as a dopant were loaded into an alumina tube, and then the alumina tube was sealed in a silica glass tube under vacuum. Fig.1 shows a schematic configuration for the growth of

LaCuOS single crystals. The evacuate silica tube was heated in a furnace and kept at high temperatures for appropriate time, and then gradually cooled down in the furnace. To obtain large crystals, several parameters on the crystal growth were varied; growth temperature from 750 to 900 °C, growth time for 6 to 120 h, cooling rate from 5 to 100 °C/h and K₂S concentration from 0.0 to 1.0 mol%. The x-ray diffraction (XRD) patterns of the obtained crystals were measured in order to identify their crystalline phase. To evaluate the obtained crystals, their optical transmission spectra were measured by a UV-VIS-NIR spectrometer and the electrical conductivities were measured at room temperature by the four probe method.

Results and discussion

Single crystal growth of LaCuOS by the flux method was attempted using two types of starting materials; one is La₂O₃, La₂S₃ and Cu₂S and the other is La₂O₂S and Cu₂S. In the case of the former starting materials, the obtained sample was a white powder when the starting materials and the flux were heated at 800 °C for 48h. The XRD measurements revealed that the sample was a polycrystalline powder of LaCuOS single phase, but its powder pattern was rather oriented in the (00 l) direction. From the observation by an optical microscope, the powder sample was composed of very small laminate crystals with the average size of 120 μm. Although further experiments were carried out by changing the growth time from 6 to 72 h, the average size of the crystals was 220 μm at most. On the other hand, in the case of the latter starting materials, several transparent laminate crystals were recognized in the sample obtained under the same growth condition without a microscope and their average size was 1.2×1.1×0.022 mm³. Obviously larger crystals were obtained when La₂O₂S and Cu₂S were used as starting materials. This clear difference in the crystal size is probably attributed to the crystal structure of La₂O₂S because La₂O₂S has the layered crystal structure that is very similar to the layered crystal structure of LaCuOS. As a result, La₂O₂S and Cu₂S were fixed as starting materials and several parameters on the crystal growth were changed as shown in Table 1 to obtain larger crystals.

In a series of sample #1~4 in Table 1, crystal growth temperature was varied from 750 to 900 °C, while growth time at each growth temperature and cooling rate were fixed to 72h and 100 °C/h, respectively. As the growth temperature rose from 750 °C to 900 °C, the average size of LaCuOS increased and became the largest at 900 °C. However, in the case of 900 °C, the silica glass tube was frequently broken up and the largest crystals were hardly reproducible. Therefore, the growth temperature was fixed at 850 °C to obtain the crystals reproducibly. At 850 °C, the average size of the single crystals was $1.9 \times 1.8 \times 0.028 \text{ mm}^3$ and their color was brownish. This coloration was supposed to originate from lattice defects such as sulfur vacancies because sulfur is easy to evaporate at high temperatures. To prevent sulfur deficiency, K₂S addition into the flux was attempted in a series of sample #3 and #5~7 changing the K₂S concentration from 0.0 mol% to 1.0 mol% under the crystal growth temperature of 850 °C and cooling rate of 100 °C/h. The average size of the crystals increased with an increase of the K₂S concentration up to 0.3 mol%, and then the size decreased gradually. Although the largest single crystals of LaCuOS were obtained at the K₂S concentration of 0.3 mol%, the brownish coloration of the obtained crystals slightly deepened. On the other hand, fairly colorless crystals were grown when the K₂S concentration was 1.0 mol%, although the average size of the crystals decreased.

In a series of sample #5 and #7~13, crystal growth time was changed from 48 to 120h, while growth temperature and cooling rate were fixed at 850 °C and 100 °C/h, respectively. The average size of the crystals increased with an increase of growth time up to 96h in the K₂S concentration of both 0.3 mol% and 1.0 mol%. However, the crystals grown for 96 h showed more brownish coloration than those grown for 72 h. When the cooling rate was varied from 5 °C/h to 100 °C/h in a series of sample #5, #7 and #14~17, growth temperature was fixed at 850 °C and growth time was set to 72h under K₂S concentration of 0.3 or 1.0 mol%. The average size of the crystals increased with an increase of cooling rate up to 10 °C/h, but much slower cooling rate at 100 °C/h did not enlarge the crystal size or decreased it. Longer growth time and slower cooling rate did not simply result in larger crystal sizes, probably because of the

deviation of chemical composition in the evacuated silica tubes. Since the silica glass tubes became clouded after the crystal growth, the chemical reaction of flux and/or sulfur with inside surfaces of silica glass tubes caused the deviation of net chemical composition in the tubes and hindered the growth of crystals.

As a consequence, large single crystals were obtained under the growth conditions of growth temperature 850 °C, growth time 96h, cooling rate 10 °C /h and K₂S concentration 0.3mol%. On the other hand, colorless crystals were grown under the growth conditions of growth temperature 850 °C, growth time 72h, cooling rate 10 °C /h and K₂S concentration 1.0 mol%. Fig.2 shows the photographs of a typical large single crystal (a) and colorless single crystal (b) grown under these growth conditions. The sizes of the single crystals were 4.1×2.7×0.036 mm³ (a) and 3.0×2.8×0.049 mm³ (b).

The XRD pattern of typical LaCuOS single crystal is shown in Fig. 3 along with a simulated powder pattern. In the XRD measurements, one surface of the laminate crystal was stuck to a sample folder using glue and incident x-ray was scanned on the opposite surface. Observed diffraction peaks were all indexed to (00*l*) planes, confirming that the sample is a single crystal and the direction of the c-axis is vertical to the surface of the laminate crystal.

The optical transmission spectra of LaCuOS single crystals are shown in Fig. 4 as well as that of polycrystalline thin film[11]. The approximate thicknesses of the single crystals were 40 μm and that of the thin film was 150 nm. The transmission of the large single crystal grown in the flux with K₂S concentration 0.3 mol% was 40%, whereas that of the colorless crystal grown in the flux with K₂S concentration 1.0 mol% was as high as 60%. Although the transmission of the crystals is slightly low in comparison to the films, the crystals showed transparency in the visible and near infrared region and fundamental absorption edges at approximately 400 nm, which is consistent with the film. The electrical conductivity of the colorless single crystal was 7.1×10⁻⁴ Scm⁻¹ at room temperature. This value is approximately one order of magnitude larger than that of a polycrystalline sample. It is, therefore, supposed that even colorless single crystals

include some defects such as Cu deficiency. Because the Seebeck coefficient of the crystal was positive, the conduction type was confirmed to be p-type.

Conclusion

The single crystals of LaCuOS were grown by the flux method using NaCl+KCl(1:1) as flux. The starting materials of La₂O₂S and Cu₂S was essential to obtain large crystals. The growth conditions were optimized; growth temperature 850 °C, growth time 96h, cooling rate 10 °C /h, K₂S 0.3mol% for large crystals, and growth temperature 850 °C, growth time 72h, cooling rate 10 °C /h, K₂S 1.0 mol% for colorless crystals. The size of the largest crystals obtained were 4.1×2.7×0.036 mm³ in the former condition and 3.0×2.8×0.049 mm³ in the latter condition. Transmission of most crystals in the visible region was in the range of 40~60%, and the intrinsic absorption edge was observed at 400 nm. The colorless single crystal showed p-type electrical conductivity of $7.1 \times 10^{-4} \text{ Scm}^{-1}$ at room temperature.

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Figure Captions

Fig.1 Schematic configurations in evacuated silica glass tube to grow LaCuOS single crystals

Fig.2 Photographs of LaCuOS single crystals; (a) large brownish single crystal (K_2S : 0.3 mol%) and (b) colorless single crystal (K_2S : 1.0 mol%).

Fig.3 XRD patterns of LaCuOS; (a) single crystal and (b) simulated powder pattern

Fig.4 Optical transmission spectra of LaCuOS single crystals and polycrystalline film.

Table 1 Samples and their growth conditions

sample No.	K ₂ S concentration (%)	growth temperature (°C)	growth time (h)	cooling rate (°C/h)	average size (mm ³)
1	0.0	750	72	100	0.3 × 0.3 × 0.020
2	0.0	800	72	100	1.2 × 1.1 × 0.022
3	0.0	850	72	100	1.9 × 1.8 × 0.028
4	0.0	900	72	100	2.4 × 1.2 × 0.021
5	0.3	850	72	100	3.0 × 2.3 × 0.028
6	0.7	850	72	100	2.4 × 1.4 × 0.027
7	1.0	850	72	100	1.6 × 1.2 × 0.023
8	0.3	850	48	100	2.6 × 1.9 × 0.028
9	1.0	850	48	100	1.4 × 1.0 × 0.018
10	0.3	850	96	100	3.2 × 2.0 × 0.044
11	1.0	850	96	100	2.5 × 1.8 × 0.071
12	0.3	850	120	100	2.3 × 1.9 × 0.053
13	1.0	850	120	100	1.6 × 1.1 × 0.022
14	0.3	850	72	10	3.1 × 1.6 × 0.042
15	1.0	850	72	10	2.6 × 2.3 × 0.043
16	0.3	850	72	5	3.0 × 2.4 × 0.059
17	1.0	850	72	5	1.7 × 1.6 × 0.038

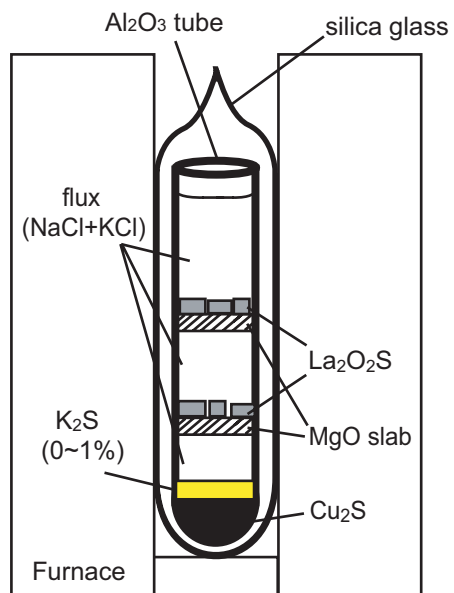
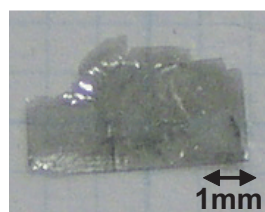
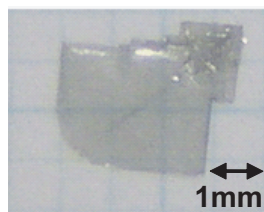


Figure 1



(a)



(b)

Figure 2

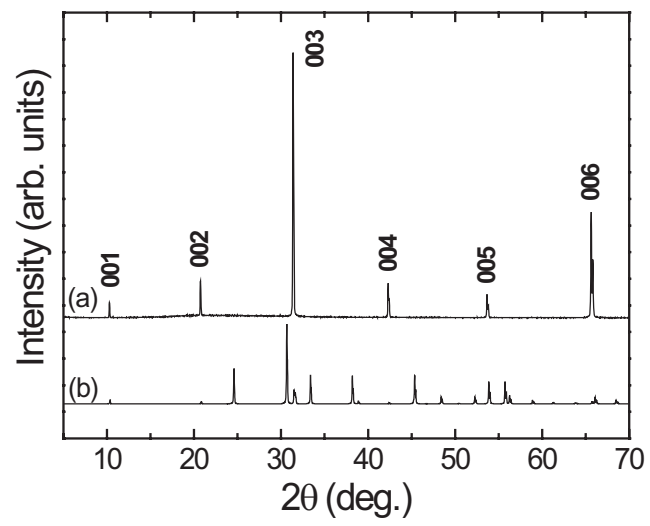


Figure 3

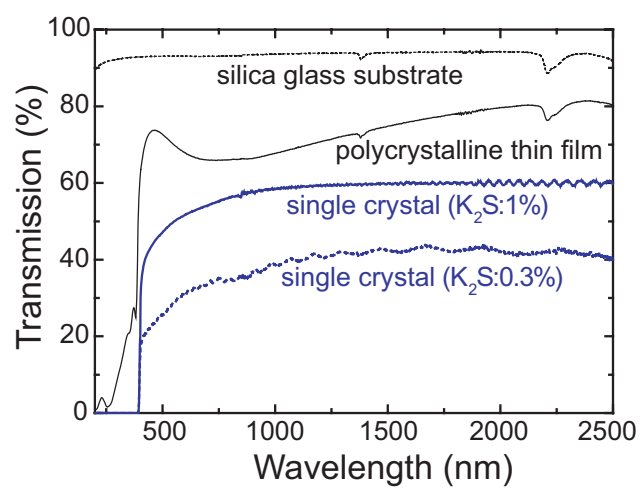


Figure 4