学 位 論 文 内 容 の 要 旨

博士の専攻分野の名称　博士（理学）　氏名　Yan Hong

学 位 論 文 題 名

Flux Crystal Growth, Crystal Structures and Optical Properties of Ga/Ge-Based Oxides and Oxysulfides
（Ga/Ge 酸化物および酸硫化物のフラックス結晶育成と結晶構造および光学特性）

Mixed-anion compounds, which have two or more different anions in a structure, have drawn a considerable attention in the inorganic solid-state science field because the coexistence of the different anionic characteristics such as oxidation numbers, electronegativity, ionic radii, and polarizability can induce unprecedented structures and chemical/physical properties inaccessible in traditional single-anion compounds. However, it is usually very difficult to stabilize mixed-anion compounds by using conventional solid-state reactions, and even if new phases could be obtained, the crystal structures, most of which are complex compared with those of single-anion compounds, could not be solved easily. Flux crystal growth method is a transitional but useful approach to obtain mixed-anion compounds including oxychalcogenide, oxyhalide, and chalcohalide phases. In addition, single crystals grown out of flux can readily allows access to the strcture determination. Although there have been many reports on flux crystal growth of mixed-anion compounds, such examples are very few tcompared with those of single-anion compounds. Therefore, further studies using the flux method are needed to deepen our understanding of mixed-anion compounds.

It is well known that Ga/Ge-based compounds with d^{10} electronic configuration possess wide optical band gaps between the valence band maximum and conduction band minimum, which afford interesting optical properties including photoluminescence, photocatalytic activity, and nonlinear optical responses. Mixing multiple anions in these wide-gap semiconductors can alter the band structure, especially the valence band mamixum composed of anions. Therefore, the anion-directed band gap engineering can be expected to greatly modify the optical properties of the trandisional single-anion compounds. This study has explored new Ga/Ge-based oxysulfide compounds using molten halide salts, resulting in the discoveries of two oxysulfides and an oxide, namely, $La_3Ga_3Ge_2S_3O_{10}$, $La_4(GaS_2O_2)_3$, and $Ce_2CaMg_2Ge_3O_{12}$. The syntheses, crystal structures, and optical properties have been discussed.

Chapter 1 introduces the general background including the mixed-anion and Ga/Ge-based compounds, their structures, and physical properties.

Chapter 2 mainly presents the experimental techniques used in this research.

Chapter 3 illustrates the mixed-anion compound of $La_3Ga_3Ge_2S_3O_{10}$, which crystallized in the hexagonal non-centrosymmetric space group *P*-62*c* with lattice constants of $a = b = 10.1406(5)$ Å and $c = 18.1645(9)$ Å. Non-centrosymmetric chalcogenide-based compounds usually have been exploited as infrared nonlinear optical materials but never been studied for the ultraviolet application due to the high energy level of chalcogen

anions leading to band gap narrowing. However, the large polarizability of chalcogenide ions is beneficial to conversion efficiency of second harmonic generation (SHG), and thus mixing chalcogenide ions with the large polarizabilities and oxide ion with short abosorption cutoff edges in a structure can be a useful approach for making chalcogenide-based compunds ultraviolet nonliniear optical materials with strong SHG response. $La_3Ga_3Ge_2S_3O_{10}$ exhibits an exceptionally wide band gap of 4.70 eV, compared with those of early reported oxychalcogenide compounds. This mainly results from the the unique anion-ordered frameworks comprising 1D $^1_\infty[(Ga_{3/5}Ge_{2/5})_3S_3O_3]$ triangular tubes and 0D $(Ga_{3/5}Ge_{2/5})_2O_7$ dimers of corner-sharing $(Ga/Ge)S_2O_2$ and $(Ga/Ge)O_4$ tetrahedra, respectively. SHG measurements revealed that $La_3Ga_3Ge_2S_3O_{10}$ was phase matchable with twice the SHG response of KH_2PO_4 benchmark compund. The results of theoretical calculations suggest that the strong SHG response is mainly attributable to the S-3*p* and O-2*p* orbitals in the occupied states. The anion-directed band-gap engineering may give insights into the application of nonlinear optical oxychalcogenides in the ultraviolet regions.

Chapter 4 presents a new germanium based oxysulfide single crystal $La_4(GeS_2O_2)_3$, which could be obtained by the flux growth method using a $BaCl_2$-$CaCl_2$ eutectic mixture. The crystal structure was determined by the single-crystal X-ray diffraction analysis. $La_4(GeS_2O_2)_3$ crystallizes in the centrosymmetric space group *R*-3 with lattice constants of $a = b = 16.8283(3)$ Å and $c = 8.4140(2)$ Å. The structure of $La_4(GeS_2O_2)_3$ is featured with a complex three-dimensional anion order and composed of unusual GeS_2O_2 tetrahedra and three types of La-centered polyhedra. The GeS_2O_2 tetrahedra form a triangular arrangement around a columnar structure of alternating face-sharing LaO_{12} and LaS_6O_6 polyhedra. The structure of $La_4(GeS_2O_2)_3$ is like that of the apatite germanate $La_{9.33}(GeO_4)_6O_2$, which features face-sharing LaO_9 columns surrounded by GeO_4 tetrahedra. The combination of UV−vis absorption measurements and first-principles calculations revealed the existence of an indirect optical band gap (Eg = 3.67 eV) between the valence band maximum composed of S 3*p* orbitals and the conduction band minimum composed of La-3*d*, La-4*f*, S-3*p*, and Ge-4*s* orbitals.

Chapter 5 shows a new germanate garnet single crystal $Ce_2CaMg_2Ge_3O_{12}$, which was synthesized via flux growth method using a $BaCl_2$-$CaCl_2$ eutectic mixture. The initial target phase was a Ge-based oxysulfide with Ce atoms, but the new garnet phase was obtained by reaction with a MgO crucible. Single-crystal X-ray diffraction analysis revealed that $Ce_2CaMg_2Ge_3O_{12}$ crystallized in a cubic garnet-type structure with lattice parameters of $a = 12.5487(3)$ Å in the space group *Ia*-3*d*. The chemical formula can be expressed as the common garnet formula of $A_3B_2C_3O_{12}$, where Ce/Ca, Mg, and Ge occupy the A, B, and C sites, respectively. A UV–Vis spectroscopy measurement on the germanate garnet exhibited a clear absorption edge corresponding to a band gap of 2.21 eV ($\lambda = 561$ nm). First-principles calculations indicated that the valence band maximum was composed of Ce 4*f* bands, whereas the conduction band minimum mainly consisted of Ce 5*d* bands. These findings explain the observed absorption edge through the Ce 4*f* to 5*d* absorption. Photoluminescence emission spectra exhibited a very broad peak centered at 600 nm, corresponding to transition from the lowest energy *d* level to the 4*f* levels.

Chapter 6 presents the general conclusion and future prospects based on this work.