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Synthesis, structure, physical properties, and electronic structure of $KGaSe_2$

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ABSTRACT

The ternary gallium selenide $KGaSe_2$ has been synthesized by solid-state reactions and good quality crystal has been obtained. $KGaSe_2$ crystallizes in the monoclinic space group $C2/c$ with cell dimensions of $a = 10.878(2)$ Å, $b = 10.872(2)$ Å, $c = 15.380(3)$ Å, and $\beta = 100.18(3)^\circ$. In the structure, adamantane like $[Ga_4Se_{10}]^{8-}$ units are connected by common corners forming two-dimensional $[GaSe_2]^-$ layers which are separated by K^+ cations. $KGaSe_2$ exhibits congruent-melting behavior at around 965 °C. It is transparent in the range of 0.47–20.0 μm and has a band gap of 2.60(2) eV. From a band structure calculation, $KGaSe_2$ is a direct-gap semiconductor. The band gap is mainly determined by the $[GaSe_2]^-$ layer.

1. Introduction

The ternary chalcogenides A/M/Q (A = alkali or alkaline-earth metal; M = Al, Ga, In; Q = S, Se, Te) have attracted much attention due to their rich structural chemistry and interesting physical properties. For example, the $LiMQ_2$ (M = Ga, In; Q = S, Se) [1–4], BaM_4Q_7 (M = Al, Ga; Q = S, Se) [5–8] compounds exhibit very large NLO response in the IR range; the $BaGa_2Q_4$ (Q = S, Se) [9,10] compounds have been widely studied as luminescent materials. The primary building units in these compounds are usually the MQ_4 tetrahedra. Exceptions include the $M(M)(Q)_3$ tetrahedra in $Na_2Ga_2Se_3$ [11], $RbIn_7S_9$ [12], and $Ba_5Ga_4Se_{10}$ [13] which contain Ga–Ga or In–In bonds and the InQ_6 octahedra in $NaInQ_2$ (Q = S, Se) [14]. As the M/A ratio decrease, the connection among the MQ_4 tetrahedra become sparse, changing from the three-dimensional framework in $BaGa_4Se_7$ [6] and KIn_5S_8 [15] etc., to two-dimensional layers in $BaIn_2Se_4$ [16] and $CsGaSe_3$ [17] etc., to one-dimensional chains in $BaGa_2Q_4$ (Q = S, Se) [9,10] and $KInTe_2$ [18] etc., and finally to zero dimensional anions in $Ba_2Ga_2S_5$ [19], $Ba_3Ga_2S_6$ [20], $Ba_4Ga_2S_7$ [20], $Ba_5Ga_2Q_8$ (Q = S, Se) [21,22], and Cs_3GaSe_3 [23] etc.

Most compounds with $AGaQ_2$ (A = alkali metal, Q = S, Se, Te) composition crystallizes in the $KInS_2$ structure type in space group $C2/c$ [24–29]. Exceptions include $LiGaQ_2$ (Q = S, Se) [3], $LiGaTe_2$ [3], and $NaGaTe_2$ [30], which adopt the $NaFeO_2$ [31] structure type, the chalcopyrite structure type [32], and the TlSe [30] structure type, respectively. The lattice constants for $KGaSe_2$ were determined in an earlier study [28]. Here we obtain good-quality $KGaSe_2$ crystals under modified reaction conditions and provide the first study on the full single-crystal structure determination, optical property, thermal property, and electronic structure of $KGaSe_2$.

2. Experimental section

2.1. Solid-state synthesis

The following reagents were used as obtained: K (Sinopharm Chemical Reagent Co., Ltd., 98%), Ga (Sinopharm Chemical Reagent Co., Ltd., 99%), and Se (Sinopharm Chemical Reagent Co., Ltd., 99%). The binary starting materials, K_2Se and Ga_2Se_3, were synthesized by stoichiometric reactions of elements in sealed silica tubes evacuated to 10^{-3} Pa at annealing temperatures of 900 °C for K_2Se and 900 °C for Ga_2Se_3, respectively.

A polycrystalline sample of $KGaSe_2$ was synthesized by solid-state reaction technique. Reaction mixtures of K_2Se and Ga_2Se_3 in the molar ratio of 1:1 were ground and loaded into fused-silica tubes under an Ar atmosphere in a glovebox, which were sealed

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under 10^{-3} Pa atm and then placed in a computer-controlled furnace. The samples were heated to 800 °C in 20 h, kept at that temperature for 72 h, and then the furnace was turned off.

X-ray powder diffraction analyses of the resultant powder samples were performed at room temperature in the angular range of $2\theta = 10–70°$ with a scan step width of 0.02°and a fixed counting time of 1 s/step using an automated Bruker D8 X-ray diffractometer with graphite monochromatized Cu K_α radiation ($\lambda = 1.5418$ Å).

2.2. Single-crystal growth

The as-prepared $KGaSe_2$ powder was loaded into a fused-silica tube under an Ar atmosphere in a glovebox, which was sealed under 10^{-3} Pa atm and then placed in a computer-controlled furnace. The sample were heated to 1000 °C in 20 h and kept at that temperature for 48 h, then cooled at a slow rate of 1 °C/h to 800 °C, and finally cooled to room temperature. The product consisted of light yellow crystals of $KGaSe_2$, which were manually selected for structure characterization. Analyses of the crystals with an EDX-equipped Hitachi S-3500 SEM showed the presence of K, Ga, and Se in the approximate molar ratio of 1:1:2. The crystals are stable in air. It should be mentioned that our crystal growth temperature is different from that of 800 °C in the earlier study [28]. According to the DSC measurement (see below), the melting point of $KGaSe_2$ is about 965 °C, so our higher crystal growth may be necessary for obtaining good-quality crystals.

2.3. Structure determination of $KGaSe_2$

Single-crystal X-ray diffraction data were collected with the use of graphite-monochromatized Mo K_α ($\lambda = 0.71073$ Å) at 93 K on a Rigaku AFC10 diffractometer equipped with a Saturn CCD detector. Crystal decay was monitored by re-collecting 50 initial frames at the end of data collection and no detectable crystal decay was observed. The collection of the intensity data was carried out with the program Crystalclear [33]. Cell refinement and data reduction were carried out with the use of the program Crystalclear [33], and face-indexed absorption correction was performed numerically with the use of the program XPREP [34].

The structure was solved with Direct Methods implemented in the program SHELXS and refined with the least-squares program SHELXL of the SHELXTL.PC suite of programs [34]. The final refinement included anisotropic displacement parameters. The program STRUCTURE TIDY [35] was then employed to standardize the atomic coordinates. Additional details and structural data are given in Tables 1–3 and further information may be found in Supplementary material.

Table 1
Crystal data and structure refinement for $KGaSe_2$.

	$KGaSe_2$
Fw	266.74
a(Å)	10.878(2)
b(Å)	10.872(2)
c(Å)	15.380(3)
β(°)	100.18(3)
Space group	$C2/c$
V(Å^3)	1790.3(6)
Z	16
T(K)	93(2)
λ(Å)	0.71073
ρ_c(g/cm^3)	3.959
μ(cm^{-1})	231.20
$R(F)$	0.0417
$R_w(F_o^2)$	0.1104

Table 2
Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for $KGaSe_2$.

Atom	x	y	z	U_{eq}[a]
K1	0.28401(17)	0.06195(17)	0.38710(13)	0.0094(4)
K2	0.46453(19)	0.31320(19)	0.10870(14)	0.0154(5)
Ga1	0.14545(8)	0.43601(8)	0.33748(6)	0.0055(3)
Ga2	0.10178(8)	0.18898(8)	0.16239(6)	0.0057(3)
Se1	0.25913(7)	0.31229(9)	0.25004(5)	0.0072(3)
Se2	0.20432(8)	0.06225(9)	0.06747(6)	0.0104(3)
Se3	0.04626(9)	0.31289(9)	0.43495(6)	0.0137(3)
Se4	0.0000	0.57185(11)	0.2500	0.0066(3)
Se5	0.0000	0.05366(12)	0.2500	0.0073(3)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

2.4. Diffuse reflectance spectroscopy

A Cary 5000 UV–visible–NIR spectrophotometer with a diffuse reflectance accessory was used to measure the spectrum of $KGaSe_2$ in the range of 250 nm (4.96 eV) to 2500 nm (0.50 eV).

2.5. Middle IR transmission spectroscopy

The middle IR transmission spectrum was measured with the use of a VERTEX 80V FTIR spectrometer in the range of 250–4000 cm^{-1} on a 1 mm-thick crystal at room temperature. The spectrum resolution is 2 cm^{-1}.

2.6. Thermal analysis

The thermal property was investigated by the differential scanning calorimetric (DSC) analysis using the Labsys™ TG-DTA16 (SETARAM) thermal analyzer (the DSC was calibrated with Al_2O_3). About 20 mg $KGaSe_2$ sample was placed in a carbon-coated silica tube with an outer diameter of 5 mm and an inner diameter of 3 mm, which was sealed under 10^{-3} Pa. The heating and the cooling rate were both 10 °C/min.

2.7. Band structure calculation

The electronic properties are calculated using the plane-wave pseudopotential method [36] implemented in the CASTEP package [37]. The local density functional (LDA) with a high kinetic-energy cutoff of 800 eV is adopted for all the calculations. The preconditioned conjugated gradient (CG) band-by-band method [38] used in CASTEP ensures a robust efficient search of the energy minimum of the electronic structure ground state. The optimized normal-conserving pseudopotentials [39] in Kleinman–Bylander form [40] for K, Ga, and Se allow us to use a small plane-wave basis set without compromising the accuracy required by our study. The 1s, 2s, and 2p electrons for potassium and the electrons below 3d orbitals for gallium are treated as the core electrons. For selenium, the 4s and 4p electrons are chosen as the valence

Table 3
Interatomic distances (Å) for $KGaSe_2$.

Atoms	Distances	Atoms	Distances	Atoms	Distances
Ga1–Se1	2.395(1)	K1–Se1	3.419(2)	K2–Se1	3.382(2)
Ga1–Se2	2.418(1)	K1–Se1	3.424(2)	K2–Se1	3.384(2)
Ga1–Se3	2.403(2)	K1–Se2	3.335(2)	K2–Se2	3.285(3)
Ga1–Se4	2.396(1)	K1–Se3	3.311(2)	K2–Se2	3.889(2)
Ga2–Se1	2.394(1)	K1–Se3	3.908(2)	K2–Se2	3.902(2)
Ga2–Se2	2.419(1)	K1–Se3	3.917(2)	K2–Se3	3.264(2)
Ga2–Se3	2.408(1)	K1–Se4	3.425(2)	K2–Se4	3.385(2)
Ga2–Se5	2.394(1)	K1–Se5	3.420(2)	K2–Se5	3.378(2)