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Journal of Alloys and Compounds 432 (2007) 69–73

Journal of ALLOYS AND COMPOUNDS

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Reactive flux syntheses, crystal structures and band gaps of $AInS_2$ (A = Rb, Cs)

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Received 7 February 2006; received in revised form 11 April 2006; accepted 5 June 2006
Available online 12 July 2006

Abstract

High-quality single crystals of $RbInS_2$, $CsInS_2$ were isolated from the halide flux as a major phase of the repeated fusion of CaS and In_2S_3 followed by slow cooling. $RbInS_2$ and $CsInS_2$ are practically isostructural with $KInS_2$. $RbInS_2$: *C*2/*c*, $a = 11.071(6)$ Å, $b = 11.068(1)$ Å, $c = 15.610(7)$ Å, $\beta = 100.36(3)^\circ$, $V = 1882(2)$ Å^3, $Z = 16$, $d_x = 3.74$ g/cm^3, $R = 6.38\%$, $R_w = 6.42\%$. $CsInS_2$: *C*2/*c*, $a = 11.197(3)$ Å, $b = 11.158(3)$ Å, $c = 16.358(4)$ Å, $\beta = 99.92(2)^\circ$, $V = 2013(2)$ Å^3, $Z = 16$, $d_x = 4.12$ g/cm^3, $R = 5.60\%$, $R_w = 6.20\%$. The $AInS_2$ (A = Rb, Cs) structure is characterized by double layers of vertex-sharing $[In_4S_{10}]$ units that each consists of four $[InS_4]$ polyhedra. The charge-balancing alkali-metal cations are stuffed into the channels created by the packing of these anionic $[In_4S_{10}]$ blocks. The optical reflectance measurements show a band gap of 3.3 eV for $RbInS_2$ and 3.4 eV for $CsInS_2$, suggesting that both are semiconductors.

Keywords: Flux; Crystal growth; Crystal structure; Band gap

1. Introduction

Materials with transparent windows extending into the far infrared region (10–14 μm) are becoming more and more important for modern optical and electronic–optical applications [1]. Most ceramic materials that are transparent in visible region contain light elements such as O, and B, and thus have vibrational excitations in the infrared region. The characteristic absorption at low frequencies of chalcogenides renders these materials excellent for long wavelength transmission. Many sulfide materials have transmission windows ranging from 0.5 to 14 μm [1]. Multinary metal sulfides are optical ceramic materials [2,3] with potential applications. In our effort to search for this type of materials [4,5], single crystals of $RbInS_2$ and $CsInS_2$ of high quality were obtained through the traditional flux method [6]. Although the X-ray powder data have been reported in literature [7], showing that $RbInS_2$, $CsInS_2$ are isostructural with $KInS_2$ [8], $KInS_2$–I [2], $KInSe_2$ [9] and $TlGaSe_2$ [10]. Recently, Huang et al. [11] reported the preparation, structures and calculated band gaps of $RbInS_2$ and $RbInSe_2$. To our knowledge, due to the lack of high-quality single crystals, the structure of $CsInS_2$ has not been reported, the physical properties of $RbInS_2$, $CsInS_2$ have not been measured by other groups yet. We present here the synthesis, crystal structure and experimental band gaps of $RbInS_2$, $CsInS_2$.

2. Synthesis and crystal growth

All starting materials were used as received.

The starting materials of 0.0670 g (0.924 mmol) CaS (99.5%) and 0.3010 g (0.924 mmol) In_2S_3 (99.95%) in the molar ratio of $CaS:In_2S_3 = 1:1$ and 1.60 g CsCl (99.95%) were ground thoroughly under a blanket of nitrogen in a drybox and then pressed into a pellet, which was subsequently sealed in an evacuated quartz tube under active vacuum. It was placed in a furnace and heated to 850 °C, held for 92 h. Then a cycle procedure com-

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doi:10.1016/j.jallcom.2006.06.010

posed of repeated heating and cooling was performed to obtain crystals of good quality. The detail of such cycle was as follows: the above reaction mixture at 850 °C was slowly cooled to 750 °C, then heated to 960 °C, soaked for 57 h, cooled to 750 °C, rapidly raised to 960 °C. This process was repeated once more, then the reaction mixture was slowly cooled to 600 °C, and finally cooled to room temperature by shutting off the furnace. The reaction mixture was then soaked in distilled water for 12 h, filtered. Pale-yellow crystals of about 0.60 g (yield 80%, based on In) were isolated.

$RbInS_2$ was prepared by the similar method by using RbBr as reactive flux. The yield was over 80% based on In.

$RbInS_2$ and $CsInS_2$ are very stable in air. The stability and purity of the as-prepared $RbInS_2$, $CsInS_2$ samples were confirmed by powder X-ray diffractions that were carried out after the crystals of $RbInS_2$, $CsInS_2$ had been obtained for 3 years. All diffraction lines observed in the X-ray powder diagrams were in agreement with those simulated ones based on the single crystal refinement results. No binary sulfide, halide or oxide was detected according to the powder X-ray diffraction or EDX analysis.

3. Crystallography

3.1. Single-crystal structure determination

Chunk-like single crystals of $RbInS_2$ (0.18 mm × 0.15 mm × 0.05 mm) and $CsInS_2$ (0.10 mm × 0.08 mm × 0.05 mm) were mounted respectively on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Programmed indexing of 25 reflections from a random search over $20° \le 2\theta \le 36°$ yielded a face-centered monoclinic cell for both compounds. Intensity data were collected using the ω–2θ scan mode and corrected for Lorentz-polarization as well as for empirical absorption using the ψ-scan technique.

The systematic absences in the data were indicative of space groups of *C*2/*c* (No. 15) or *Cc* (No. 9), the centrommetric *C*2/*c* was assumed, and subsequent structure solution and refinement confirmed the choice of this space group.

The structures were solved by the direct methods and difference Fourier synthesis. Final full-matrix least-squares refinements of all variables (coordinates and anisotropic thermal parameters) resulted in the following agreement factors: $R = 0.0613$, $R_w = 0.0666$, $S = 1.48$ for $RbInS_2$; $R = 0.0560$, $R_w = 0.0620$, $S = 1.35$ for $CsInS_2$. All calculations were performed using the MolEN package [12]. The final difference electron density showed the highest residual peak of 2.739 eV/Å^3 and the lowest of −0.934 eV/Å^3, the maximum residual is 1.48 Å away from Rb(2) atom and 2.69 Å away from In(1) for $RbInS_2$. While for $CsInS_2$, the maximum and minimum residual peaks in the final difference electron density were 1.964 and −0.783 eV/Å^3, respectively. The maximum residual is 2.98 Å away from Cs(2) atom, 2.19 Å away from In(2) and 1.53 Å away from S(5).

Some details of the data collection and refinements are summarized in Table 1, the positional coordinates and isotropic equivalent thermal parameters are given in Table 2, and important bond distances are given in Table 3. Further details of the crystal structure investigations can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49 7247 808 666; e-mail: crysdata@fiz-karlsruhe.de) on quoting the depository number CSD-415553 for $CsInS_2$ and CSD-415554 for $RbInS_2$.

Table 1
Crystal data and experimental details for $RbInS_2$ and $CsInS_2$

Compound	$RbInS_2$	$CsInS_2$
Formula weight	264.42	311.85
Crystal system	Monoclinic	Monoclinic
Space group	*C*2/*c* (No. 15)	*C*2/*c* (No. 15)
Cell parameters		
a (Å)	11.071(6)	11.197(3)
b (Å)	11.068(1)	11.158(3)
c (Å)	15.610(7)	16.358(4)
β	100.36(3)	99.92(2)
V (Å^3)	1882(2)	2013(2)
Z	16	16
F(0 0 0)	1888	2176
Density (calculated) (Mg/m^3)	3.74	4.12
Temperature (K)	293	293
μ(Mo Kα) (mm^{-1})	15.61	12.32
Crystal shape, color	Chunk, pale-yellow	Chunk, pale-yellow
Crystal size (mm)	0.175 × 0.15 × 0.05	0.10 × 0.08 × 0.05
2θ range(°)	2–80	2–80
T_{min}/T_{max}	0.652/0.995	0.704/0.996
h, *k*, *l* Range	$-20 \le h \le 20$, $0 \le k \le 20$, $-28 \le l \le 0$	$-20 \le h \le 0$, $0 \le k \le 20$, $-29 \le l \le 29$
Decay (%)	6.1	0.4
Total reflection data collected	6030	6461
Observed data (with $I > 3.0\sigma(I)$)	2121	2499
R_{int}	0.162	0.025
No. of variables	74	74
Weighting scheme	$w = 1/\sigma^2(F_o)$	$w = 1/\sigma^2(F_o)$
Goodness of fit *S*	1.48	1.35
R, R_w	0.0613, 0.0666	0.0560, 0.0620
$(\Delta/\sigma)_{max}$	0.0005	0.0004
High/low residual (eV/Å^3)	2.74/−0.93	1.96/−0.78

$S = \left[\sum \frac{w(|F_o|-|F_c|)^2}{(N_{obs}-N_{var})}\right]^{1/2}$. $R = \frac{\sum ||F_o|-|F_c||}{\sum |F_o|}$. $R_w = \left[\frac{\sum w(|F_o|-|F_c|)^2}{\sum w|F_o|^2}\right]^{1/2}$.

3.2. X-ray powder diffraction

The powder diffraction patterns were recorded on a STOE powder diffractometer (Stoe, Darmstadt), using germanium-monochromatized Cu Kα radiation (λ = 1.54057 Å) with the powdered samples enclosed in sealed glass capillaries.

3.3. UV–vis diffuse reflectance spectroscopy

Optical diffuse reflectance spectra of powdered $RbInS_2$ and $CsInS_2$ were performed at room temperature using a Perkin-Elmer Lambda 900 UV–vis spectrophotometer equipped with