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Structural characterization and low-temperature physical properties of p-type single-crystal $K_8Ga_{8.5}Sn_{37.5}$ grown by self-flux method

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ABSTRACT

Single-crystal $K_8Ga_{8.5}Sn_{37.5}$ was synthesized employing a self-flux method where Ga and Sn were used as fluxes. Single-crystal X-ray diffraction analyses revealed that this composition crystallizes in a cubic structure with the $Pm\bar{3}n$ space group (#223, $a=11.9345(16)$ Å, $V=1699.9(4)$ Å^3, $Z=1$, and $R/wR=0.0187/0.0382$). A large dynamic disorder and anisotropic atomic displacement parameters were observed for K atoms inside the larger polyhedra in the crystal structure of $K_8Ga_{8.5}Sn_{37.5}$. Electrical properties measurements indicate p-type conduction with onset of minority charge carrier conduction at temperatures above 270 K.

1. Introduction

Inorganic clathrates continue to be of interest for thermoelectric [1–3], magnetocaloric [4,5], and photovoltaic applications [6–9], as a result of their interesting physical properties, including a very low thermal conductivity [1,10], magnetism [11,12], and superconductivity [13,14]. Investigations into the intrinsic structural and physical properties of these materials requires new compositions in single-crystal form, and in many cases new synthetic techniques such as the spark plasma sintering [15,16], or vapor-phase intercalation of alkali-elements with graphite [17,18], reported recently. Another approach for single-crystal growth is the flux-method [19]. The role of fluxes in materials synthesis is to dissolve the elemental constituents of the desired product, as well as to serve as a transport medium facilitating the diffusion processes [19]. Ga or Sn can be used as fluxes due to their relatively low melting temperatures and the large difference between their respective melting and boiling temperatures [19]. In the so-called self-flux synthesis, Sn or Ga, for example, appear as reactants and can be incorporated as constituents in the product of the reaction. Crystals grown from Ga or Sn fluxes are typically recovered by centrifugation [20,21]. There is a large number of alkali-earth and rare-earth transition-metal stannides that have been prepared using Sn flux [22]. Single-crystal clathrates have been grown by the flux method and stoichiometric elemental solid-state reaction [23–29]. The type-I clathrate $K_8Ga_8Sn_{38}$ is one example [24,27]. In this report we demonstrate that p-type $K_8Ga_{8.5}Ga_{37.5}$ type-I clathrate can be synthesized using a two-flux method whereby excess amounts of Ga and Sn are used as fluxes. Structural characterization of this composition was performed employing single-crystal XRD, and the electrical and thermal properties were also investigated.

2. Experimental section

The single-crystal $K_8Ga_{8.5}Sn_{37.5}$ clathrate was synthesized by using both Sn and Ga as fluxes. The pure elements K (Alfa Aesar, 98%), Ga (Alfa Aesar, 99.99999%) and Sn (Alfa Aesar, 99.999%) were mixed in a K:Ga:Sn ratio of 8:50:90 and reacted in a tungsten crucible enclosed in a stainless steel canister which was sealed in a quartz ampoule. The mixture was heated up to 550 °C at a rate of 25°/min and held at this temperature for 15 h. It was then slowly cooled to 450 °C at a rate of 1°/min followed by air quenching. The single crystals were manually recovered from the Ga and Sn-rich matrix and ultrasonicated in a mixture of ethanol and distilled water to remove any surface contamination from the crystals (Fig. 1a).

Preliminary examination and data collection were performed on a Bruker X8 Apex II diffractometer equipped with 4 K CCD detector and graphite-monochromatized Mo $K\alpha$ radiation ($\lambda=0.7107$ Å). The initial positions for all atoms were obtained using SHELXS97 [30] and the structure was refined by full-matrix least-squares techniques with the use of SHELXL97 [30] in the

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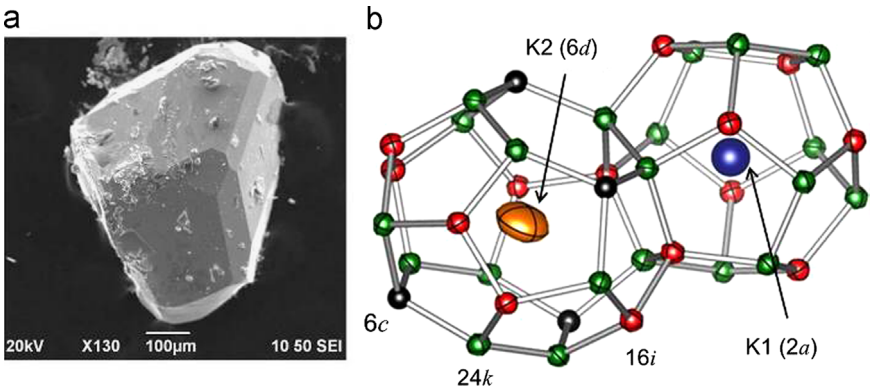

Fig. 1. (a) SEM image of a single-crystal $K_8Ga_{7.5}Sn_{37.5}$. (b) A fragment of the crystal-structure of $K_8Ga_{8.5}Sn_{37.5}$ from single-crystal XRD. K1 at 2*a* and K2 at 6*d* crystallographic sites are shown in blue and orange, respectively; Ga and Sn share the 6*c* (black), 16*i* (red) and 24*k* (green) crystallographic sites. Thermal ellipsoids are shown with 99% probability. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

WinGX program package [31]. The final cycle of refinement performed on F_o^2 with 619 unique reflections afforded residuals, w*R*2, of 0.0382 and a conventional *R* index based on 569 reflections having $F_o^2 > 2\sigma\,(F_o^2)$ of 0.0187. The highest peak (0.940 e/Å^3) and deepest hole (−1.492 e/Å^3) in the residual electron density (Table 1) are located 0.48 Å and 0.11 Å from Sn3/Ga3 and Sn2/Ga2, respectively, and are likely due to data truncation errors ($2\theta \approx 66.6^\circ$) and the empirical absorption correction that was used for this irregularly shaped crystal.

Scanning electron micrographs (SEM) were collected using a JEOL JSM-6390LV, and energy dispersive X-ray spectroscopic (EDS) data were collected using an Oxford INCA X-Sight 7582 M. Wavelength-Dispersive Spectrometry (WDS) analyses were performed using a Cameca SX-100 by Cameca probe, using elemental Sn, GaAs and orthoclase mineral as Sn, Ga, and K standards, respectively.

Steady-state thermal conductivity, κ, and four-probe resistivity, ρ, measurements on a single-crystal of approximate dimensions $0.2 \times 0.3 \times 0.4$ mm from 12 to 300 K were conducted in a custom radiation-shielded vacuum probe [32]. Conservative estimates of the room temperature maximum uncertainties in the measurements of both κ and ρ are 30%. The large uncertainties estimated for these measurements are due to the relatively large contacts as compared to the size of the crystals.

3. Results and discussion

Crystallographic and structure refinement results from single-crystal XRD data are given in Table 1. The refined composition of the specimen was $K_8Ga_{8.5}Sn_{37.5}$ with a lattice parameter of 11.9345 (16) Å, slightly smaller than that of the n-type $K_8Ga_8Sn_{38}$ [24]. This composition was corroborated by WDS analyses performed on the same crystal used for single-crystal XRD. An average K/Ga/Sn ratio of 8/8.2(3)/37.4(2) was calculated from ten points analyzed quantitatively with the electron microprobe at 15 kV, 7 nA, with a 5 μm raster.

$K_8Ga_{8.5}Sn_{37.5}$ is cubic with the type-I clathrate crystal structure, space group $Pm\bar{3}n$. Ga and Sn share the framework 6*c*, 16*i* and 24*k* crystallographic sites to form two types of covalently-bonded polyhedra: two dodecahedra, E_{20}, and six tetrakaidecahedra, E_{24}, (E=Ga, Sn) encapsulating K1 and K2 at the interstitial 2*a* and 6*d* crystallographic sites, respectively (Fig. 1b and Table 2).

Refined occupancies, atomic coordinates, and isotropic atomic displacement parameters (ADPs), U_{eq}, are given in Table 2, and refined anisotropic ADPs, U_{ij}, are given in Table 3. Listed in Table 4 are selected bond angles for the framework atoms, with an average value close to the ideal sp^3 hybridization angle of 109.5°.

Table 1
Crystallographic and structure refinement results for $K_8Ga_{8.5}Sn_{37.5}$.

Refinement composition	$K_8Ga_{8.5}Sn_{37.5}$
Space group	$Pm\bar{3}n$
Lattice parameter, (Å)	11.9345(16)
Volume, (Å^3)	1699.9(4)
Density	5.256 g/cm^3
Absorption coefficient, μ	17.259 mm^{-1}
θ limits	$2.41^\circ \le \theta \le 33.30^\circ$
Dada collected	$-18 \le h \le 18$, $-17 \le k \le 18$, $-18 \le l \le 18$
Goodness-of-fit on F^2	1.154
R_1, $I > 2\sigma(I)$	0.0187
wR_2, all data	0.0382
Largest diff. peak	0.940 ē/Å^3
Largest diff. hole	−1.492 ē/Å^3

Both the interstitial and framework crystallographic sites are found to be fully occupied. The framework sites are shared between Sn and Ga in the following Sn/Ga ratios: 0.49/0.51 for the 6*c*, 0.93/0.07 for the 16*i*, and 0.82/0.18 for the 24*k* site (Table 2). K1 and K2 fully occupy the interstitial 2*a* and 6*d* sites.

U_{eq} of the K2 atoms are more than three times larger than those of the K1 atoms (Table 2), due to the larger size of the E_{24} polyhedra as compared to the size of E_{20}. This is corroborated by the larger Sn3/Ga3–Sn3/Ga3 distances as compared to the other bond distances (Table 4) and the larger number of Sn3/Ga3–Sn3/Ga3 bonds per unit cell. This is in contrast with the type-I $K_{7.5}Si_{46}$ clathrate [18], where U_{eq} for both K atoms inside Si_{20} and Si_{24} were found to be similar. U_{eq} of the K atoms in $K_8Ga_{8.5}Sn_{37.5}$ are approximately two times smaller than those of $K_8Ga_8Sn_{38}$ [24], consistent with the lower lattice parameter of the former composition as compared to the latter. Also U_{eq} for the Sn/Ga atoms in $K_8Ga_{8.5}Sn_{37.5}$ are smaller than those of $K_8Ga_8Sn_{38}$ [24]. Substitution of Ga for Sn in the framework of $K_8Ga_8Sn_{38}$ presumably results in an increase of the restoring force on the Sn/Ga atoms due to the shorter Sn/Ga–Sn/Ga distances in $K_8Ga_{8.5}Sn_{37.5}$ as compared to the Sn–Sn distances in $K_8Ga_8Sn_{38}$ [24]. A typical Si3–Si3 distance in the crystal lattice of $K_{7.5}Si_{46}$ is 2.39 Å [18], as compared to Sn3/Ga3–Sn3/Ga3 with a bond distance of 2.81 Å for $K_8Ga_{8.5}Sn_{37.5}$ (Table 4). This is a result of the larger E_{24} polyhedra in the later composition, as compared to the Si_{24} in the former, and is an indication that there is more "room" for the K atoms to oscillate about their equilibrium positions inside E_{24} in $K_8Ga_{8.5}Sn_{37.5}$. This also results in a larger U_{eq} (Table 2). The single-crystal XRD data in Table 2 indicate that U_{eq} for K are much larger than that of the Sn and Ga forming the framework. This dynamic disorder is isotropic