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Thermoelectric Properties of $\text{Ca}_2\text{Sn}/\text{Ca}_3\text{SnO}$

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We measured thermopower, thermal conductivity and electrical resistivity for Ca_2Sn sample across 4–350 K temperature range. Contrary to expectations from recent DFT based calculations the thermopower is not particularly large, reaching $7 \mu\text{V}$ at 350 K. The thermoelectric figure of merit renders this material in unmodified form practically unusable for thermoelectric applications.

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1. Introduction

This type of materials was first synthesized in 1961 (Eckerlin), and its structure was determined by XRD measurements [1]. There are little experimental studies of thermodynamic and electrical properties of these compounds [2–4], as even in the first paper it was observed that these materials within a very short time turn into black powder after exposure to air. That powder contains mainly oxidation products. Recently, these materials were studied using ab-initio calculations and they were predicted to possess very promising thermopower [5–10]. Its real crystal structure is also a matter of debate [3, 8, 9]. The usability of thermoelectric material for thermoelectric applications depend on figure of merit, where high thermopower, small thermal conductivity and low resistivity is expected from a prospective material [11, 12]. Due to recent ab-initio studies we decided to revisit Ca_2Sn , and measure its thermoelectric properties.

2. Experimental details

The sample was melted using argon arc from 99,5% Ca, 99,95% Sn elements. The stoichiometric amount of constituent Ca and Sn elements were weighted with 5% Ca surplus in order to compensate for evaporation loss. After melting, the samples had shiny outlook and looked homogenous. The loss of weight during melting was lower than 4%. Thermoelectric properties were measured using Thermal Transport Option (TTO) for Quantum Design PPMS system. Several previous attempts [1–3] has shown that these samples turn into powder after contact with air within few minutes. As we do not have the possibility to transfer the sample to PPMS platform without contact with air (note that in order to perform thermoelectric measurements, the sample must have the correct shape) after melting we covered the sample with mineral oil, polished to correct shape, than cleaned oil residues and installed within TTO option. The time, when the

sample has contact with air was therefore reduced to 1–2 minutes. The contacts were glued to the sample using Epo-Tek H2OE silver conducting epoxy and the sample was measured using two terminal method. The conducting epoxy was cured very fast by the touch of soldering iron set to about 220°C . The samples just after measurement in PPMS were solid and exhibited only slight surface oxidation (the thermal measurements are performed in vacuum). Afterwards, we performed powder x-ray diffraction studies (XRD) of the prepared sample. Part of the sample was ground to powder in a mixture with Apiezon N grease under argon atmosphere. Measurement was done in the 2θ range of $7\text{--}70^\circ$ at normal thermodynamic conditions. We performed four succeeding XRD measurements through 24 hours, and we observed sample degradation even though the air impact was limited.

3. Results and discussion

We identified two crystallographic phases in the prepared alloy. However the identification of Ca_2Sn phase was difficult because compound have 6 inequivalent (Wyckoff 4c) positions for Ca1, Ca2 and Sn atoms. Lattice parameters were reported by Eckerlin in 1961 and this compound do not exist in any crystallographic databases like COD or PDF-4. We analysed XRD measurements comparing the results with simulated XRD patterns and estimated the lattice parameters. We didn't manage to perform La Bail or Rietveld refinement for this sample.

We found that the sample is a mixture of at least 3 phases, Ca_2Sn , Ca_3SnO and probably CaSn . Those phases dominate, and we suppose their equal amount in the sample. Ca_3SnO exhibits a perovskite type structure with probable good thermoelectric properties [14].

We calculated spectra for two suspected phases and compared them with experimental data in Fig. 1. Estimated lattice parameters of Ca_2Sn and Ca_3SnO , are collected in Table I. It is worth nothing that the previous experimental reports [1–3] shows very different values of lattice parameters (parameter a varies in different reports from 7.5 \AA to 12.15 \AA). During the 24 hour XRD measurement the concentration of Ca_2Sn phase diminished and the concentration of Ca_3SnO phase increased despite

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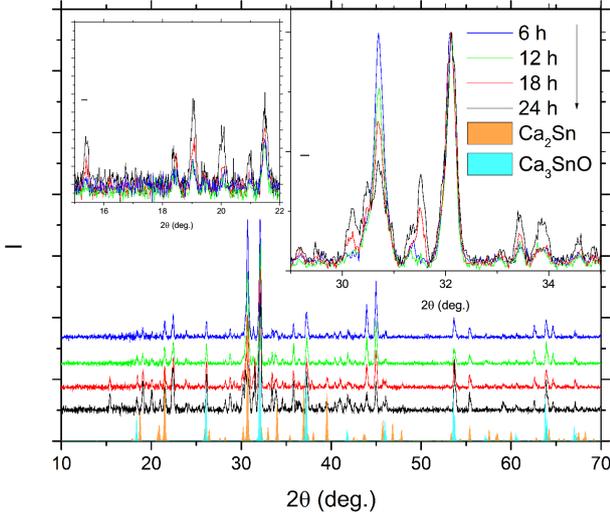


Fig. 1. Powder X-ray diffraction patterns measured for 6, 12, 18 and 24 hours. Results were compared to simulations of Ca_2Sn (orange) and Ca_3SnO (cyan) phases. Inset shows detailed regions of the diffractograms and changes in intensities caused by oxidation.

the sample was covered by Apiezon N grease. Moreover, it is very probable that previous reported samples have different amount of oxidised phases. To our knowledge no XRD patterns were published for Ca_2Sn phases. XRD experiment shows that the thermal conductivity of material should stay at low level due to phonon scattering on concurrent phases.

TABLE I

Lattice parameters of Ca_2Sn and Ca_3SnO phases.

Phase	a [Å]	b [Å]	c [Å]
Ca_2Sn	8.501	5.820	9.460
Ca_3SnO	4.834	4.834	4.834

Figure 2 shows thermal conductivity of the sample. Sudden drop of thermal conductivity below 75 K is visible due to the net effect. Below 75 K impurities and defects become the main limiting factor [13]. Electronic contribution to thermal conductivity was estimated using Wiedemann-Franz formula with the Sommerfeld value of the Lorenz number [13].

The lattice thermal conductivity dominates in whole temperature range. That result confirms earlier predictions [6-10] that the phonons are the main mechanism for thermal conductivity and thus lattice modification through reducing of material dimensionality is reasonable [7]. Moreover calculations show presence of soft phonons modes suppressing thermal energy in material [5, 6, 9]. The value of thermal conductivity is also low because of multiphase structure of the sample[11].

The resistivity of Ca_2Sn is shown in Fig. 3. It is large with the residual resistivity of about 75.22 mΩcm and typical metallic behaviour which can be fitted with Bloch-Grüneisen formula:

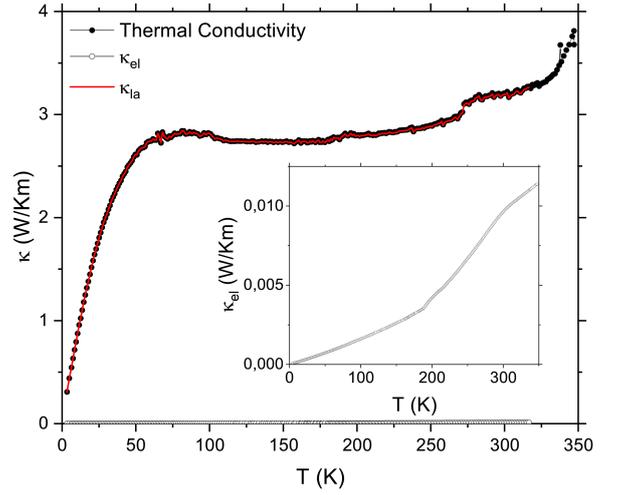


Fig. 2. Thermal conductivity of Ca_2Sn . Figure presents lattice κ_{la} (red line) and electronic contribution κ_{el} (black circles) to thermal conductivity κ . Inset displays electronic contribution κ_{el} in details.

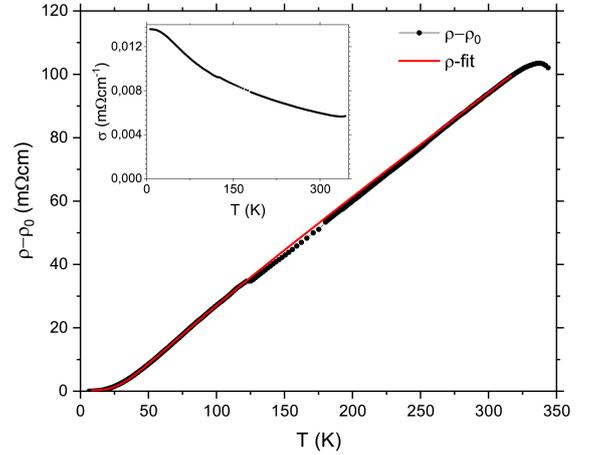


Fig. 3. Resistivity of Ca_2Sn reduced by value of residual resistivity (ρ_0) Red line represents Bloch-Grüneisen function fit to experimental data. Inset shows electrical conductivity of measured sample.

$$\rho(T) = \rho_0 + A \left(\frac{T}{\Theta_R} \right)^n \int_0^{\frac{\Theta_R}{T}} \frac{x^n}{(e^x - 1)(1 - e^{-x})} dx$$

TABLE II

Fitting parameters from Bloch-Grüneisen function where ρ_0 - residual resistivity, Θ_R — Debye temperature, n — interaction constant, A — constant.

ρ_0 [mΩcm]	A	Θ_R [K]	n
75.217	0.072	181.738	5

We clearly see that resistivity does not exhibit semi-conducting behaviour expected for material with high thermopower due to band-gap at Fermi level as predicted by Migas [10].

In Fig. 4 we present thermopower, which is positive. The sign of thermopower determines the type of the

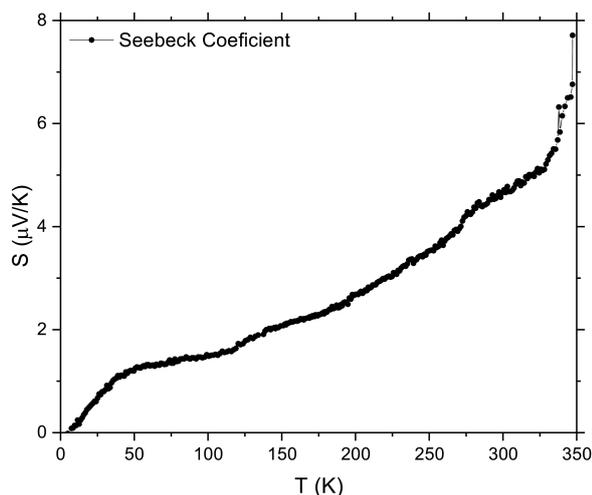


Fig. 4. Seebeck coefficient (thermopower) of Ca_2Sn .

majority carriers — here these dominant carriers are holes. At room temperature the thermopower S is about $4 \mu\text{V}/\text{K}$ whereas at 350 K the thermopower reaches $7 \mu\text{V}/\text{K}$. As the thermopower enters the ZT formula in squared form, the ZT calculated from these measurements is very low, of the order of 2.2×10^{-5} .

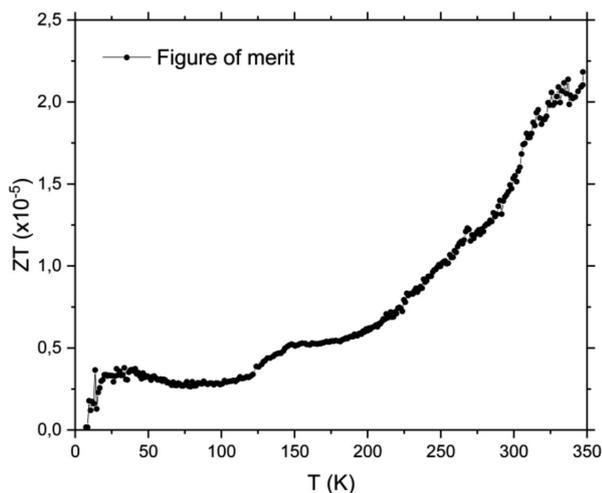


Fig. 5. Calculated thermoelectric figure of merit of Ca_2Sn .

4. Conclusions

Our experimental studies have shown that the Ca_2Sn prepared by arc melting possess significant amount of foreign phases and our sample in contrast to previous reports based on ab-initio calculations had very poor thermoelectric properties. It is caused by too high resistivity, and too small thermopower. The structure of the sample

was analyzed using XRD technique and shows multiphase structure, and high concentration of Ca_3SnO , perovskite phase. EDS analysis was not possible to perform, as our samples oxidized rapidly in air, and the protecting Apiezon N grese layer which we use to deter oxidation is dangerous for high vacuum instruments which uses ion pump like EDS.

The thermal conductivity have low value enough for good thermoelectric material. The thermopower of the disordered sample can be lower than a thermopower of a proper crystal, it is however not very probable that the difference is so large so that the material has S in the hundreds of $\mu\text{V}/\text{K}$ range.

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