Experimental report

20/09/2022

Proposal:	**7-01-564**	**Council:**	4/2021

Title: Inelastic neutron scattering studyof the lattice dynamics of the green semiconducting calcium silicidesfor thermoelectric applications

Research area: Materials

This proposal is a new proposal

Main proposer: **Doaa ALI**

Experimental team: Romain VIENNOIS

Local contacts: Michael Marek KOZA
Clemens RITTER

Samples: Ca3Si4
Ca14Si19

Instrument	Requested days	Allocated days	From	To
IN5	2	2	11/10/2021	13/10/2021
D2B	2	2	22/09/2021	24/09/2021
PANTHER	3	3	24/09/2021	27/09/2021

Abstract:

We wish to study the lattice dynamics, phonon anharmonicity, and structural characteristics of Ca3Si4 and Ca14Si19 by inelastic neutron scattering and neutron diffraction. Ca3Si4 and Ca14Si19 are semiconducting Zintl compounds showing electronic and transport properties marking them excellent materials for thermoelectric applications. One key feature contributing to their excellent thermoelectric behavior is their very low lattice thermal conductivity. To date, their depleted thermal transport has not been understood and only a few attempts have been undertaken to shed light on the microscopic mechanism of the low thermal conductivity. Here we ask for temperature-dependent inelastic and diffraction experiments to study the vibrational properties responsible for thermal transport in the compounds in every detail.

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Diffraction Instrument: Highest-resolution diffractometer D2b
INS Instruments: Cold and thermal time-of-flight spectrometers IN5, and PANTHER
T [K]: 10, 150, 300, 450, 550@D2b; 100, 200, 300, 400, 550@IN5; 2, 100, 200, 300@Panther
Incident E_i [meV]: $\approx$ 32.2@D2b(1.59 Å); 1.3, 3.3@IN5; 40, 76@PANTHER
Environment: CF Cryofurnace (D2b, IN5), CO Cryostat (Panther)
Samples: Ca_3Si_4 and $Ca_{14}Si_{19}$
Sample Can: Vanadium cylinder (D2b), niobium cylinder (IN5 and PANTHER)

The abundance, low cost, and non-toxicity of alkaline earth silicides have sparked high interest in thermoelectric material (TEM) research. Among those silicide compounds, Ca_3Si_4 and $Ca_{14}Si_{19}$ may be good TEM candidates due to their carrier concentration being within the semiconducting regime and their narrow electronic bandgaps of 0.56 and < 0.1 eV, respectively. Their structural complexity is supposed to promote a low lattice thermal conductivity k_l and raise their TEM figure of merit $ZT = S^2\sigma T/(k_\mathrm{e} + k_\mathrm{l})$ (S Seebeck coefficient, σ electronic condutivity, k_e electronic thermal conductivity, T absolute temperature). Notably, lattice dynamics calculations indicate the presence of non-propagating optical phonons in the energy range of the heat carrying acoustic phonons. Thus, the interaction of localized and propagating modes shall further enhance phonon-phonon scattering and reduce thermal transport. So far, no experimental studies have been carried out to shed light on the vibrational dynamics of these compounds nor on the response to temperature variation. Our measurements were intended to monitor structural and phonon properties from the base temperature, for the ground state properties of the compounds, up to the T regime of their potential applications.

The structural properties were investigated with the diffractometer D2b in the T range 10-550 K. The applied T points are detailed above. We indicate the quality of the data in Fig. 1 with the compound Ca_3Si_4. The phonon response was recorded at the spectrometers IN5 and PANTHER. PANTHER was utilized for monitoring ground state properties up to 300 K at the Stokes line with neutrons of incident energies of $E_\mathrm{i} = 40, 76$ meV. IN5 spectrometer was exploited for high-resolution spectra with $E_\mathrm{i} = 1.3, 3.3$ meV. Temperatures between 100 and 550 K were applied and the anti-Stokes line was analyzed.

Both powder specimens weighed $\approx$ 2.3 g. Standard cylindrical vanadium and niobium sample holders were utilized for the D2b and spectroscopy measurements, respectively. D2b data were measured for 4 hours each. The quality of the data allows to extract through Rietveld fits the cell parameters, fractional coordinates and isotropic thermal parameters with high precision. We confirm that the specimens consisted of 86 % Ca_3Si_4 and 14 % CaSi on one hand, and 91.2 % $Ca_{14}Si_{19}$ and 8.8 % CaSi, on the other hand.

The inelastic spectra were recorded between 2 and 4 hours with acquisition periods adapted to the counting statistics and, thus, the applied T. We indicate the data quality in Fig. 3 reporting the temperature evolution of the generalized density of states (GDOS) of Ca_3Si_4 followed at both spectrometers.

From the analysis of the data we conjecture that in the sampled temperature range the structural and vibrational properties of both compounds follow a quasi-harmonic behaviour. The temperature dependence of lattice and isotropic thermal parameters is sufficiently well approximated by our ab initio results. The recorded renormalization of characteristic phonon energies is in line with the detected volume expansion of the compounds.

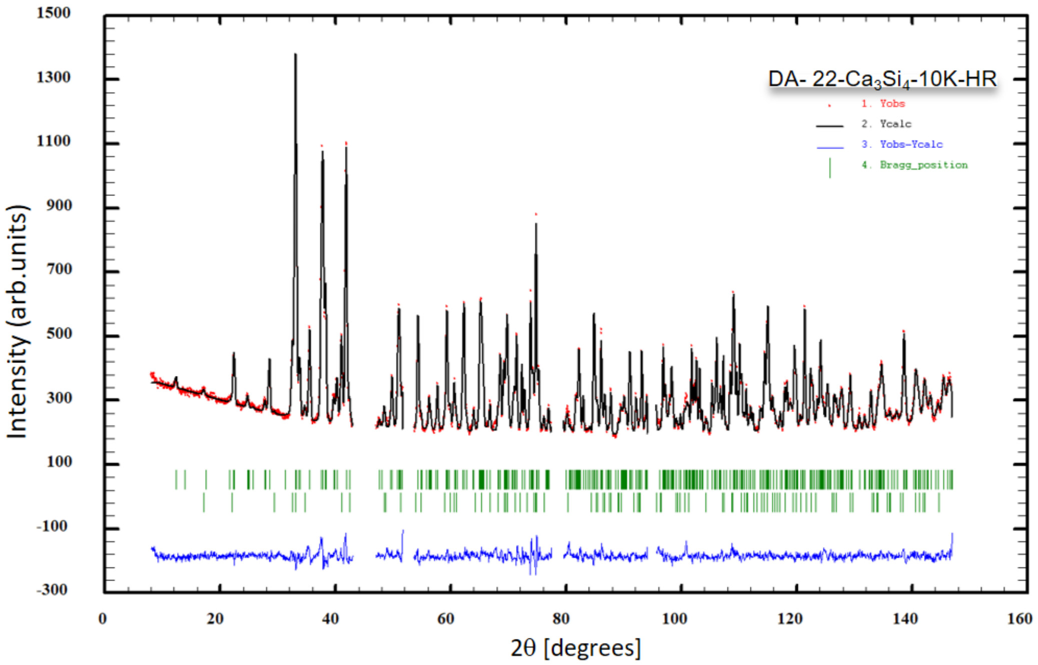

Figure 1: Diffraction data of Ca_3Si_4 recorded at D2b at $T = 10$ K. Rietveld fits to the data are indicated. Note that the specimen consisted of 86 % Ca_3Si_4 and 14 % CaSi.

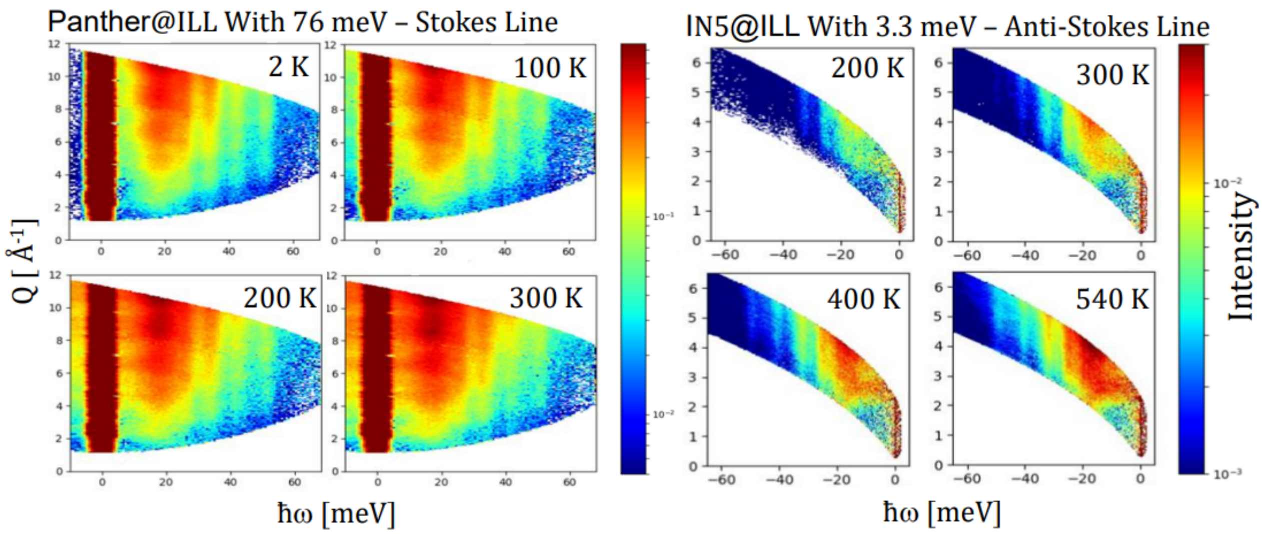

Figure 2: Signal evolution and phase space coverage with PANTHER (left panel) and IN5 (right panel) at the indicated temperatures for Ca_3Si_4.

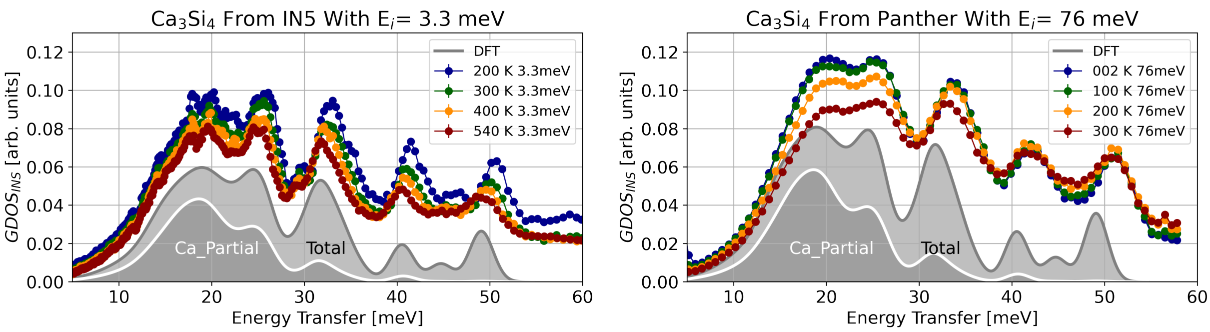

Figure 3: GDOS of Ca_3Si_4 from IN5 (left) and PANTHER (right). Our lattice dynamics results are indicated as gray-shaded areas. Data are broadened for the resolution of the applied PANTHER setup. Note the fine texture on the high-resolution IN5 response giving evidence of the complexity of the vibrational response in the acoustic phonon regime below 20 meV.