

Thermal Properties of Thermochemical Heat Storage Materials

Julianne E. Bird,^a Terry D. Humphries,^{a*} Mark Paskevicius^a, Lucas Poupin^a and Craig E. Buckley^a

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

The thermal conductivity, thermal diffusivity and volumetric specific heat of materials are all vital properties in the determination of the efficiency of a thermal system. However, the thermal transport properties of heat storage materials are not consistent across previous studies, and are strongly dependent on sample composition and measurement method. A comprehensive analysis of thermal transport properties using consistent preparation and measurement method is lacking. This study aims to provide the foundation for a detailed insight into thermochemical heat storage material properties with consistent measurement methods. The thermal transport properties of pelletised metal hydrides, carbonates and oxides were measured using the transient plane source method to provide the thermal conductivity, thermal diffusivity and volumetric heat capacity. This information is valuable in the development of energy storage and chemical processing systems that are highly dependent on the thermal conductivity of materials.

Introduction

Climate change is a subject undergoing intense study in scientific communities with a growing sense of urgency to take action.¹ With a major contributor of CO₂ being societal dependence on fuel, coal and 'dirty energy',²⁻⁴ international research is underway to investigate renewable, carbon neutral and carbon negative energy sources.⁵ Hence, the development of a sustainable and cost-efficient fuel source is a pressing issue in modern society. Many renewable energy sources have been explored although Concentrated Solar Power (CSP) coupled with thermochemical energy storage is a promising avenue for baseload 'green' energy.^{6,7}

To allow 24/7 energy production, thermal energy storage technology (or thermal batteries) have been implemented in CSP plants including the Crescent Dunes installation in Nevada, USA.⁸ Current thermal batteries utilise molten salts with a normal composition of 60:40 NaNO₃:KNO₃, but these degrade above 600 °C and so are limited to 565 °C. Increasing the maximum operating temperature of the thermal batteries would allow for an increased efficiency and as such second generation materials are being investigated. Thermochemical energy storage has been shown to have a greater energy density than the sensible heat storage of molten salts and is highly competitive in price.⁹⁻¹¹ Metal hydrides, carbonates and oxides have been shown to be ideal candidates by using their reversible gas storage reactions to store and release thermal energy and generate electricity^{10,12}. However, the efficiency of thermal exchange varies between different powder beds (i.e. packing densities).^{13,14} Hence, in the screening of materials for

large scale thermal storage operations, bulk thermal conductivity (λ) is a key property to be assessed.

Thermal conductivity is a material's ability to internally transfer heat due to the net flux from a hotter to a colder body (W/m.K),¹⁵ which operates with respect to the steady-state flow of heat via phonon interactions.¹⁶ The thermal conductivity of powder beds is called the effective conductivity.¹⁷ Thermal conductivity can be used in conjunction with thermal diffusivity to describe the thermal transport properties of materials. Thermal diffusivity is defined as the rate at which heat transfer occurs (m²/s).¹⁸ The relationship between crystalline density (ρ) and thermal conductivity is linear per Eq. 1.^{19,20} Hence, the thermal diffusivity (k) can also be calculated from the thermal conductivity (λ) and heat capacity per unit volume (C), Eq. 1.²¹

$$k = \frac{\lambda}{c} \quad (1)$$

The mechanism for thermal conductivity in solids is phonon propagation. Phonons interact via boundary scattering, mass-defect scattering and phonon-phonon scattering. Phonon interactions cause the thermal conductivity of a crystalline structure to vary along different crystallographic axes.²² At room temperature, anharmonic phonon scattering is a prominent mechanism in thermal conductivity as well as scattering mechanisms arising from crystalline imperfections.²³ These imperfections include point defects, as the defects influence host atoms due to mass differences and altered interatomic force constants.²³ Interstitial defects also affect the phonon scattering mechanisms, including vacant lattice sites and interstitial substitutions. Hence, the presence of defects in a sample's crystalline structure will affect its thermal conductivity, where increased scattering results in lower thermal conductivity. In anisotropic materials, such as polyimide film,²⁴ bonds that are aligned in the direction of phonon propagation allow for greater thermal conductivity.^{23,25,26}

In powders, lower thermal conductivities are expected when compared to single crystals due to the presence of voids that

^a Department of Physics and Astronomy, Fuels and Energy Technology Institute, Curtin University, GPO Box U1987, Perth, WA 6845, Australia.

* E-mail: terry_humphries81@hotmail.com

act to constrict heat flow between grains or fibres. In heat storage applications, particle refinement additives can be introduced at the sample preparation stage to affect particle morphology to improve gas release/absorption properties. These changes often adversely affect the thermal conductivity of materials such as metal hydrides, which can be overcome by introducing additional materials with favourable thermal transport properties, e.g. exfoliated natural graphite (ENG).²⁷⁻³⁰ In addition, a non-linear relationship between mole fraction of molten halide mixtures and thermal conductivity has been studied at 1100 K.³¹ Conversely, eutectic salt mixtures have been shown to feature a linear relationship between the mol.% of a LiNO₃-NaNO₃ system and its thermal conductivity.³² These studies suggest that the relationship between heterogeneous materials and their thermal transport properties are dependent on the material being studied.

To measure the thermal transport properties of a material, there are two broad methods: transient or steady state. Steady-state techniques perform measurements with a constant temperature difference, while transient methods perform *in-situ* measurements with transient temperature differences.³³ Determining which method to employ is dependent on the amount of sample and operational temperatures. For thermal characterisation of bulk material, both steady-state and transient methods can be employed, whereas thin-film measurements are conventionally measured with the transient method.

In steady-state measurements, a solid sample is heated at a constant rate from one side (steady state heat flow) while the temperature difference over a known perpendicular distance is measured. This process produces a temperature gradient, which is measured to calculate the thermal transport properties.³⁴ Steady state methods include heat flow meter (HFM), guarded hot plate (GHP), unguarded hot plate (UHP), and linear heat flow (LHF). This process can be used to measure thin film (via electrical heating methods) or bulk material (through the parallel conductance, absolute, comparative or radial heat flow methods).

In transient measurements, heat pulses are periodically applied to one end of a sample. This causes heat wave propagation, and consequentially an observable temperature difference between the ends. This temperature gradient is plotted against time to calculate the thermal conductivity. Transient methods include Angstrom, Time Domain Thermoreflectance (TDTR), Transient Plane Source (TPS) and Frequency Domain Thermoreflectance (FDTR).

Thermal transport properties are extremely susceptible to changes in applied pressure during sample preparation, composition (including purity, structure etc.), temperature, input power, and method of measurement. Often, thermal properties available in the literature are measured at incomparable temperatures, pressures, phases, or purities. Additionally, the thermal diffusivity of many materials has not yet been systematically studied by the transient plane source technique. This causes comparison between thermal properties to be extremely difficult. Table 1 displays a range of literature values available for materials of interest. The variability and

range of reported thermal properties is indicative of the difficulty in drawing comparisons between different systems based on literature data alone. The reporting of uncertainties is non-existent in most of the literature, and the report of significant figures varies between publications.

Experimental

The following chemicals were used as received with no additional purification: CaH₂ 95% purity, Sigma Aldrich; CaO reagent grade, Sigma Aldrich Australia; K₂CO₃ 99% purity, Sigma Aldrich; KBH₄ 99.9 % purity, Sigma Aldrich; LiBH₄ 90% purity, Sigma Aldrich; LiH 95% purity from Sigma Aldrich; Na₂CO₃ 99.5% purity, Sigma Aldrich; NaAlH₄ 93% purity, Sigma Aldrich; NaBH₄, 99% purity, Sigma Aldrich; NaF >99% purity, Sigma Aldrich; NaH 95% purity, Sigma Aldrich.

The synthesis and manipulation of the following metal hydride compounds was undertaken in an argon atmosphere using an Mbraun Unilab glovebox to prevent air exposure and to minimize oxygen (O₂ < 1 ppm) and water (H₂O < 1 ppm) contamination. LiAlH₄ (95% purity from Sigma Aldrich) was purified by soxhlet extraction with diethylether. Mg₂FeH₆ was synthesised by reacting 2 moles of Mg (Sigma-Aldrich, >99%, powder) with one mole of Fe (Sigma-Aldrich, >99%, powder). The mixture was ball milled for 2 hours, under an argon atmosphere, in a 316 stainless steel Turbula T2C shaker mill with a ball to powder ratio of 5:1. The milled powder was then placed in a 316 stainless steel reactor and cycled 3 times at 460 °C with absorption carried out under 60 bar H₂ pressure and desorption under dynamic vacuum. Mixtures of Mg₂FeH₆ with additional Fe (10 wt % and 25 wt % Fe) were prepared by manually mixing the relevant ratios of Mg₂FeH₆ and Fe. NaMgH₃ was synthesised by first ball milling, an equimolar mixture of NaH and Mg, using stainless steel vials and balls. The ball to powder ratio was 30:1 and the process was performed in an Across International Planetary Ball Mill (PQ-N04), under argon for 240 min. NaMgH₃ formation was observed after annealing the reactants at 380 °C under a minimum pressure of 20 bar H₂ for 6 hours. For samples tailored with exfoliated natural graphite (ENG, 2.5–10 mm, SGL carbon), the addition was prior to the ball milling step. The ENG was previously outgassed for 12 h at 500 °C under dynamic vacuum.

A TPS 500S (Hot Disk, Thermtest) was used for thermal analysis, featuring a double nickel spiral sensor, laminated by electrically insulating Kapton. A C7577 (2 mm radius) sensor was employed and calibrated using stainless steel, polystyrene and NaCl standards. All measurements were conducted in an argon filled glove box.

The required pellet volume was calculated using the target probing depth, which is based on the sensor radius. The probing depth (d_p) of the heat wave is constrained by the sample thickness (h), dye diameter (D) and the sensor radius (r),²¹

$$r \leq h \leq 2 \cdot r \quad (2)$$

$$4 \cdot r \leq D \leq 6 \cdot r \quad (3)$$

$$d_p = \frac{D}{2} - r = h \quad (4)$$

ARTICLE

Table 1. Literature values of thermochemical heat storage materials with thermal conductivity (λ), thermal diffusivity (k), heat capacity per unit volume (C) and crystallographic density (ρ). C_p is the specific heat capacity.

Material	λ (W/m.K)	k (mm ² /s)	C (MJ/m ³ .K)	ρ (g/cm ³)	Notes
BaH ₂	–	–	1.37 ³⁵	4.16 ³⁵	<ul style="list-style-type: none"> 1.37 MJ/m³.K calculated at 298 K using $C_p = 46.0$ J/mol.K using $\rho = 4.16$ g/cm³.³⁵
CaCO ₃	2.259 ³³	1.04 ³³	2.18 ³³	2.61 ³³	<ul style="list-style-type: none"> –
CaH ₂	–	–	1.66 ³⁵	1.7 ³⁵	<ul style="list-style-type: none"> 1.66 MJ/m³.K calculated at 298 K using $C_p = 41.0$ J/mol.K using $\rho = 1.7$ g/cm³.³⁵
CaMg(CO ₃) ₂	2.929 – 5.1 ^{33, 36}	1.18 ³³	–	2.7 ³³	<ul style="list-style-type: none"> 5.1 W/m.K, 3.1 W/m.K: at 313.65 K (dry air saturated samples) for medium (10 – 60 μm pore size) and fine grain (0.01 – 1 μm pore size) respectively.³⁶
CaO	0.318 – 13.807 ³³	0.25 – 6.05 ³³	1.28 – 2.51 ^{33, 35, 37}	3.34 ^{35, 37}	<ul style="list-style-type: none"> 0.318 W/m.K; 0.25 mm²/S; 1.28 MJ/m³.K calculated from $C_p = 0.753$ J/g.K and $\rho = 1.7$ g/cm³ for a packed powder.³³ 13.807 W/m.K; 6.05 mm²/S; 2.28 MJ/m³.K calculated from $C_p = 0.753$ J/g.K and $\rho = 3.03$ g/cm³ for a pressed powder.³³ 2.51 MJ/m³.K: at room temperature, calculated using C_p of 0.75 J/g.K and ρ of 3.37 g/cm³. C_p measured using DSC, STA and LFA.³⁷ 2.51 MJ/m³.K calculated at 298 K using $C_p = 42$ J/mol.K using $\rho = 3.34$ g/cm³.³⁵
Fe	72.0 – 72.4 ^{33, 38}	20.4 ³³	3.54 ³⁵	7.87 ³⁵	<ul style="list-style-type: none"> 3.5 MJ/m³.K calculated at 298 K using $C_p = 25.1$ J/mol.K using $\rho = 7.87$ g/cm³.³⁵ 72.4 W/m.K measured at 303.15 K, using the absolute radial heat flow method.³⁸
K	35.4 – 44.9 ³⁹	–	–	0.700 – 0.795 ³⁹	<ul style="list-style-type: none"> 35.4 W/m.K: at 873 K and 44.9 W/m.K: at 473 K.³⁹
K ₂ CO ₃	–	–	1.90 ³⁵	2.29 ³⁵	<ul style="list-style-type: none"> 0.11 MJ/m³.K calculated at 298 K using $C_p = 114.4$ J/mol.K using $\rho = 2.29$ g/cm³.³⁵
KBH ₄	0.96 ⁴⁰	–	1.98 ³⁵	1.11 ³⁵	<ul style="list-style-type: none"> 0.96 W/m.K: at 300 K.⁴⁰ 1.98 MJ/m³.K calculated at 298 K using $C_p = 96.1$ J/mol.K using $\rho = 1.11$ g/cm³.³⁵
LiAlH ₄	0.09 – 0.28 ⁴¹	–	2.01 – 2.03 ^{35, 41}	0.917 ³⁵	<ul style="list-style-type: none"> 0.09 W/m.K: powder using modified transient plane source by C-Therm TCi Thermal Conductivity analyser.⁴¹ 0.28 W/m.K: powder pressed with 6 tonnes using modified transient plane source by C-Therm TCi Thermal Conductivity analyser.⁴¹ 2.03 MJ/m³.K measured at 298.3 K by DSC calculated using 84.22 J/mol.K⁴¹ using $\rho = 0.917$ g/cm³.³⁵ 2.01 MJ/m³.K calculated at 298 K using $C_p = 83.2$ J/mol.K using $\rho = 0.917$ g/cm³.³⁵
LiBH ₄	1.23 – ~2.8 ^{40, 42}	–	2.50 – 5.36 ^{35, 42}	0.67 ³⁵	<ul style="list-style-type: none"> 1.23 W/m.K: at 300 K.⁴⁰ ~2.8 W/m.K: at ~340 K of 99 % purity using hot wire method.⁴² 4.4 to 5.4 MJ/m³.K: ⁴² at 340 K of 99 % purity using hot wire method and $\rho = 0.66$ g/cm³.³⁵ 2.50 MJ/m³.K calculated at 298 K using $C_p = 82.6$ J/mol.K using $\rho = 0.66$ g/cm³.³⁵

LiH	6.95 – 15.06 ⁴³⁻⁴⁶	–	2.83 ⁴⁴	0.78 ³⁵	<ul style="list-style-type: none"> 6.95 W/m.K: compact LiH at 323.15 K in hydrogen using axial heatflux.^{43, 44} 7.28 W/m.K: converted from 6.26 kcal/mh.°C solid LiH⁴³ using radial heat flux in helium. 7.49 W/m.K: converted from 0.075 W/cm.°C at 323.15 K⁴⁵ in helium using radial heat flux.⁴⁴ 12.49: W/m.K: converted from 0.125 W/cm.°C crystal LiH at 323.15 K⁴³ in hydrogen using axial heat flux.⁴⁴ 15.06 W/m.K: cold pressed LiH.⁴⁶ 2.74 MJ/m³.K calculated at 298 K using $C_p = 27.9$ J/mol.K using $\rho = 0.78$ g/cm³.³⁵
MgH ₂	0.4 – 1.21 ⁴⁷⁻⁴⁹	–	1.95 ³⁵	1.45 ³⁵	<ul style="list-style-type: none"> 0.40 W/m.K: nanocrystalline, with DSC.⁴⁷ 0.70 W/m.K: 100 MPa compressed MgH₂ pellet.⁴⁸ 1.21 W/m.K: 100 MPa compressed MgH₂ pellet, cold rolled and ball milled (30 minutes) (rolled sample was reduced to powder after rolling).⁴⁹ 1.95 MJ/m³.K calculated at 298 K using $C_p = 35.4$ J/mol.K using $\rho = 1.45$ g/cm³.³⁵
MgCO ₃			2.70 ³⁵	3.01 ³⁵	<ul style="list-style-type: none"> 2.70 MJ/m³.K calculated at 298 K using $C_p = 75.5$ J/mol.K using $\rho = 3.01$ g/cm³.³⁵
MgH ₂ + ENG	1.2 – 9.3 ^{14, 48, 50, 51}	–	–	–	<ul style="list-style-type: none"> 1.20 W/m.K: axial conductivity of 100 MPa compressed MgH₂ pellet with 5 wt % ENG.⁴⁸ 1.50 W/m.K: axial thermal conductivity of 100 MPa compressed MgH₂ disk with ENG.⁴⁸ 1.60 W/m.K: with 10 wt % ENG.⁴⁸ 1.77 W/m.K: with 10 wt % ENG at 100 MPa and under 0.4 MPa H₂.¹⁴ 1.90 W/m.K: radial thermal conductivity of uniaxially compressed compacts + ENG flakes (average size = 200 μm) with 1 bar hydrogen pressure.⁵⁰ 1.90 W/m.K: with 10 wt % ENG 100 MPa in air and <1 bar H₂.¹⁴ 3.40 W/m.K: radial thermal conductivity of uniaxially compressed compacts + ENG flakes (average size=200 μm) with 1 bar hydrogen pressure.⁵⁰ 4.20 W/m.K: radial thermal conductivity of 100MPa compressed MgH₂ pellet 5 wt % ENG.⁴⁸ 4.40 W/m.K: radial thermal conductivity of uniaxially compressed compacts + ENG flakes (average size=200 μm) with 1 bar hydrogen pressure.⁵⁰ 7.60 W/m.K: radial thermal conductivity of 100 MPa compressed MgH₂ disk with ENG.⁴⁸ 8.60 W/m.K: mechanically mixed with 25 w.t% graphene.⁵¹ 9.00 W/m.K: with 20 wt % ENG 100 MPa in air and < 1 bar H₂.¹⁴ 9.30 W/m.K: augmented with compacts at 1 bar hydrogen with ENG flakes (20 wt % ENG).⁵⁰
MgO	29.4 – 61.923 ^{33, 52}	18.8 ³³	3.3	3.58 ^{33, 52}	<ul style="list-style-type: none"> 29.4 W/m.K at 397.8 K; 12.3 W/m.K at 897.3 K.⁵² One sided hot plate. Sintered disks of polycrystalline MgO. 61.923 W/m.K, 18.8 mm²/s, 3.58 g/cm³: Polyxtal 100D.³³ 3.3 MJ/m³.K calculated at 298 K using $C_p = 37.2$ J/mol.K using $\rho = 3.58$ g/cm³.³⁵
Na	66.8 – 181 ^{39, 53}	–	–	0.731 – 0.903 ³⁹	<ul style="list-style-type: none"> 128.2 W/m.K at 360 K, 141.0 W/m.K at 280 K and 181 W/m.K at 40 K.⁵³ 81.5 W/m.K at 473 K and 66.8 W/m.K at 773 K³⁹
Na ₂ CO ₃	0.83 ⁵⁴	0.34 ⁵⁴	2.44 – 2.69 ^{35, 54}	2.54 ³⁵	<ul style="list-style-type: none"> 2.69 MJ/m³.K calculated at 298 K using $C_p = 106.0$ J/mol.K using $\rho = 2.54$ g/cm³.³⁵

NaAlH ₄	0.06 – 4.5 ^{40, 41,} 55-59	1.23 ^{40, 60}	0.11 – 1.98 ^{35, 41, 60}	1.24 ³⁵	<ul style="list-style-type: none"> 0.06 W/m.K: powder using modified transient plane source by C-Therm TCi Thermal Conductivity analyser.⁴¹ 0.20 W/m.K: during sorption of hydrogen from powdered sodium alanate.⁵⁵ 0.21 W/m.K: powder pressed with 6 tonnes using modified transient plane source by C-Therm TCi Thermal Conductivity analyser.⁴¹ 0.35 to 0.50 W/m.K: non-catalysed alanate powder.⁵⁶ 0.40 to 0.60 W/m.K: 293.15 K to 513.15 K at pressures 1 to 100 bar with platinum transient hot wire method.⁵⁷ 0.50 W/m.K: 9.5 diameter pellet, powder form with 63.3 % void volume.⁵⁸ 0.51 W/m.K: thermal conductivity averaged over 5 cycles with 1 atm H₂ using thermal probe method in powder form.⁵⁵ 0.8 to 1.2 W/m.K: 303.15 to 473.15 K at pressures 1 to 50 bar with nichrome transient hot wire method.⁵⁹ 2.48 W/m.K: 9.5 mm diameter pellet, 69 MPa die pressure with 42.5 % void volume.⁵⁸ 4.5 W/m.K: 9.5 mm diameter pellet, 138 MPa die pressure with 38.4 % void volume.⁵⁸ 1.94 W/m.K: at 300 K, extrapolated to atmospheric pressure.⁴⁰ 1.23 mm²/s: calculated from refs [40] and [60]. 1.96 MJ/m³.K: C_p of 85.51 J/mol.K⁶⁰ converted to MJ/m³.K using $\rho = 1.24 \text{ g/cm}^3$.³⁵ 1.98 MJ/m³.K: at 298.3 K using modified transient plane source by C-Therm TCi Thermal Conductivity analyser⁴¹ presented as 1.60 J/g.K converted to MJ/m³.K using $\rho = 1.24 \text{ g/cm}^3$.³⁵ 1.98 MJ/m³.K: at 298.3 K using DSC⁴¹ presented as 86.24 J/mol.K converted to MJ/m³.K using $\rho = 1.24 \text{ g/cm}^3$.³⁵
NaBH ₄	0.96 ⁴⁰	–	2.45 ³⁵	1.07 ³⁵	<ul style="list-style-type: none"> 0.96 W/m.K: at 300 K.⁴⁰ 2.45 MJ/m³.K calculated at 298 K using C_p = 86.8 J/mol.K using $\rho = 1.07 \text{ g/cm}^3$.³⁵
NaCl	4.12 – 8.16 ^{33, 61-} 66	2.93 – 7.82 ^{33, 63-} 67	0.77 – 2.26 ^{33, 35}	2.16 – 2.17 ^{35, 63}	<ul style="list-style-type: none"> 4.12 W/m.K: at 382 K, using a steady state method.⁶¹ 5.79 W/m.K: 0.1 MPa stress and by calculating C_p with $\rho = 2164 \text{ kg/m}^3$⁶³ and C_p = 850.2 J/kg.K⁶⁷ 6.02 W/m.K: Using transient hot wire method, 0 to 2 MPa, powders of ≥ 99.5 % purity⁶⁶ dried at 473.15 K (for 24 h) in a vacuum oven and then compacted in a steel die (0.1 GPa) forming polycrystalline plates then dried. Performed in an argon atmosphere glove box in the presence of P205.⁶⁴ 7.50 W/m.K: Avery Island Salt, 99.1 % NaCl, 0.7 % water insoluble, 0.2 % CaSO₄, 0.02 % water, at 10 MPa.⁶⁵ 4.80 mm²/s: Avery Island Salt, 99.1 % NaCl, 0.7 % water insoluble, 0.2 % CaSO₄, 0.02 % water, at 10 MPa.⁶⁵ 7.82 mm²/s: calculated using values for λ and C_p (6.02 W/m.K and 0.77 MJ/m³.K respectively).⁶⁴ 0.77 MJ/m³.K: Using transient hot wire method, 0 to 2 MPa, powders of ≥ 99.5 % purity,⁶⁶ dried at 473.15 K (24h), compacted in a steel die (0.1 GPa) forming polycrystalline plates then dried. Performed in an argon atmosphere glove box in the presence of P205.⁶⁴ 1.59 MJ/m³.K: calculated using C_p = 770 J/kg.K and $\rho = 2070 \text{ kg/m}^3$.³³ 1.84 MJ/m³.K: 0.1 MPa stress and by calculating C_p with $\rho = 2164 \text{ kg/m}^3$⁶³ and C_p = 850.2 J/kg.K.⁶⁷ 1.88 MJ/m³.K: Opaque Impure crystal, calculated using C_p = 870 J/kg.K and $\rho = 2165 \text{ kg/m}^3$.³³ 1.88 MJ/m³.K: Clear crystal, calculated using C_p = 870 J/kg.K and $\rho = 2165 \text{ kg/m}^3$.³³ 2.26 MJ/m³.K calculated at 298 K using C_p = 50.5 J/mol.K using $\rho = 2.17 \text{ g/cm}^3$.³⁵
NaF	10.502 ³³	3.69 ³³	2.85 – 3.10 ^{33, 35}	2.558 – 2.78 ^{33, 35}	<ul style="list-style-type: none"> 2.847 MJ/m³.K calculated using C_p = 1113 J/kg.K using $\rho = 2.558 \text{ g/cm}^3$.³³ 3.10 MJ/m³.K calculated at 298 K using C_p = 46.9 J/mol.K using $\rho = 2.78 \text{ g/cm}^3$.³⁵
NaH	–	–	0.49 – 50.95 ⁶⁸⁻⁷¹	1.4 ^{69, 70}	<ul style="list-style-type: none"> 2.12 MJ/m³.K: calculated using 36.37 J/mol.K⁶⁸ and $\rho = 1.4 \text{ g/cm}^3$.^{69, 70} 0.49 MJ/m³.K: C_p of 0.35 J/g.K⁷¹ $\rho = 1.4 \text{ g/cm}^3$.^{69, 70}

SrCO ₃	1.90 ³⁵	3.785 ³⁵	• 1.90 MJ/m ³ .K calculated at 298 K using $C_p = 81.4$ J/mol.K using $\rho = 3.785$ g/cm ³ . ³⁵
-------------------	--------------------	---------------------	---

The volume of the cylindrical pellet is determined by,

$$V = \pi hr^2 \quad (5)$$

The measured probing depth can be used to calculate the thermal diffusivity (k) of the sample ²¹, where t is the sampling time,

$$d_p = 2\sqrt{k \cdot t} \quad (6)$$

This relationship can be represented in terms of the sensor radius,²¹

$$2 \cdot r = 2\sqrt{k \cdot t} \quad (7)$$

$$\frac{r^2}{t} = k \quad (8)$$

Finally, the input power can be calculated using three different methods. For a highly conducting sample, the input power can be determined by,²¹

$$P = \frac{2\pi^2 r \lambda}{50000} \quad (9)$$

For a poorly conducting sample, the input power can be found by,²¹

$$P = \frac{\pi^2 r \lambda}{100} \quad (10)$$

For all other materials, the input power can be calculated by,²¹

$$P = \frac{\pi^2 r \lambda}{500} \quad (11)$$

In these measurements, the transient plane source (TPS) method was adopted. The TPS method measures the thermal conductivity, diffusivity, and volumetric heat capacity with small sample masses (approximately 1.5 g per pellet). The planar Kapton sensor is sandwiched between two isothermal sample pellets (treated as a bulk sample measurement). By increasing the input current, the TPS records the sensor's resistance and temperature increase. This allows the thermal conductivity, thermal diffusivity and volumetric heat capacity to be calculated from a single transient recording. This method assumes that the sensor is in an infinite medium, and that there is a relationship between diffusivity, measurement time and sensor radius.

Prior to analysis, all commercial materials were ground using a mortar and pestle until a consistently fine powder resulted. Using a 13 mm diameter die and 2 mm radius sensor, approximately 4 mm of radial probing depth and height is required per pellet (see Eq. 6). Each pellet was pressed using a manual hydraulic press with 370 MPa of pressure for 5 minutes. The pellets have an apparent density of 80% ± 10% of the crystalline density. Measurements were undertaken in an argon-atmosphere at ambient temperature, measured by an

external thermocouple. The Kapton sensor was lightly clamped concentrically between two pellets of test material.

In these experiments, the geometric mean of the axial thermal conductivity, diffusivity and volumetric specific heat (in the probed sample volume), and the standard deviations were calculated by the TPS software (Hot Disk, Sweden). A radial flow method was applied to avoid the low temperature issues with a longitudinal method.³⁴ Samples were measured over 2.5 s at 0.133 W. Ten thermal transport property measurements per sample were conducted with the TPS, with 15 minutes wait time between each measurement to allow the sample and sensor to cool to a steady-state.

Results and Discussion

The thermal conductivities (λ), thermal diffusivities (k), heat capacity per unit volume (C) of various relevant compounds were measured and are presented in Table 2. The values reported in this study allow a direct comparison between materials due to the identical method of sample preparation and measurement environment, whereas previous studies have been conducted under incomparable conditions.

The majority of the materials measured in this study hold potential application as thermal energy storage materials. Therefore a relatively high thermal conductivity value is required for heat to be transferred effectively in and out of the materials so that energy can be generated upon demand. Very little information has been published on determining a threshold limit of λ for powder bed applications although a study on a hydrogenated sample of LaNi_{4.9}Al_{0.3} determined that 5 W/m.K allows for optimal hydrogen absorption kinetics, while a larger value only has a minor incremental influence.⁷² As can be seen from Table 2 the values for materials without additives range from 0.55 W/m.K for K₂CO₃ to 11.0 W/m.K for LiH. Despite the majority of the materials measured in this study being below 5 W/m.K, the λ of the material will alter upon desorption/absorption of gas. Metal hydrides often decompose into metals of metallic alloys,^{11, 73, 74} which will likely improve the thermal transfer within the powder bed during technological application. For instance, Mg₂FeH₆ has a thermal conductivity of 1.80 ± 0.02 W/m.K, while this increases to 2.20 ± 0.04 W/m.K in its metallic form (2Mg + Fe) at room temperature. One further example is sodium hydride which has a $\lambda = 5.00 \pm 0.07$ W/m.K at room temperature, but upon hydrogen release at ~500 °C,⁷⁵ Na is formed which has a $\lambda = 66.8 \pm 0.7$ W/m.K at 500 °C.³⁹

Compared to many of the materials measured in this study, sodium hydride has a respectable λ of 5.00 ± 0.07 W/m.K. However, other sodium hydride based materials including sodium borohydride or sodium aluminium hydride have a lower λ of 0.97 ± 0.01 W/m.K and 1.90 ± 0.02 W/m.K, respectively.

This is due to the phonon interactions within the compound and the high symmetry possessed by the heteronuclear diatomic molecule of NaH, which resides in a cubic crystallographic space group. This observation is reinforced by the measured thermal conductivity of NaF of 9.4 ± 0.1 W/m.K, which is higher than NaH due to the fact that NaF has a greater ionic character than NaH.⁷⁶

Methods to increase thermal transport in poorly conducting powder beds have been investigated including with the addition of materials with higher λ . Graphite or exfoliated natural graphite (ENG) have been the material of choice in many studies,^{9, 14, 48, 77} while Al foams and metal fins have also been investigated.⁷⁸ In this study, ENG was added to Mg₂FeH₆. An increase in the thermal conductivity from $\lambda = 1.80 \pm 0.02$ W/m.K for the pure hydride, to $\lambda = 4.43 \pm 0.05$ W/m.K and 6.76 ± 0.03 W/m.K resulted for 5 and 10 wt% ENG equivalents, respectively. Addition of 20 wt% ENG to NaMgH₃ also caused an increase in thermal conductivity, with an improvement from 1.90 ± 0.02 to 5.15 ± 0.07 W/m.K. These results agree well with those measured by Chaise *et al.*, who noted a linear increase of thermal conductivity with mass ratio of ENG when added to MgH₂.⁴⁸ It was previously considered that the addition of ENG is only effective if the sample is compressed and the effect is also unidirectional.⁴⁸ For instance, if MgH₂ is measured as an uncompressed powder without ENG, $\lambda = 0.65$ W/m.K (measured under 1 bar H₂)¹³ and $0.1337(6)$ W/m.K with 20 wt% ENG and 2 mol% TiB₂ (measured under Ar background).¹⁴ Although λ is greater without ENG, the difference between the values is small and is attributed to the greater thermal conductivity of H₂ (0.182 W/m.K at 1 bar) compared to Ar (0.017 W/m.K).^{50, 79, 80}

The unidirectional effect on thermal conductivity on MgH₂ pellets containing 10 wt% ENG is exemplified with radial $\lambda = 7.5$ W/m.K, whereas axial $\lambda = 1.6$ W/m.K, which is attributed to the alignment of the ENG flakes during compression. This effect is not encountered in this present study and in fact, ENG particle size may have a larger effect than previously assumed. The ENG particle size used by Chaise *et al.* was on the millimetre scale,⁴⁸ whilst being micrometre in this study. This means that the graphite particles are less likely to organise in parallel to the compression axis.

An excess of iron in Mg₂FeH₆ has also been investigated to potentially improve thermal conductivity. However, the addition of up to 25 wt% did not cause an increase in λ . As the density of iron is almost three times greater than the density of Mg₂FeH₆ (7.87 and 2.74 g/cm³, respectively),^{35, 81} the volume of iron in excess seems negligible as to have a significant impact on the heat transfer in the compressed hydride.

Conclusions

The axial thermal conductivity, thermal diffusivity and volumetric heat capacity of various metal hydrides, carbonates and oxides were measured using a TPS 500S. Each material was measured under identical conditions allowing a direct comparison between materials that was not previously possible. The majority of results previously reported have been under a variety of conditions including atmosphere, compression and temperature, all of which greatly affect the thermal transport properties of materials. In addition to the

Table 2: Thermal conductivity (λ), thermal diffusivity (k), heat capacity per unit volume (C) and crystallographic densities (ρ) of selected materials. Standard deviations are in parentheses.

Material	λ (W/m.K)	k (mm ² /s)	C (MJ/m ³ .K)	ρ (g/cm ³)
CaH ₂	3.10 (± 0.07)	1.8 (± 0.1)	1.7 (± 0.2)	1.90 ^a
CaO	0.83 (± 0.01)	0.40 (± 0.02)	2.10 (± 0.09)	3.34 ^a
K ₂ CO ₃	0.55 (± 0.01)	0.37 (± 0.02)	1.50 (± 0.07)	2.29 ^a
KBH ₄	1.03 (± 0.01)	0.70 (± 0.01)	1.50 (± 0.03)	1.11 ^a
LiAlH ₄	1.30 (± 0.01)	0.66 (± 0.04)	1.9 (± 0.1)	0.917 ^a
LiBH ₄	1.30 (± 0.01)	0.54 (± 0.05)	2.4 (± 0.2)	0.67 ^a
LiH	11.0 (± 0.3)	1.1 (± 0.2)	9.0 (± 0.1)	0.78 ^a
2 Mg + Fe	2.20 (± 0.04)	1.8 (± 0.1)	1.20 (± 0.08)	2.98 ^a
Mg ₂ FeH ₆	1.80 (± 0.02)	1.29 (± 0.07)	1.39 (± 0.07)	2.74 ^b
Mg ₂ FeH ₆ + 10 wt% Fe	1.72 (± 0.03)	1.4 (± 0.1)	1.3 (± 0.1)	-
Mg ₂ FeH ₆ + 25 wt% Fe	1.73 (± 0.03)	1.45 (± 0.08)	1.20 (± 0.08)	-
Mg ₂ FeH ₆ + 5 wt% ENG	4.43 (± 0.05)	2.57 (± 0.08)	1.73 (± 0.07)	-
Mg ₂ FeH ₆ + 10 wt% ENG	6.76 (± 0.03)	1.8 (± 0.2)	3.7 (± 0.3)	-
Na ₂ CO ₃	0.56 (± 0.01)	0.36 (± 0.02)	1.60 (± 0.08)	2.54 ^a
NaAlH ₄	1.90 (± 0.02)	0.88 (± 0.06)	2.2 (± 0.2)	1.24 ^a
NaBH ₄	0.97 (± 0.01)	0.40 (± 0.03)	2.4 (± 0.1)	1.07 ^a
NaF	9.4 (± 0.1)	1.8 (± 0.2)	5.5 (± 0.6)	2.78 ^a
NaH	5.00 (± 0.07)	1.1 (± 0.1)	4.7 (± 0.4)	1.39 ^a
NaMgH ₃	1.90 (± 0.02)	3.2 (± 0.2)	0.58 (± 0.04)	1.47 ^c
NaMgH ₃ + 20 wt% ENG	5.15 (± 0.07)	2.16 (± 0.14)	2.4 (± 0.2)	-

^a Ref 35; ^b Ref 81; ^c Ref 82

Journal Name

ARTICLE

characterisation of pure materials, the enhancement of thermal transport properties was also examined using additives. A compilation of literature values is also reported, allowing for a comparison between the results collated in this study. With the high precision of these experimental results, a more streamlined material selection processes and in-depth analysis of thermal energy storage materials is possible. This information will enable rational selection and design of better thermal energy storage systems.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

CEB, LP and TDH acknowledge the financial support of the Australian Research Council for ARC Linkage grant LP150100730. CEB and MP acknowledge the financial support of the ARC for DP150101708. CEB, TDH, MP and MVS acknowledge financial support from the Department of Industry Innovation and Science for the 2019 Global Innovation Linkage (GIL73589) grant. JB acknowledges the Department of Physics and Astronomy at Curtin University for providing support through the Summer Physics and Astronomy Scholarship. MP acknowledges the financial support of ARC Future Fellowship FT160100303.

Notes and references

- W. N. Adger, in *Der klimawandel*, VS Verlag für Sozialwissenschaften, 2010, pp. 327-345.
- R. Ewing, K. Bartholomew, S. Winkelman, J. Walters, D. Chen, B. McCann and D. Goldberg, *Ann Trop Med Parasitol*, 1997, **71**, 219-226.
- N. P. Myhrvold and K. Caldeira, *Environ. Res. Lett.*, 2012, **7**, 014019.
- B. K. Bose, *IEEE Trans. Ind. Electron.*, 2010, **4**, 6-17.
- United Nations, Paris Agreement*, Le Bourget, 2015.
- A. Z'Graggen, P. Haueter, D. Trommer, M. Romero, J. C. de Jesus and A. Steinfeld, *Int. J. Hydrogen Energy*, 2006, **31**, 797-811.
- D. N. Harries, M. Paskevicius, D. A. Sheppard, T. E. C. Price and C. E. Buckley, *Proc. IEEE*, 2011, **100**, 539-549.
- U. S. Department of Energy, Report - 'Sunshot Vision Study', 2012, <http://energy.gov/eere/sunshot/downloads/sunshot-vision-study-february-2012-book-sunshot-energy-efficiency-renewable>, (accessed 06/05/2019).
- L. Poupin, T. D. Humphries, M. Paskevicius and C. E. Buckley, *Sustain Energy Fuels*, 2019, **3**, 985-995.
- K. Manickam, P. Mistry, G. Walker, D. Grant, C. E. Buckley, T. D. Humphries, M. Paskevicius, T. Jensen, R. Albert, K. Peinecke and M. Felderhoff, *Int. J. Hydrogen Energy*, 2019, **44**, 7738-7745.
- D. A. Sheppard, M. Paskevicius, T. D. Humphries, M. Felderhoff, G. Capurso, J. B. von Colbe, M. Dornheim, T. Klassen, P. A. Ward, J. A. Teprovich, C. Corngale, R. Zidan, D. M. Grant and C. E. Buckley, *Appl. Phys. A*, 2016, **122**, 395.
- K. T. Møller, T. R. Jensen, E. Akiba and H.-w. Li, *Prog. Nat. Sci.*, 2017, **27**, 34-40.
- R. Albert, R. Urbanczyk and M. Felderhoff, *Int. J. Hydrogen Energy*, 2019, **44**, 29273-29281.
- D. Dong, T. D. Humphries, D. A. Sheppard, B. Stansby, M. Paskevicius, M. V. Sofianos, A.-L. Chaudhary, M. Dornheim and C. E. Buckley, *Sustain. Energy Fuels*, 2017, **1**, 1820-1829.
- NETZSCH, Definition Thermal Conductivity, <https://www.netzsch-thermal-analysis.com/en/landing-pages/definition-thermal-conductivity/> (accessed October 28, 2019, 2018).
- C. Kittel, P. McEuen and P. McEuen, *Introduction to solid state physics*, Wiley New York, 1976.
- S. Suda, in *Encyclopedia of Materials: Science and Technology*, eds. K. H. J. Buschow, R. W. Cahn, M. C. Flemings, B. Ilshner, E. J. Kramer, S. Mahajan and P. Veysière, Elsevier, Oxford, 2001, pp. 3970-3976.
- NETZSCH, Definition Thermal Diffusivity, <https://www.netzsch-thermal-analysis.com/en/landing-pages/definition-thermal-diffusivity/>, (accessed October 28, 2019, 2019).
- A. van Roekeghem, J. Carrete, C. Oses, S. Curtarolo and N. Mingo, *Phys. Rev. X*, 2016, **6**, 041061.
- M. F. Ashby and D. Cebon, *Le Journal de Physique IV*, 1993, **3**, C7-1-C7-9.
- Hot-Disk, *Hot disk thermal constants analyzer: Instruction manual* Hot Disk AB, Sweden, 7.3 edn., 2016.
- A. Mathew, unpublished work.
- J. E. Parrott and A. D. Stuckes, *Thermal conductivity of solids*, Pion, London, 1975.
- R. J. Samuels and N. E. Mathis, *J. Electron. Packag.*, 2001, **123**, 273.
- A. A. Balandin, *MRS Bulletin*, 2014, **39**, 817-823.
- A. C. Henry, Gang; Plimpton, Steven J.; Thompson, Aidan, *Phys. Rev. B*, 2010, **82**, 144308.
- E. Rönnebro, G. Whyatt, M. Powell, M. Westman, F. Zheng and Z. Fang, *Energies*, 2015, **8**, 8406.
- H. Yokota and M. Ibukiyama, *J. Eur. Ceram. Soc.*, 2003, **23**, 55-60.
- A. Karaipekli, A. Sari and K. Kaygusuz, *Renew. Energ.*, 2007, **32**, 2201-2210.
- Y. Lin, Y. Jia, G. Alva and G. Fang, *Renew. Sustain. Energy Rev.*, 2018, **82**, 2730-2742.
- M. V. Smirnov, V. A. Khokhlov and E. S. Filatov, *Electrochim. Acta*, 1987, **32**, 1019-1026.
- T. Omotani and A. Nagashima, *J. Chem. Eng. Data*, 1984, **29**, 1-3.
- Thermtest, Thermal Properties Materials Database, <https://thermtest.com/materials-database>, (accessed 22/10/19, 2019).
- D. Zhao, X. Qian, X. Gu, S. A. Jajja and R. Yang, *J. Electron. Packag.*, 2016, **138**, 040802.

- 35 W. M. Haynes, *CRC Handbook of Chemistry and Physics, 96th Edition (Internet Version 2016)*, CRC Press/Taylor and Francis, Boca Raton, FL, 2016.
- 36 J. Thomas Jr, R. R. Frost and R. D. Harvey, *Eng. Geol.*, 1973, **7**, 3-12.
- 37 NETZSCH, Thermal Properties of Ceramics, <http://www.netzsch.com/TPoC> (accessed October 28, 2019, 2019).
- 38 R. W. Powell, *Proceedings of the Physical Society*, 1939, **51**, 407-418.
- 39 C. T. Ewing, J. A. Grand and R. R. Miller, *J. Am. Chem. Soc.*, 1952, **74**, 11-14.
- 40 B. Sundqvist and O. Andersson, *Int. J. Thermophys.*, 2009, **30**, 1118-1129.
- 41 S. D. Beattie, A. Harris, A. Levchenko, J. Rudolph, C. D. Willson and G. S. McGrady, presented in part at the ITCC Proceedings, 2009.
- 42 V. Dmitriev, Y. Filinchuk, D. Chernyshov, A. Talyzin, O. Andersson, B. Sundqvist and A. Kurnosov, *Phys. Rev. B*, 2008, **77**, 174112.
- 43 C. E. Messer, *A survey report on lithium hydride*, Tufts Univ., Medford, Mass., 1960.
- 44 E. Shpil'rain, K. Yakimovich, T. Medl'nikova and A. Polishchuk, *Springer Science & Business Media*, 1987, 174-176.
- 45 I. Fieldhouse, *Thermodynamic Transport Properties of Gases, Liquids and Solids*, ASME, 1959, 391.
- 46 C. W. Hamill, F. B. Waldrop and H. T. Kite, *Metal hydrides for shielding applications*, Union Carbide Nuclear Co. Y-12 Plant, Oak Ridge, Tenn., 1961.
- 47 C. P. Camirand, *Thermochim. Acta*, 2004, **417**, 1-4.
- 48 A. Chaise, P. De Rango, P. Marty, D. Fruchart, S. Miraglia, R. Olives and S. Garrier, *Int. J. Hydrogen Energy*, 2009, **34**, 8589-8596.
- 49 J. Lang, M. Eagles, M. S. Conradi and J. Huot, *J. Alloys Compd.*, 2014, **583**, 116-120.
- 50 J.-H. Shim, M. Park, Y. H. Lee, S. Kim, Y. H. Im, J.-Y. Suh and Y. W. Cho, *Int. J. Hydrogen Energy*, 2014, **39**, 349-355.
- 51 G. Xia, Y. Tan, X. Chen, D. Sun, Z. Guo, H. Liu, L. Ouyang, M. Zhu and X. Yu, *Adv. Mater.*, 2015, **27**, 5981-5988.
- 52 A. J. Slifka, B. J. Filla and J. M. Phelps, *J Res Natl Inst Stand Technol*, 1998, **103**, 357-363.
- 53 J. G. Cook, M. P. V. d. Meer and M. J. Laubitz, *Can. J. Phys.*, 1972, **50**, 1386-1401.
- 54 Y. Du and Y. Ding, *Chem. Eng. Process.*, 2016, **108**, 181-188.
- 55 D. E. Dedrick, M. P. Kanouff, B. C. Replogle and K. J. Gross, *Journal of Alloys Compounds*, 2005, **389**, 299-305.
- 56 D. L. Anton, D. A. Mosher and S. M. Opalka, *High density H₂ storage demonstration using NaAlH₄-based complex compound hydrides*, Berkley, C.A., 2003.
- 57 M. D. Christopher, Application of the Transient Hot-Wire Technique for Measurement of Effective Thermal Conductivity of Catalyzed Sodium Alanate for Hydrogen Storage, Virginia Tech, 2006.
- 58 M. Sulic, M. Cai and S. Kumar, *Int. J. Hydrogen Energy*, 2012, **37**, 15187-15195.
- 59 Y. Ishido, M. Kawamura and S. Ono, *International Journal of Hydrogen Energy*, 1982, **7**, 173-182.
- 60 B. Bonnetot, G. Chahine, P. Claudy, M. Diot and J. Letoffe, *J. Chem. Thermodyn.*, 1980, **12**, 249-254.
- 61 H. M. Brown, The thermal conductivity of sodium chloride at elevated temperatures, Missouri, 1955.
- 62 C. L. Yaws, *Chemical properties handbook*, McGraw-Hill, 1999.
- 63 M. Straumanis, *Zeitschrift für Physik*, 1949, **126**, 49-64.
- 64 B. Håkansson and P. Andersson, *J. Phys. Chem. Solids*, 1986, **47**, 355-362.
- 65 W. B. Durham, A. E. Abey and D. A. Trimmer, in *Thermal Conductivity 16*, Springer, 1983, pp. 181-192.
- 66 M. Windholz, *The Merck Index*, Merck & Co, Rahway, NJ 10th Ed edn., 1983.
- 67 K. Clusius, J. Goldmann and A. Perlick, *Z. Naturforsch. A*, 1949, **4**, 424-432.
- 68 M. Chase Jr, *J Phys. Chem. Ref Data, Monograph*, 1998, **9**.
- 69 S. Budavari, M. J. O'Neil, A. Smith and P. E. Heckelman, *The merck index*, Merck Rahway, NJ, 1989.
- 70 R. C. Weast, *CRC Handbook of Chemistry and Physics. 1979-1980*, CRC Press Inc, Boca Raton, Fl. , 1979.
- 71 D. R. Lide, *CRC Handbook of Chemistry and Physics*, New York: CRC Press, 2002.
- 72 H. Choi and A. F. Mills, *Int. J. Heat Mass Transfer*, 1990, **33**, 1281-1288.
- 73 T. D. Humphries, D. A. Sheppard and C. E. Buckley, *Coord. Chem. Rev.*, 2017, **342**, 19-33.
- 74 K. T. Møller, D. A. Sheppard, D. Ravnsbæk, C. E. Buckley, E. Akiba, H.-W. Li and T. R. Jensen, *Energies*, 2017, **10**, 1645.
- 75 T. D. Humphries, G. N. Kalantzopoulos, I. Llamas-Jansa, J. E. Olsen and B. C. Hauback, *J. Phys. Chem. C*, 2013, **117**, 6060-6065.
- 76 R. Varunaa and P. Ravindran, *J. Phys. Chem. C*, 2017, **121**, 21806-21820.
- 77 M. Paskevicius, D. A. Sheppard, K. Williamson and C. E. Buckley, *Energy*, 2015, **88**, 469-477.
- 78 S. Mellouli, H. Dhaou, F. Askri, A. Jemni and S. B. Nasrallah, *Int. J. Hydrogen Energy*, 2009, **34**, 9393-9401.
- 79 E. Suissa, I. Jacob and Z. Hadari, *J. Less-Common Met.*, 1984, **104**, 287-295.
- 80 P. Mukhopadhyay and A. K. Barua, *Br. J. Appl. Phys.*, 1967, **18**, 1307-1310.
- 81 J. J. Didisheim, P. Zolliker, K. Yvon, P. Fischer, J. Schefer, M. Gubelmann and A. F. Williams, *Inorg. Chem.*, 1984, **23**, 1953-1957.
- 82 E. Rönnebro, D. Noréus, K. Kadir, A. Reiser and B. Bogdanović, *J. Alloys Compd.*, 2000, **299**, 101-106.