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RESEARCH PAPER



Effect of Different Processing Routes on the Power Factor of the Filled Skutterudite $Sm_v(Fe_xNi_{1-x})_4Sb_{12}$ (x = 0.50-0.80; y = 0.12-0.53)

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The effect of varying the applied pressure during the processing by spark plasma sintering (SPS) of samples belonging to the Sm_y(Fe_xNi_{1x})₄Sb₁₂ system has been investigated by evaluating the power factor of the obtained filled skutterudite. A strong dependence of both the electrical conductivity and the Seebeck coefficient on the applied pressure has been observed. The highest power factor was detected at different pressures for the different compositions, being the optimal value 180 MPa for the sample with x = 0.80, and 400 MPa for the samples with x = 0.50 and x = 0.63. Relying on the present results, a possible further improvement of power factor of samples with x = 0.50 and x = 0.63 by enhancing the applied pressure above 400 MPa cannot be excluded.

Keywords: Thermoelectricity; filled skutterudites; processing; spark plasma sintering; power factor

Received 6 February 2019, Accepted 7 May 2019

DOI: 10.30919/esmm5f221

1. Introduction

The PGEC (Phonon Glass Electron Crystal) concept rules the search for materials with outstanding thermoelectric properties. It states that such a material should ideally conduct heat like a glass and electricity like a crystal, thus have low thermal conductivity (λ) and high electrical conductivity (σ). The manipulation of σ aimed at the enhancement of the power factor ($PF = S^2 \sigma$, where S is the Seebeck coefficient) led in particular to the investigation of paracostibite. Yet, the most commonly pursued phenomenological approach directed toward the search for high-quality thermoelectric materials consists in the depression of thermal conductivity through the reduction of the phonon mean free path, which can be accomplished by introducing into a cavity of the hosting structure an ion of proper size, disturbing the transmission of vibration quanta through its rattling movement. In this framework, Heusler and half-Heusler phases, clathrates and filled skutterudites⁻ are currently studied as promising thermoelectrics among intermetallic

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materials.

Filled skutterudites RM4X12, in particular, are of significance because of the high ZT values of some of them (for instance ZT ~ 1.8 in *n*-type (Sr,Ba,Yb)Co₄Sb₁, and ZT ~ 1.3 in *p*-type DD_{0.7}Fe₂CoSb₁, at 800 K), coupled to the easy tunability of their electronic properties, which gives rise to the opportunity of obtaining a large number of members belonging to this family, such as Ni-, Fe/Ni-"and Fe/Cobased compounds, even limiting to antimonides. They crystallize in a cubic cell belonging to the Im3 space group (Pearson symbol cI32, isotypic crystal: CoAs₃), having three atomic sites: $8c (\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$, 24g (0, y, z) and 2a position (0, 0, 0) occupied by M, X and R, respectively. The X_{12} icosahedral cage built around the 2*a* site is of the utmost importance, due to its ability to host atoms such as alkaline-earths or lanthanides, responsible for lowering the phononic part of thermal conductivity and for determining the n- or p- conduction regime of the resulting material. Electrons contributed by the filler ion, in fact, tune the electronic count of the skutterudite; previous studies indicated the p/n crossover in Sm₄(Fe₁Ni_{1-x})₄Sb₁₂ to be located at $x \sim 0.63$.¹⁶ It is noteworthy that the filler amount (y) can hardly be forced to a certain desired value, being it strictly correlated to the electronic count determined by the Fe/Ni ratio. Previous studies show in fact that, taking different filler ions in the same oxidation state, y values at a certain Fe/Ni ratio are comparable,^{13,16,19,} thus suggesting that the filler fraction is essentially related to electronic issues, rather than to the chemical identity of the filler itself.

In addition to intrinsic transport properties, which are mainly determined by electronic factors, such as the carrier density and mobility, even extrinsic features contribute to the thermoelectric performance of a material. The lowering of thermal conductivity, for instance, was pursued by acting on numerous factors, such as enhancing density, controlling porosity, nanostructuring, mesostructuring and grain boundary engineering through precipitation of nano-sized secondary phases like oxides, Sb, antimonides, multi-walled carbon nanotubes and others. All these actions aim at exploiting different mechanisms of phonon scattering by introducing additional defects and interfaces, and point at the importance of proper processing of skutterudites. In addition to thermal conductivity, even the electrical contribution to ZT, *i.e.* the power factor, can be strongly affected by the processing route, due to the modification of both the Seebeck coefficient (S) and the electrical conductivity (σ) as a consequence of the variation in the degree of grain connection and the introduction of defects. A proper choice of the processing technique, as well as a careful recognition of the best experimental conditions, can in fact promote a significant enhancement of both S and .

In this work a comparative approach is employed to evaluate the effectiveness of different spark plasma sintering (SPS) processing parameters on the power factor enhancement of the filled skutterudite $Sm_y(Fe_xNi_{1-a})_4Sb_{12}$. SPS is often used to this purpose, since it allows to strongly enhance grain connection and to better control porosity, *i.e.* to manage two factors which are responsible for the enhancement of . The cited system was chosen as its structural, thermoelectric and mechanical properties were recently widely investigated by the present research group.¹⁶— The melting-sintering technique was used to obtain porous bulk samples, which were subsequently densified by SPS applying three different pressure values; the results of the power factor measurements collected on all the samples are discussed.

2. Experimental section

2.1 Synthesis and processing

Three formulations belonging to the Sm₂(Fe_xNi_{1,x})₄Sb₁₂ system were prepared with nominal x = 0.50, 0.63 and 0.80; x values were chosen in order to extend the present study to a p- (x = 0.80) and a n-type (x =0.50) skutterudite, as well as to a composition close to the p/n crossover (x = 0.63). Small pieces of pure elements Fe (Alfa-Aesar, 99.99 wt.%), Ni (Alfa-Aesar, 99.99 wt.%), Sm (NewMet, 99.9 wt.%) and Sb (Mateck, 99.99 wt.%) were weighed in due amounts and placed into a quartz tube subsequently sealed under vacuum; the starting mixture was treated at 1223 K for 3 hours, and then quenched in a salted iced water bath. The Sm amount to be employed was calculated taking into account results obtained in;¹⁶ Sb was used in a slight excess to avoid possible leakage caused by its considerable vapour pressure (0.133 Pa at 873 K). As-cast samples were then annealed in vacuum at 873 K for 7 days.

Samples were subsequently ball milled at a rotation speed of 150 rpm using a steel jar and steel balls; the process duration was set to 1 hour; powders were then densified by spark plasma sintering (SPS). SPS was employed under three different sets of conditions, as reported in Table 1. Samples prepared by applying pressure of 50 MPa were

sintered in Toyota TI laboratory using SPS machine CSP-KIT-02121 by S.S. alloy corporation, Japan, while samples treated by applying 180 MPa and 400 MPa were sintered in Pavia University laboratory (Italy), using a home-made SPS machine. Discs were obtained having diameters ranging between 5 and 20 mm (depending on the applied pressure), and thickness 3 mm.

Specimens are named Fe50_ann, Fe63_SPS180, and so on, according to the Fe % amount with respect to the total (Fe + Ni) content, and to the process they were submitted to: annealing treatment or SPS at 50, 180 or 400 Mpa.

The density of the so obtained samples was measured by the Archimedes method through water immersion; the relative density was calculated by considering the theoretical value for each formulation.

2.2 Morphological and compositional characterization

Polished surfaces of bulk annealed samples were analyzed by scanning electron microscopy (SEM) equipped with energy dispersive x-ray spectroscopy (EDS) (Zeiss EVO 40, with Oxford Instruments Pentafet Link, software package: Oxford-INCA v. 4.09, standard: Co, acceleration voltage: 20 kV, working distance: 8.5 mm, live time: 40 s) with the aim to detect the Fe/Ni elemental ratio and the Sm content, and to identify the possible presence of extra phases. Dense samples were analyzed too, in order to evaluate grain connection. In particular, analyses were carried out on the top of the disc after metallographic polishing, as well as on a polished cross section.

Annealed samples were also subjected to x-ray diffraction: they were ground, and the powder was set on a zero-background Si sample-holder and analyzed by a Bragg-Brentano powder diffractometer (X'pert MPD, Cu K_u radiation in the 20 range $10^{\circ}-90^{\circ}$ with angular step 0.02°).

2.3 Evaluation of microhardness

Microhardness properties of dense samples were evaluated by means of a Leica VMHT MOT microhardness tester provided with a Vickers indenter. A test load of 10 g was applied with a dwell time of 15 seconds, and at least 20 measurements were performed on each sample; indentations were selectively done on the skutterudite matrix, in order to provide an estimate of microhardness associated to the sole main phase.

2.4 Transport properties measurements

All the dense samples were cut by a diamond saw to obtain slabs. Electrical conductivity was analyzed by the four probes technique, while Seebeck coefficient was measured by a custom-built set-up using a nanovoltmeter (Keithley 2182A), a current source (ADCMT 6144), a tube furnace, NI DAQ system and k-type thermocouples. A thermal gradient of about 5 K, necessary for the evaluation of Seebeck

Set of onditions	Temperature increasing rate [K/min]	T [K]	t [min]	Applied pressure [MPa]	Vacuum pressure [Pa]	Applied current [A]	Series name
1	30	773	20	50	5*10 ⁻²	200	FeXX_SPS 50
2	200	773	5	180	10	300	FeXX_SPS 180
3	200	773	5	400	10	300	FeXX_SPS400

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coefficient, was generated by flowing N₂ gas through a stainless pipe in proximity to one of the two edges of the rectangular-shaped sample. These parameters were measured in the temperature range 300 K - 500 K under moderate vacuum (10^{-2} Pa). Constantan and platinum standards were used to validate the home made setup before proceeding to the evaluation of samples. The result uncertainty is about 2% for electrical conductivity and 5% for Seebeck coefficient, which is overall about 12% for power factor.

3. Results and discussion

3.1 Structural and morphological characterization of porous and dense samples

The experimental composition of samples, as revealed by EDS analyses performed on annealed specimens, is reported in Table 2. It is noteworthy that the Fe/(Fe + Ni) content generally coincides or is very close to the nominal value, while the Sb/(Fe,Ni) ratio always slightly

exceeds 3, thus suggesting that the Sb atomic site (24g) is fully occupied, while the one of Fe/Ni (8*c*) is not. Small amounts of extra phases, such as (Fe,Ni)SmSb₃ in Fe50_ann and SmSb₂ in Fe80_ann, are detected in addition to traces of Sb; the presence of the cited additional phases can be observed in SEM microphotographs of all the samples (see Fig. 1). Fig. 2 shows the diffraction patterns of the three samples; it can be observed that by this technique the only recognizable secondary phase is Sb in Fe50_ann, meaning that the amount of the other additional phases is tiny. As expected, the position of diffraction peaks moves toward lower angles with increasing the Fe content, due to the larger size of this element with respect to Ni (see inset to the figure).

SEM microphotographs of the polished surface of porous samples point at the presence of wide holes, due to the scarce compaction degree of annealed specimens; see for example Fig. 1 a), b) and c), taken by backscattered electrons on Fe50_ann, Fe63_ann and Fe80_ann, respectively.



 Table 2 Experimental composition of annealed samples as revealed by EDS analyses.

Sample	Experimental composition	Additional phases
Fe50_ann	$Sm_{0.12(3)}(Fe_{0.47(1)}Ni_{0.47(1)})_4Sb_{12}$	Sb, (Fe,Ni)SmSb ₃
Fe63_ann	$Sm_{0.33(3)}(Fe_{0.60(1)}Ni_{0.34(1)})_4Sb_{12}$	
Fe80_ann	$Sm_{0.53(4)}(Fe_{0.74(1)}Ni_{0.20(1)})_4Sb_{12}$	Sb, SmSb ₂

A significant densification of all the samples was obtained by SPS, as testified by the results of density measurements as a function of the applied pressure, which are reported in Fig. 3 for all the samples. The relative density appears to remarkably increase up to the application of 180 MPa, while at the highest pressure it does not change or it slightly decreases, most probably due to the formation of fine microcracks, as already observed on similar skutterudite systems []. A confirmation of the density increase at the intermediate pressures is provided by SEM microphotographs. In Fig. 4 the ones taken by backscattered electrons on the specimens treated at 50 MPa are collected: a significant reduction in the pores amount can be clearly observed with respect to bulk samples (see Fig. 1). By observing images taken at a higher magnification (see Fig. 5), the uniformity in the color of the obtained microphotographs allows to infer that SPS also improved phase homogeneity.

The increase of density with the applied pressure is also indirectly observed by microhardness measurements performed on all the samples, which are reported in Fig. 6. Noteworthy is that microhardness does not significantly increase with increasing applied pressure, while standard deviations remarkably decrease, thus pointing at a reduction in the amount of pores, which are responsible for the data spread observed in annealed porous samples.

3.2 Electrical resistivity and Seebeck coefficient

The thermoelectric performance of a material is properly evaluated by considering ZT, which accounts both for electrical and thermal properties. Nevertheless, even the sole electrical resistivity (ρ) and Seebeck coefficient (S) can be of help for a preliminary screening of the material quality in terms of thermoelectric performance. The two cited parameters are closely related to each other, being the higher , the higher



Fig. 2 Diffraction patterns of samples Fe50 ann, Fe63 ann and Fe80 ann. Inset: enlargement of the pattern in the angular range $35^\circ \le 2\theta \le 45^\circ$.



Fig. 3 Relative density of all the samples as a function of pressure applied during SPS.





Fig. 4 SEM microphotograph taken by backscattered electrons on a) Fe50_SPS50, b) Fe63_SPS50 and c)





Fig. 5 SEM microphotograph (higher magnification) taken by backscattered electrons on a) Fe50_SPS50, b) Fe63_SPS50 and c) Fe80_SPS50.

S; moreover, factors contributing to an improvement of the electrical features, also affect the thermal ones. Thus, hints on the overall thermoelectric behavior can be deduced from power factor.

Two competing effects can be expected to act on the power factor of a material as a consequence of a pressure application: on one hand, the augmented grain connection should promote a resistivity decrease; on the other hand, the introduction mainly at the grain boundary of dislocations and defects due to the SPS treatment, is expected to cause a resistivity rise. This precondition allows to hypothesize that the optimum applied pressure value can be different for each formulation, depending on the interplay between the aforementioned factors, namely grain connection and defects introduction.

Fig. 7 a), b) and c) report the resistivity trend as a function of temperature of samples Fe80, Fe63 and Fe50, respectively, at each applied pressure. It can be observed that with increasing pressure, resistivity decreases for samples Fe80 and Fe63, meaning that the higher degree of grain connection prevails over the introduction of defects. A more complex behavior occurs for sample Fe50, which shows a



Fig. 6 Vickers microhardness data as a function of the applied pressure during SPS.





Fig. 7 Resistivity trend as a function of temperature of samples a) Fe80, b) Fe63, and c) Fe50 at each pressure applied. Error bars are sometimes hidden by data markers.

resistivity increase on going from 50 to 180 MPa and the minimum resistivity value when applying 400 MPa. This evidence suggests that the introduction of defects prevails over the enhanced grain connection at low pressure, while the opposite occurs between 180MPa and 400 MPa. By closer inspection, it can also be noticed that Fe63 and Fe50 are characterized by a typical semiconducting trend of resistivity, while in Fe80 the pressure increase is responsible for the transition from a metal-like behavior (Fe80_SPS50 and Fe80_SPS180) to a semiconducting one (Fe80_SPS400). This evidence was already observed in the similar system $DD_{0.30}Yb_{0.04}Fe_{3.1}Ni_{0.9}Sb_{12}$ (DD: didymium, a mixture of Nd and Pr) as a consequence of hot pressing at 56 MPa.³⁹

Seebeck coefficients are of great significance for the large amount of information they provide about the electronic properties of the material and its thermoelectric features. Fig. 8 a), b) and c) clearly indicate that the conduction regime is mainly hole-like in Fe80 and Fe63, and electron-like in Fe50, being the sign of S positive for the former and negative for the latter at each pressure applied. With regard to samples Fe80 and Fe50, this result is in good agreement with the refined Sm content obtained from crystallographic data collected on the Sm_y(Fe_xNi_{1,x})₄Sb₁₂ system,¹⁶ which point at an overcompensation of electrons for *x*<-0.63 and an electron deficiency for *x*>-0.63 with respect to the electronic count of a compensated semiconductor, thus suggesting the *n*-character of the former compositions and the *p*character of the latter. As aforementioned, relying on structural data, Fe63 results to be located close to the p/n crossover;¹⁶ therefore, the positive Seebeck coefficients appearing in Fig. 8 b) could at a first glance seem to contradict this conclusion. Conventionally, in fact, the crossover from the p- to the n-conduction regime occurs at the composition where the Seebeck coefficient changes its sign. Nevertheless, it has to be considered that in the crossover region the Seebeck coefficient of a multiband semiconductor, such as the present one, is characterized by a complex dependence on two factors originating from both holes and electrons, according to the following expression:

$$S = \frac{\sum_{i} \sigma_{i} S_{i}}{\sum_{i} \sigma_{i}} = \frac{n_{e} \mu_{e} S_{e} + n_{h} \mu_{h} S_{h}}{n_{e} \mu_{e} + n_{h} \mu_{h}}$$
(1)

Being *S*, *S_e* and *S_h* the overall, electron and hole Seebeck coefficient, respectively, σ the electrical conductivity, *n_e* and *n_h* the negative and positive charge carriers, respectively, and μ_e and μ_h the mobility of electrons and holes, respectively. This means that not only the charge carrier amount, but also the carrier mobility contributes to *S*, what in principle does not allow to easily locate the position of the *p/n* crossover. On the other hand, the Seebeck coefficient is inversely proportional to the number of charge carriers, as described by the following equation:

$$S = \frac{\pi^2 k_B^2 2m_e}{|e|\hbar^2 (3n\pi^2)^{2/3}} T$$
(2)



Fig. 8 Trend of the Seebeck coefficient as a function of temperature of samples a) Fe80, b) Fe63, and c) Fe50 at each pressure applied. Error bars are sometimes hidden by data markers.



where m_e is the electron mass and *n* the number of charge carriers.

Therefore, due to the described involvement of mobilities, the p/n crossover is better identified by the composition at which *S* assumes the maximum value. In this respect, as shown both in this work and in,¹⁶ Seebeck coefficients of Fe63 are generally higher than for both the other samples, meaning that the cited composition is located close to the p/n transition.

In agreement with electrical resistivity, it can be observed that S decreases with increasing applied pressure for sample Fe80 and partly for Fe63. A more complex behavior appears when the trend of sample Fe50 is analyzed: in this case, in fact, S of the sample treated at 180 MPa appears to be the lowest one, at least up to \sim 460 K.

Seebeck coefficients reveal a roughly linear behavior as a function of temperature for each sample, meaning that within the considered temperature range just one conduction regime applies. The case of sample Fe80 is particularly interesting since, according to Seebeck data, it acts as a metal-like conductor at each pressure applied; comparing these results to resistivity data, which show a semiconducting conduction regime at 400 MPa and a slightly metallic one at the other pressure values, it can be thus concluded that this composition is located at the metal/semiconductor transition, and that the cited crossover is promoted by a pressure application.

Resistivity and Seebeck coefficients can be then used to build power factor values of all the samples at each temperature and pressure applied. In Fig. 9 a), b) and c) the described results are collected. It can be observed that for samples Fe63 and Fe50 an increase in the applied pressure, at least up to 400 MPa, promotes a power factor improvement; this evidence leads to the hypothesis that the application of an even higher pressure could be of help to further increase the thermoelectric performance of the material. On the contrary, sample Fe80 presents the highest power factor at 180 MPa, due to the high Seebeck coefficient of Fe80 SPS180.

In conclusion, no general rules can be easily identified for the choice of the most proper pressure to be applied during the processing of filled skutterudites, and experimental studies are generally needed to determine the best experimental conditions. The optimum pressure value can in fact be hardly estimated, since it depends in a complex way on all the factors ruling both Seebeck coefficient and electrical conductivity.

4. Conclusions

With the aim to improve the thermoelectric performance of filled skutterudites, the effect of the processing route on the power factor of three compositions belonging to the Sm₂(Fe_xNi_{1,x})₄Sb₁₂ system has been investigated by varying the pressure applied during spark plasma sintering (SPS). The three formulations have been chosen in order to account both for a *p*- (x = 0.80) and a *n*-type (x = 0.50) skutterudite, as well as for a composition close to the *p*/*n* crossover (x = 0.63). Since power factor is related both to Seebeck coefficient and to electrical conductivity, it is the complex interplay between factors acting on these parameters which rules the dependence of power factor on the pressure applied during processing. In particular, it has been found out that resistivity generally decreases with increasing the applied pressure, due





Fig. 9 Trend of the power factor as a function of temperature of samples a) Fe80, b) Fe63, and c) Fe50 at each pressure applied. Error bars are sometimes hidden by data markers.

to the prevailing effect of the grain connection enhancement, while the Seebeck coefficient shows a more complicated behavior as a function of pressure. As a consequence of the mutual interaction between electrical conductivity and Seebeck coefficient, the optimal pressure value for the sample with x = 0.80 results to be 180 MPa, while for samples with x = 0.50 and x = 0.63 it is 400 MPa, *i.e.* the maximum applied pressure. The latter result suggests that power factor could probably be further enhanced by applying an even higher pressure.

Conflict of interest

There are no conflicts to declare.

Acknowledgements

Prof. P. Manfrinetti (University of Genova, Italy) is kindly acknowledged for his help in preparing samples. G. L. thanks prof. S. Hirai, Director of Research Center for Environmentally Friendly Materials Engineering, for providing experimental facilities during her stage in Muroran Institute of Technology. G. L., S. S. and P. M. thank gratefully Prof. A. Kamegawa and Dr. T. Kimura of Research Center for Environmentally Friendly Materials Engineering, Muroran Institute of Technology, for providing ball milling facility and giving assistance in the ball milling experiment.

References

- G. A. Slack, in *CRC Handbook of Thermoelectrics*, ed. D.M. Rowe, Taylor and Francis, Boca Raton, 1st edition, 1995, **34**, 407-440.
- R. Carlini, C. Artini, G. Borzone, R. Masini, G. Zanicchi and G.A. Costa, J. Therm. Anal. Calorim. 2011, 103, 23.
- R. Chmielowski, S. Bhattacharya, W. Xie, S. Jacob, K. Moriya, A. Weidenkaff, G. K. H. Madsen and G. Dennler, *J. Mater. Chem. C* 2016, 4, 3094.
- I. Pallecchi, M. Pani, F. Ricci, S. Lemal, D. I. Bilc, P. Ghosez, C. Bernini, N. Ardoino, G. Lamura and D. Marré, *Phys. Rev. Mater.* 2018, 2, 075403.
- A. Tavassoli, F. Failamani, A. Grytsiv, G. Rogl, P. Heinrich, H. Müller, E. Bauer, M. Zehetbauer and P. Rogl, *Acta Mater*. 2017, 135, 263.
- V. V. Romaka, P. F. Rogl, R. Carlini and C. Fanciulli, in *Alloys and Intermetallic Compounds From Modeling to Engineering*, ed. Cristina Artini, CRC Press, Taylor & Francis Group, Boca Raton, 1st edition, 2017, chapter 2.7, 286-323.
- J. Fu, X. Su, Y. Yan, W. Liu, Z. Zhang, X. She, C. Uher and X. Tang, J. Solid State Chem. 2017, 253, 414.
- B. C. Sales, in *Handbook on the Physics and Chemistry of Rare Earths*, ed. K. A. Gschneidner Jr., J. C. G. Bünzli and V. K. Pecharsky, North Holland, 1st edition, 2003, chapter 33, 1-34.
- C. Uher, in *Thermoelectrics Handbook Macro to Nano*, Ed. D.M. Rowe, CRC Press, Taylor & Francis Group, Boca Raton, 1st edition, 2006, chapter 34, 1-15.
- R. Carlini, C. Fanciulli, P. Boulet, M. C. Record, V. V. Romaka and P. F. Rogl, in *Alloys and Intermetallic Compounds – From Modeling to Engineering*, ed. Cristina Artini, CRC Press, Taylor & Francis Group, Boca Raton, 1st edition, 2017, chapter 2.8, 324-355.
- G. Rogl, A. Grytsiv, K. Yubuta, S. Puchegger, E. Bauer, C. Raju, R. C. Mallik and P. Rogl, *Acta Mater*. 2015, 95, 201.

- G. Rogl, A. Grytsiv, F. Failamani, M. Hochenhofer, E. Bauer and P. Rogl, J. Alloys Compd. 2017, 695, 682.
- 13. L. Chapon, D. Ravot and J. C. Tedenac, J. Alloys Compd. 1999, 282, 58.
- A. Kaltzoglou, P. Vaqueiro, K. S. Knight and A.V. Powell, J. Solid State Chem. 2012, 193, 36.
- S. Choi, K. Kurosaki, Y. Ohishi, H. Muta and S. Yamanaka, J. Appl. Phys. 2014, 115, 023702.
- C. Artini, G. Zanicchi, G. A. Costa, M. M. Carnasciali, C. Fanciulli and R. Carlini, *Inorg. Chem.* 2016, 55, 2574.
- G. Rogl, A. Grytsiv, P. Heinrich, E. Bauer, P. Kumar, N. Peranio, O. Eibl, J. Horky, M. Zehetbauer and P. Rogl, *Acta Mater*. 2015, 91, 227.
- F. Duan, L. Zhang, J. Dong, J. Sakamoto, B. Xu, X. Li and Y.Tian, J. Alloys Compd. 2015, 639, 68.
- B. Bérardan, E. Alleno, C. Godart, O. Rouleau and J. Rodriguez-Carvajal, *Mater. Res. Bull.* 2005, 40, 537.
- R. Liu, J. Y. Cho, J. Yang, W. Zhang and L. Chen, J. Mater. Sci. Technol. 2014, 30, 1134.
- 21. X. Li, Q. Zhang, Y. Kang, C. Chen, L. Zhang, D. Yu, Y. Tian and B. Xu, J. Alloys Compd. 2016, 677, 61.
- A. U. Khan, K. Kobayashi, D. M. Tan, Y. Yamauchi, K. Hasegawa, M. Mitome, Y. Xue, B. Jiang, K. Tsuchiya, D. Golberg, Y. Bando and T. Mori, *Nano Energy* 2017, **31**, 152.
- 23. G. Rogl and P. Rogl, Curr. Opin. Green Sust. Chem. 2017, 4, 50.
- M. Benyahia, V. Ohorodniichuk, E. Leroy, A. Dauscher, B. Lenoir and E. Alleno, *J. Alloys Compd.* 2018, 735, 1096.
- 25. G. Rogl and P. Rogl, Mater. Today Phys. 2017, 3, 48.
- 26. W. Zhao, Z. Liu, Z. Sun, Q. Zhang, P. Wei, X. Mu, H. Zhou, C. Li, S. Ma, D. He, P. Ji, W. Zhu, X. Nie, X. Su, X. Tang, B. Shen, X. Dong, J. Yang, Y. Liu and J. Shi, *Nature* 2017, **549**, 247.
- 27. J. Ding, H. Gu, P. Qiu, X. Chen, Z. Xiong, Q. Zheng, X. Shi and L. Chen, J. *Electron. Mater.* 2013, **42**, 382.
- 28. H. Li, X. Tang, X. Su and Q. Zhang, Appl. Phys. Lett. 2008, 92, 202114.
- 29. G. Tan, H. Chi, W. Liu, Y. Zheng, X. Tang, J. He and C. Uher, *J. Mater: Chem. C* 2015, **3**, 8372.
- P. Che, B. Wang, C. Sun, Y. Han and W. Li, J. Alloys Compd. 2017, 695, 1908.
- N. Shaheen, M. Sufyan Javed, H. Ullah Shah, S. Hussain, M. Ashfaq Ahmad, R. Raza, M. Saleem and X. Zhou, *Ceram. Int.* 2018, 44, 12610.
- 32. C. Artini and R. Carlini, J. Nanosci. Nanotechnol. 2017, 17, 1634.
- C. Artini, A. Castellero, M. Baricco, M. T. Buscaglia and R. Carlini, *Solid State Sci.* 2018, 79, 71.
- 34. C. Artini, C. Fanciulli, G. Zanicchi, G. A. Costa and R. Carlini, *Intermetallics* 2017, 87, 31.
- R. Carlini, N. Parodi, F. Soggia, G. Latronico, M. M. Carnasciali and C. Artini, J. Mater. Eng. Perform. 2018, 27, 6266.
- C. Artini, N. Parodi, G. Latronico and R. Carlini, J. Mater. Eng. Perform., 2018, 27, 6259.
- R. Carlini, A. U. Khan, R. Ricciardi, T. Mori and G. Zanicchi, J. Alloys Compd. 2016, 655, 321.
- R. C. Weast, Handbook of Chemistry and Physics, CRC Press, Cleveland, 1976.
- G. Rogl, A. Grytsiv, E. Royanian, P. Heinrich, E. Bauer, P. Rogl, M. Zehetbauer, S. Puchegger, M. Reinecker and W. Schranz, *Acta Mater.* 2013, 61, 4066.

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