

Phase diagram calculation, a tool for design of thermoelectric materials. A Calphad contribution to multicomponent antimonide-based systems.

Jean Claude Tedenac¹, Hongxiao Li^{1,2}, Suzana Gomes-Fries³, M.C. Record¹, R.M. Marin-Ayral¹, and
Didier Ravot¹

1-Université Montpellier 2 LPMC-UMR-CNRS-5617, Montpellier, France

2- on leave from University of Science and Technology Shenyang (Liaoning), P.R. China

3-ACCESS e. V., RWTH-Aachen, Intzestrasse 5, D52072 Aachen, Germany

Abstract

High ZT thermoelectric modules can be obtained by a good knowledge of the materials involved in their fabrication. The phase transformations of new materials are still unknown and a thermodynamic study of these systems is needed. The development of thermodynamic and kinetic databases of such practical materials is important for the microstructural evolution of the materials during processing and service for improving the knowledge.

This paper will show how the Calphad method can be used to study multicomponent materials and to determine the best processes for their synthesis (single crystals growth, powder metallurgy,...).

Advanced thermoelectric materials are semi-conductors as: $Ce_yFe_{4-x}Co_xSb_{12}$, $TiNi_xCo_{(1-x)}Sb$ and $(CdZn)_4Sb_3$. They are studied from a thermodynamic point of view and we will show some interesting relationships between calculated phase diagram, microstructure constitution and processes.

Cobalt-Antimony, Iron-Antimony, Zinc antimony, Cerium-Antimony and Cerium-Iron systems are five relevant systems of the previously quoted semi-conductors. We will show in this study the method used for studying the ternaries built with those systems:

Introduction

The efficiency of a solid-state thermoelectric engine primarily depends on the chemical compositions of materials and then of phase stabilities. The improvement of the figure of merit in thermoelectric materials depends on multiple factors regarding the microstructures and the physical properties (1).

Thermoelectric materials are typically multicomponent systems and a thermodynamic approach is necessary to study such systems (2).

The processes involved in the fabrication of a thermoelectric component lead to other problems:

a - Solidification processes cause segregations in single phases and, depending on the composition of the melt, eutectic precipitations.

b - Pressure dependence of the material composition (in tellurides and selenides as well) causes point defects leading to imperfect electronic properties.

c - Hot pressing processes cause element diffusion in the grains and at the boundaries leading to non-equilibrium material with properties changing with time and temperature.

Phase transformations and process modelling of the new materials presently studied for thermoelectricity are still unknown.

In this paper we present a computational approach to the phase equilibria in multicomponent systems used in thermoelectric materials. Phase diagrams are useful for thermoelectricity and help to build a thermodynamic database of antimonides based materials.

To gain a better understanding of thermoelectric materials and to help to resolve the problems listed above we present thermodynamic calculations based on the CALPHAD method (3).

The CALPHAD approach uses Gibbs energy descriptions in order to calculate phase equilibria as an aid to optimize performance, design and tailoring of the materials (4). As a result, these multicomponent databases can be used to determine the microstructures of materials, calculate equilibria, add to the understanding of solidification and the resulting microstructures can be obtained by hot pressing or ball milling processes.

Materials microstructures after sintering and thermal behaviour are checked with the isothermal section at high temperature. Moreover, Gulliver-Scheil simulations (5,6) (infinite diffusion in liquid phase and no diffusion in solid phase) can be used to determine the solid fractions in a solidification process and the final microstructure.

In this paper we present a contribution to the CALPHAD approach for intermetallic based semi-conductors suitable for thermoelectric applications.

Phase diagrams determination in thermoelectric materials.

The CALPHAD method has been widely developed for metallic systems, for oxide systems and, in the past 10 years, to some semi-conductor systems as, for example, gallium arsenide, cadmium telluride and lead telluride systems (7,8,9)

Moreover, it is very important to introduce the point defects in the modeling into the phases in order to map the defects as a function of chemical composition. Due to its difficulty, this characteristic, important for physical applications, was not taken into account in previous assessment of semi-conductor systems. Recently, the defect modelling in semi-conductors has been introduced and used for the Cd-Te modelling (8).

Introducing the CALPHAD method.

The calculation of phase equilibria of a multicomponent system is obtained by the minimization of the total Gibbs energy, where G is a summation of the Gibbs energy of all phases that take part in each equilibrium as is expressed by equation (1):

$$G = \sum_{i=1}^p n_i G_i^0 = \min. (1)$$

The thermodynamic description of the whole system requires the assignment of thermodynamic functions to each phase. The main interest of the CALPHAD method is the use of a variety of models to describe the free-energy functions of the various phases of the system as a function of temperature, pressure and composition. Then the Gibbs energy function of a phase j can be written as in equation (2):

$$G_m = \sum_i x_i (G_i^0 - G_0^0)^{phys} + G_m^{phys} - T S_m^{ideal} + G_m^{ex} (2)$$

The effects of particular physical phenomena (as magnetism) are taken into account by subtracting them from the description of the end-members (reference state) and it is introduced for the solution through the contribution G_m^{phys} . The last term on the right hand side is the excess term.

Usually the temperature dependence of the Gibbs energy

$$G = a + bT + cT \cdot \ln(T) + \sum d_n T^n (3)$$

is expressed as a power series of T where a, b, c and d_n are coefficients and n are integers (3). The pure elements are represented by the same function according to the database of A. Dinsdale (10).

By taking into account all the parameters the Gibbs

$$G^0 = G^{ref} + G^{ideal} + G^{xs} (4)$$

energy of phases are then represented by three contributions as expressed in equation (4).

The first term of the right-hand side corresponds to the Gibbs energy of a mechanical mixture of the components, the second one corresponds to the entropy of mixing for an ideal solution and the third term, the so-called excess term, represents all the deviations from ideality.

Thermodynamic modeling of phases is the core of the CALPHAD approach. Most systems have few strictly stoichiometric compounds, so it is important to model phases deviating from the ideal stoichiometry. The most used model for solution phases are random substitutional, or ordered sublattices. In ordered solid phases, the Wagner-Shottky model is used for describing small deviations from stoichiometry (which are non-interacting defects).

Intermetallic binary compounds are generally non-stoichiometric and can exist in a large range of composition. In this case the most used model is the sublattice model (2). All the models can be used for ternary to multicomponent systems by adding high order interactions terms in the expression of the excess free energy.

In such high ordered systems the Gibbs energy must be calculated from extrapolation of the excess quantities of constituent sub-systems. Several methods can be used and among them the geometrical Muggianu method is the most used (2). Consequently the Gibbs energy of a n-component solution phase must be determined by the n-1 energies using the method given by Figure 1.

$$G = \sum x_i G_i^0 + RT \sum x_i \ln x_i + G^{ex}$$

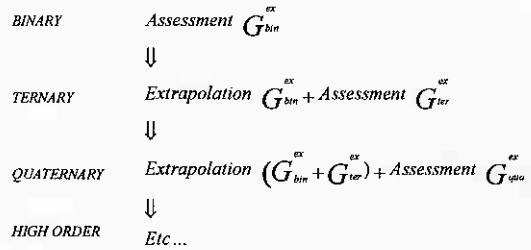


Figure 1 The extrapolation method used in the Gibbs energy calculation.

In fact relationship between chemical potentials of the phases and the system gives non linear equations that can be solved by numerical methods such as Newton-Raphson methods. The CALPHAD type packages use mathematical methods to minimize the Gibbs functions.

Modelling antimonide systems for thermoelectric applications

The next generation of thermoelectric materials will be built up with intermetallic phases. Many of these materials are based on antimony systems such as Sb-Zn or Co-Sb and they should be multicomponent in order to optimize thermoelectric properties. Over this last decade a number of skutterudite materials have been synthesized and studied. Large ZT values have been obtained for $CeFe_{(1-x)}Co_xSb_{12}$ (11,12). The problem for these materials is the optimization of the fabrication processes and it will be performed by phase diagram modeling.

Phase diagrams useful for thermoelectricity.

A well known thermoelectric material family studied in number laboratories is built up on the solid solutions $(Bi_{1-x}Sb_x)_2Te_3$ by introducing antimony in bismuth telluride or vice-versa.

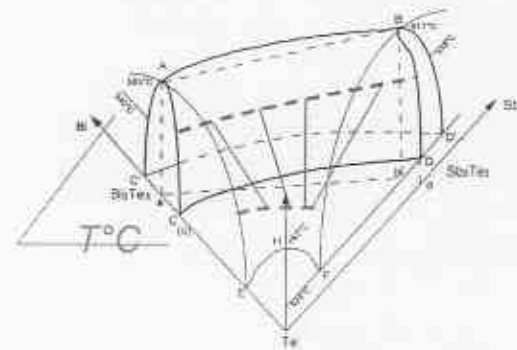


Figure 2 The tellurium rich part of the Bi-Sb-Te system according to the reference 13. An hypothetical isothermal section is draw for showing the tie lines solid-liquid.

As it is shown in figure 2, the two compounds Bi_2Te_3 and Sb_2Te_3 are narrow band-gap semi-conductors and display complete solubility in the whole composition range (13). Regarding the ternary phase diagram in the tellurium rich

corner (figure 2) the two binary compounds present an homogeneity range allowing the possibility of modification of the carriers concentrations by changing the chemical compositions. This composition modification is obtained in the ternary solid-solution.

Unfortunately the phase relationships are not simple and numbers of experimental efforts were necessary to understand the modification of the properties. The calculation of this ternary system should be an aid in the study of those thermoelectric materials.

A second example concern a material used in power generation: lead telluride. The p- material is built up with lead, tin and tellurium. In such a case it is necessary to use the ternary Pb-Sn-Te. This system is simpler than the previous Bi-

Sb-Te and it has been calculated recently (9). The two intermetallic compounds PbTe and SnTe are narrow band-gap semi-conductors and display complete solubility in the whole composition range. The carriers concentration in PbTe materials changes with the chemical composition (p-type in the metal rich side and n-type in the tellurium rich side). The free energy function description of the system is made with a two sublattices model according to reference (9), neutral and charged vacancies are included in this model in order to satisfy electrical neutrality and to describe the departure from stoichiometry at all temperatures. This description allowed us to calculate the ternary phase diagram using Thermocalc and the PbSnTe database provided by H.L. Lukas (9).

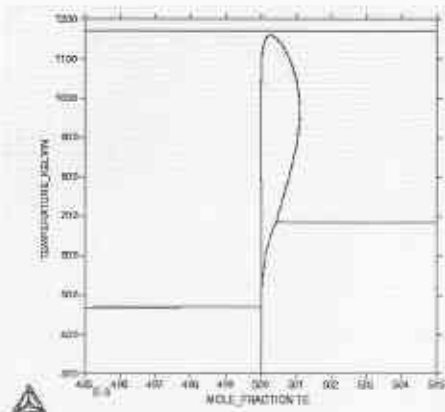


Figure 3 The central part of the isopleth section $\text{Sn}_{30}\text{Pb}_{70}\text{Te}$ of the Pb-Sn-Te phase diagram showing the homogeneity range of the solid-solution.

Usually ternary alloys based on 30-35 mol% of tin are studied for thermogenerator materials (14). Some important problems can be approached with the corresponding database. The definition of the homogeneity range of PbSnTe materials in the whole range of temperature can easily be made by a thermodynamic description of the section. The figure 3 shows the central part of the isopleth section where the material $\text{Sn}_{30}\text{Pb}_{70}\text{Te}$ is contained. In the central part of the phase diagram one can see the homogeneity zone of the thermoelectric material and this description is very useful for determining precisely the conditions of quenching and preparing the material without tellurium precipitations.

Phase diagram determination in antimony zinc ternary systems.

The problem existing in zinc antimony materials was due to difficulties in the crystal growth of materials. Having initially a high figure of merit, those T.E. materials could have better properties with some achievement in the metallurgical processes (15). These difficulties are easily explained by a complicated phase diagram. Up to our recent paper (16) the different phase equilibria determinations lead to 6 different versions of this phase diagram. These differences were due to real difficulties in the phase equilibria determination. With a Calphad analysis we have determined the phase relationship in this binary and explained the behaviour of the material. The figure 4 presents the calculated phase diagram obtained by this way. All the important informations for crystal growth (temperatures, compositions, liquidus shape,...) are indicated.

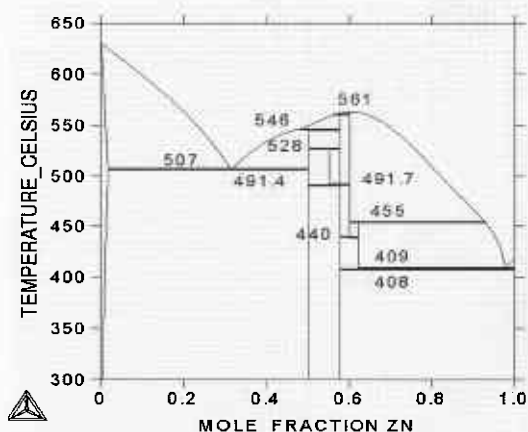


Figure 4 The calculated phase diagram Sb-Zn.

It was demonstrated that the enhancement of the thermoelectric properties of Zn_4Sb_3 is obtained by additions of cadmium element (15). In such a case an analysis of the ternary system is necessary to determine all the possibilities of doping by departure to the stoichiometry.

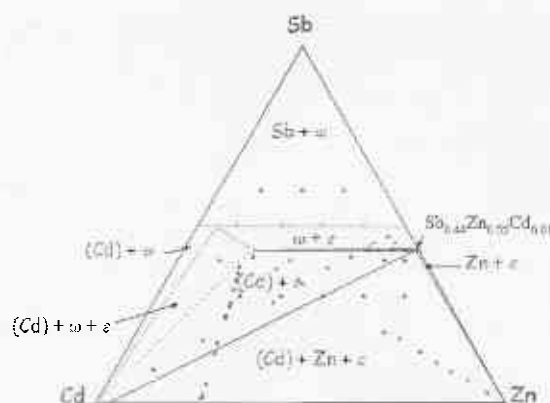


Figure 5 Isothermal section at 250°C of the experimental phase diagram Cd-Sb-Zn.

An experimental determination of the ternary was made by our group and it is presented in figure 5. The ternary extension of the ϵ -Zn₄Sb₃ has been accurately determined (17).

The quaternary $Ce_yFe_{1-x}Co_xSb_{12}$

The optimized skutterudite materials are contained in the Ce-Co-Fe-Ni-Sb system. The so-called optimized skutterudites (2) belongs to the section $CoSb_3$ - $FeSb_3$ - $CeFe_4Sb_{12}$ in that multicomponent system. The purpose of our laboratory is to build a multicomponent database with five elements in order to improve the materials behaviour. In this aim, it is necessary to assess the binaries and ternaries as reported in a general CALPHAD procedure (section 1).

The key system for studying these materials where the skutterudite phase should exist with a certain homogeneity range is the Co-Fe-Sb with two interesting border binaries.

Most of the binary systems with the skutterudite structure have been experimentally studied but no assessments have been available until now. Moreover, among the $CoAs_3$ type phases which are possibly involved in thermoelectrics the only that appears thermodynamically stable is cobalt triantimonide, but the iron materials appear unstable. Some thermodynamic discussion can explain this behaviour. We have modeled the two binaries and made some experimental determinations in order to extend the models to the ternary system.

In the Cobalt-Antimony system three intermetallic compounds are formed: $CoSb$, $CoSb_2$ and $CoSb_3$. In Iron-Antimony only two compounds are formed: $CoSb$, and $CoSb_2$. For applications, it is interesting to determine the homogeneity range of the skutterudite phase in the ternary. This determination lead to a maximum content of 7.5 at% in Fe in the ternary triantimonide (figure 6).

Modelling the binary systems.

As it was explained in section 1, modelling a ternary system need to know the binaries. In that case one can observe that a phase is dominant (the 1:1 nickel arsenide phase) and a good modelling of the ternary and related binaries depends on the model used in this phase.

By a fine solid state analysis of some compositions we have determined the crystal structure of the $\{CoSb-Fe_{0.56}Sb_{0.44}\}$ mixtures (17). It was shown that a solid solutions existing in the whole range of composition and the iron atoms are partially in interstitial positions.

The choice of the model for the Gibbs energy calculations should be a four sublattice model with two metal sublattices (Co_1 , Co_2) including vacancies, and two antimony sublattices (Sb_1 and Sb_2) associated with its interstitials.

By applying this model to the ideal NiAs type structure we obtain $CorCorSbqVaqSbqVaq$, (r and q are the stoichiometric coefficients) leading to the 1:1 stoichiometry wich is present for $CoSb$ with $r=q$). By adding some iron atoms on interstitials positions of the structure they can be partially occupied leading finally to $Fe_{0.56}Sb_{0.44}$.

This model can be generalized to all the compounds derived from NiAs. By ordering the vacancies (all sites of Co_2 are vacant) it lead to the 1:2 stoichiometry ($CorVarSbqSbqVaq$), $CoSb_2$ related to CdI_2 . All the interstitials of antimony are occupied by cobalt

($CorCorSbqSbqCoqCoq$ or $CorCorSbqCoqSbqCoq$ leading to Co_2Sb) related to Ni_2In .

Using these results we have described the Gibbs energy functions in the systems Co-Sb and Fe-Sb.

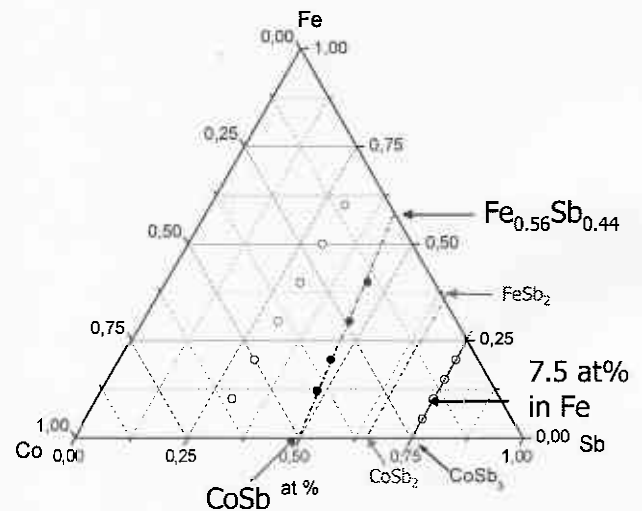


Figure 6 The ternary Co-Fe-Sb.

Experimental data used for these calculations are those concerning the phase diagram measurements, enthalpy of formation of the compounds, C_p for $CoSb$ and chemical potentials measured by electrochemistry. According to the description adopted in the SGTE database the Gibbs energy of pure elements is taken with reference to the enthalpy of the elements in the SER state (standard element reference), the elements in their stable state at 10^5 Pa and 298.15 K. In this assessment the regular solution model was adopted for the liquid and terminal solution solids.

Concerning the intermetallic compounds the Gibbs energy of $CoSb_2$, $FeSb_2$, $CoSb_3$ and $FeSb_3$ are stoichiometrically modeled and described by a sub-regular model. The 1:1 compound was described with a four sublattice model in order to take into account the departure from stoichiometry on the both sides of the solid solution.

The modeled phase diagrams are presented in Figure 7 and 8. The figure 9 represent the shape of the Gibbs energy functions at 1000 K for the binary Co-Sb, showing the good relevance of the models.

The liquidus curve and the invariant temperatures are known to good accuracy. This result will be an aid for understanding the thermodynamic behaviour of the ternary and quaternary phases. It has been possible to calculate the temperature of the metastable melting point of $CoSb_3$ (1285K instead of 1210K for the peritectic decomposition of the 1:2 phase). One can observe that these temperatures are not so far and it could explain the problems occurring in the fabrication of the materials as well as the lack of 1:3 compounds for iron and nickel systems.

The most useful result is the shape of the phase diagram around CoSb_3 . In the binary the liquidus curve and the invariant temperatures are known to good accuracy. This result will be an aid for understanding the behaviour of the ternary and quaternary phases which are presently in progress.

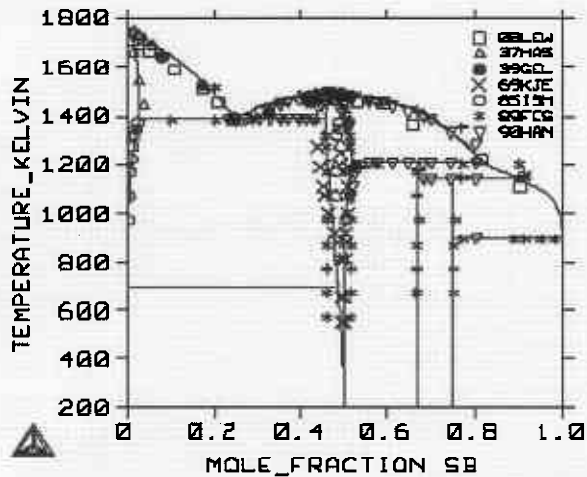


Figure 7 The calculated phase diagrams Fe-Sb.

Conclusions

Using the CALPHAD method we have described phase diagrams of some thermoelectric materials and show the possibilities of this kind of study for the fabrication processes. We have modelled the Sb-Zn, Co-Sb and Fe-Sb phase diagrams which are the first step of the constitution of our database. The ternary Co-Fe-Sb is experimentally determined and the modelling is presently in progress.

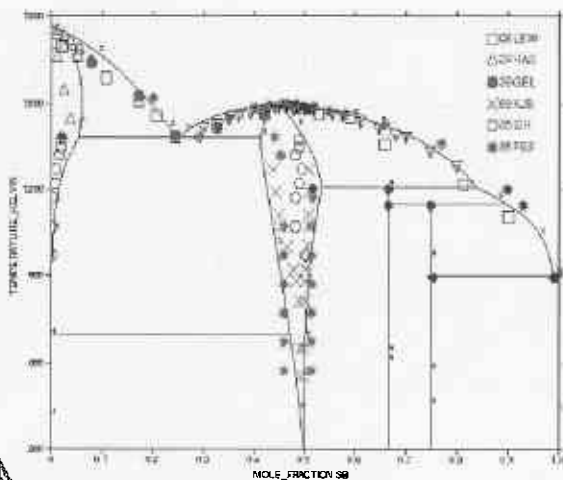


Figure 8 The calculated phase diagrams Co-Sb.

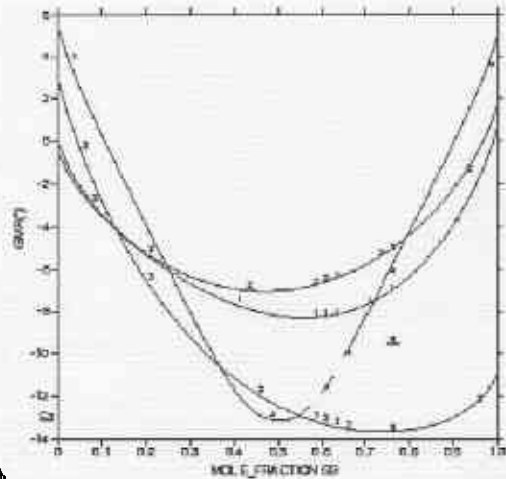


Figure 9 The Gibbs energy function vs composition at 1000 K.

References

1. Fleurial J.P., Caillat T., Borshevsky A., Morelli D.T. and Meisner, Proc. 15 th Intl Conf. on Thermoelectrics, Piscataway, NJ, (1996), p 9.
2. Tedenac J.C., Marin-Ayral R.M., Ravot D., Record M.C. Proc. XX Int. Conf. On Thermoelectrics, ICT'01, (2001) 371-374
3. Saunders N, Miodownik P. "CALPHAD, a comprehensive guide", Pergamon (Exeter, 1998), p 261.
4. Katner U., J.O.M., 49 (12), (1997), 14-19.
5. Scheil E. Z. fur Metallkunde Vol.34, (1942), pp 70
6. Gulliver G.H. Metallic alloys, Verlag griffin, Vol.25, (1922), pp. 120-157.
7. Ansara I., Chatillon C., Lukas H L., Nishizawa T., Ohtani H., Ishida K., Hillert M., Sundman B., Argent B. B., Watson A., Chart T. G., Anderson T.. Calphad, 18-2, (1994), 177-222.
8. Chen Q., Hillert M., Sundman B., Oates W.A., Fries-Gomes S.G., Schmid-Fetzer R., J of Elec. Mat., Vol 27 No 8, (1998), pp 961-971.
9. Kattner U., Lukas H.L., Petsow G., Gather B., Irle E., Blachnik R. Z. fur MetallK. Vol. 79, (1988), pp 32-40,
10. Dinsdale A. Calphad, Vol.15, (1991), pp 317-425.
11. Sales B.C., Mandrus D., Williams R.K. Science 272, (1996), p 1325.
12. Fleurial J.P., Caillat T., Borshevsky A., Morelli D.T. and Meisner, Proc. 15 th Intl Conf. on Thermoelectrics, Piscataway, NJ, (1996), p 9.
13. Scherrer H., Lenoir R., Dauscher A., Scherrer S, Proc. XX Int. Conf. on Thermoelectrics, ICT'01, (2001) 13-17
14. Bouad N., Ph. D Thesis Montpellier (France) 2001
15. Izard V. , Ph. D Thesis Montpellier (France) 2001
16. Record M.C., Izard V., Tedenac J.C., Gomes-Fries S. Calphad 25-2, (2001), 567-581.
17. Record M.C., Izard V., Bulanova M., Tedenac J.C. Intermetallics 11(11) (2004), 1189-1194