# Chemistry of Materials a Tool for Skutterudite Based Materials Tailoring. Application to Cobalt Based System

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**Abstract**

The ternary Co-Fe-Sb system is one of the border systems of the quaternary (Cobalt-Cerium-Iron-Antimony) which is useful for the study of new thermoelectric materials. Indeed, the skutterudite phases ($Fe_xCo_{1-x}Sb_3$) present in this ternary system is one of the best thermoelectric materials. However, the precipitation of secondary phases changes the electronic properties notably; therefore the conditions of synthesis must be improved.

On another hand, in many applications the phase equilibria determination (in stable as well as in metastable states) is very useful for the preparation of optimized materials and systems.

The application of the Calphad method to that ternary system will be shown. A determination of the phase equilibria including metastable equilibria is fundamental for the improvement of the properties and the physical behavior of such materials.

The phase stabilities, the ternary fields of solubility are defined and they will be presented in order to explain the materials fabrication.

**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).

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

In this paper, we present a recent study of the phase equilibria of the Co-Fe-Sb system using a CALPHAD procedure.

The Co-Fe-Sb ternary system was first studied in 1939 by Geller (3) After that very few investigations were done on this system (4,5,6) although a quite relevant amount of experimental data was determined for the Fe-Co, Fe-Sb and Co-Sb constituent binaries.

Three intermetallic phases are present in this system:

The B8 phase, prototype NiAs, appears as stable phase in the Fe-Sb and Co-Sb binaries. In Fe-Sb, *B8* stabilizes off-stoichiometry by an excess of Fe, in Co-Sb, however, the homogeneity range of *B8* spreads into the both sides of the 1:1 ideal composition at high temperature and is reduced to the equimolar stoichiometry at room temperature. The rich metal range stability is explained by iron occupying interstitial sites in the hexagonal antimony sublattice. The extension to the antimony rich side in Co-Sb system is explained by vacancies in the metal sublattice. As a matter of fact, these defects are known in the literature (7) as the mechanism making the connection between NiAs, $InNi_2$ and $CdI_2$ structures types. The occupation of all hexagonal interstitial sites in the antimony sublattice by the metal atoms leads to the $InNi_2$ structure and the increasing ordering of the vacancies resulting in an empty layer in the metal sublattice leads to the $CdI_2$ structure.

The *C18* phase, prototype $FeS_2$, also appears in both binaries with a very narrow homogeneity range.

The skutterudite phase, *D0*$_2$ prototype $CoAs_3$, stabilizes only in the Co-Sb system and constitutes a relevant material for thermoelectric applications, which makes important the knowledge of the phase equilibrium in this system. The experimental investigation of the stability and defect mechanism understanding in the ternary phases applied to a Gibbs energy modelling is the objective of this study.

**Experimental techniques**

In order to guide the modelling of the ternary fourteen samples were prepared and analyzed by DTA, X-ray determination as well as by metallography and EPMA measurements. They have been presented in (8). In that work, the experimental investigations of those samples belonging to three sections were made in order to establish the phase relationship in the system. The different phase fields of the ternary have been determined. The three sections studied in this ternary are shown in the figure 1.

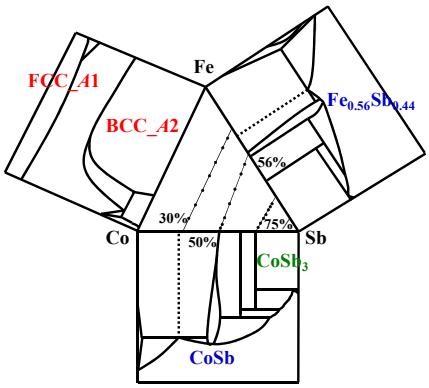



Figure 1. Sections of the ternary studied in the work.

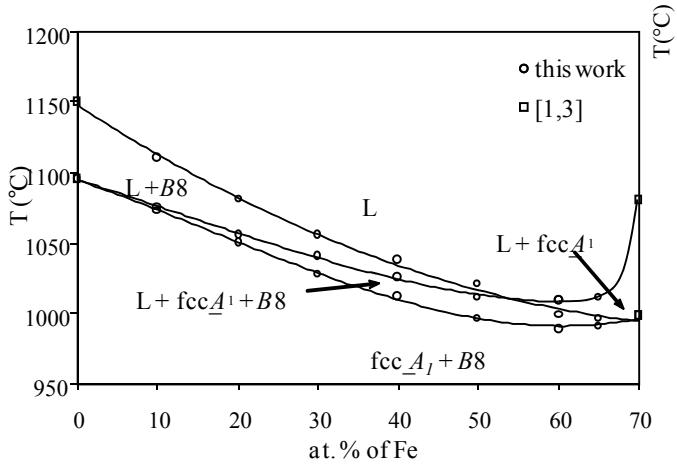
The first samples are in the section at 30 at% in antimony. It lays at a point richer in antimony than the Co-

Sb eutectic ($e_1$) and at a point poorer than the Fe-Sb eutectic ($e_2$). It normally crosses the univariant line in the metal rich part of the diagram and gives information about the reaction temperatures. The second section connects the two binary B8 compounds and do not correspond to an isopleths section. The third one corresponds to the skutterudite composition in each binary (Sb at%= 75).

**Results**

**The section at 30 at % Sb.**

Figure 2. The section at 30 at% in antimony.




This section is very important for the determination of the relationships between four phases: liquid, fcc-*A1*, bcc-*A2* and B8. The figure 2 shows the phase diagram that can be drawn by analysing the thermal events measured by heating rate in the range temperature: 900-1200°C. One can remember that the fcc-*A1* phase transforms into the bcc-*A2* at lower temperature. One observes the trace of the monovariant valley, crossing this section at ~55 at% in antimony. The phase fields present there are four: liquid+ *A1*, liquid+*B8*, liquid +*A1*+*B8* and *A1*+*B8*.

By X-Ray analysis, we have observed for the samples of the section and some other in the quadrilateral Co-Fe- CoSb - $Fe0_{.56}Sb_{0.44}$ that only two phases are present: *A2* obtained from the decomposition of *A1* and *B8*.

**The diagram between CoSb and $Fe0_{.56}Sb_{0.44}$.**

This part of the diagram is bordered by the two B8 compounds. Although these compounds are congruently melting, it is impossible to observe a quasi binary section, the composition is moving from one side to the other as a function of the fraction $X_{Fe}/( X_{Fe}+ X_{Co})$. The question that arises is the extension of the solid solution in the ternary. Understanding this section one needs to refer to a former study made on the determination of the crystal structure of the alloys (9). In that paper, it was shown that the iron atoms are situated on both positions: on the 2a Wyckoff site for one part and on the 2d for the other part, this position is a interstitial one. It has also been shown that the interstitial position is filled from the compositions between 15 at% of iron and 56%. Below this range, iron is in substitution of the cobalt. In such a case, the determination of the thermal characteristics of this solid solution is necessary. Figure 3 represents the two phase-region liquid+*B8* determined by heating ramps of DTA measurements. It is shown that, at high temperature the *B8* phase exists in the whole composition range.

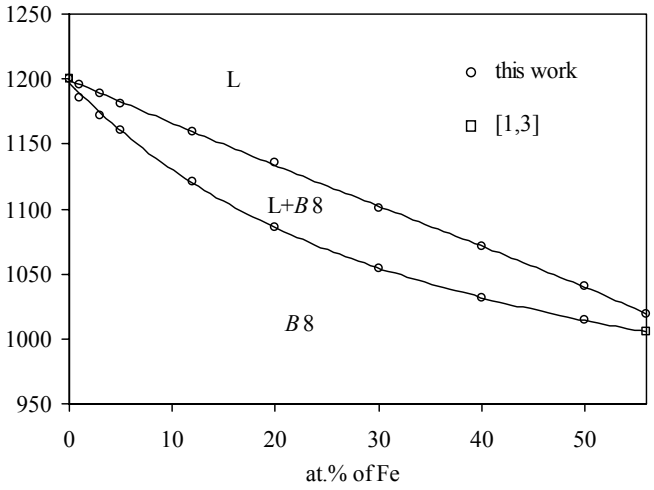



Figure 3. The phase equilibria in the system CoSb - $Fe0_{.56}Sb_{0.44}$.

At lower temperature, and after long annealing periods reproduced three times we did not evidenced any phase separation at temperature over 400°C , showing definitively the chemical homogeneity of the solid solution.

**The section at 75 at % Sb or Skutterudite section.**

This section is the most interesting for thermoelectric applications. It corresponds to the skutterudite composition: $D0_2$.

Due to the fact that only $CoSb_3$ exists in the binaries and not $FeSb_3$, we have studied ten samples by thermal analysis, X-Ray diffraction and EPMA in the aim of determining the phase relationships as a function of temperature. These experiments were reproduced three times.

A second problem related to the phase relationships concerns the determination of the limit of solubility of iron in $CoSb_3$ (which is very important for thermoelectric materials).

In figure 4 we report the lattice constant of the studied samples as a function of the composition in iron. As one can see iron solubility is ranging from 0 to 5 at% in iron. For higher iron content, the samples are bi or triphased, depending of the iron content.

As a result of our investigations the figure 5 represent the interpretation of the phase equilibria in respect with the phase rule.

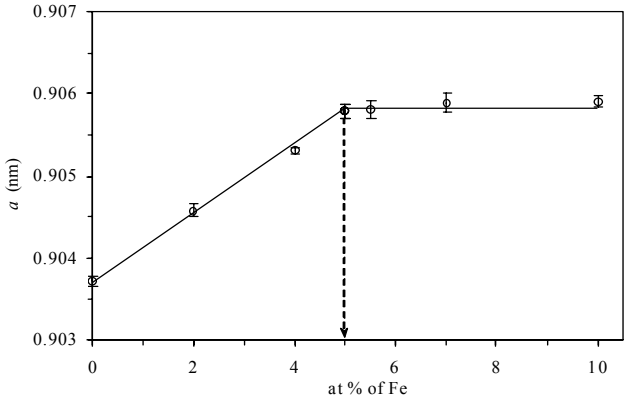



Figure 4. Lattice parameter *a* of $D0_2$ phase in isopleth at 75 at.% of Sb.

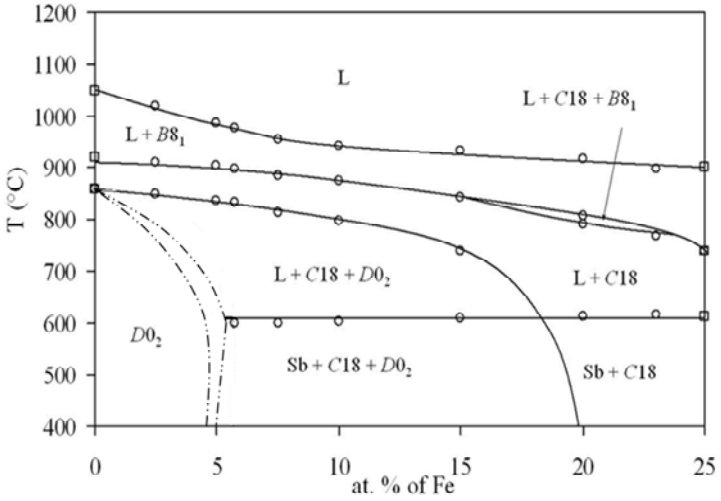



Figure 5 . The $CoSb_3$-$FeSb_3$ section of the ternary (dotted lines represent the phase boundaries wich are not determine with hign precision.)

**Modelling the ternary system.**

The ternary system was modeled according to the Calphad recommendations (10, 11).The assessed excess Gibbs energies of the constituent subsystems have been extrapolated to the three component system. Experimental data used for these calculations are those concerning the phase diagram measurements , enthalpy of formation of the compounds, Cp for CoSb and chemical potentials measured by electrochemistry. They have been taken from the literature as well as from our own measurements (8,9).

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

The modeled phase diagrams of the three binaries are obtained and put together in order to built the ternary system. All the sections (isopleth as well as isotherms can be calculated), solidification paths are obtained by this way. As an example, figure 6 shows the calculated isothermal section for the temperature of 1000 K. In this picture we can see some particularity of the system. Due to the shape of the luiquidus and solidus surfaces (presence of a minimum in the ternary), the skutterudite phase is always in equilibrium with the *B8* and *C18* phases. It explain the existence of impurities in some fabrication processes and thus, one can understand the difficulties to synthesize single phase samples of skutterudites.

**Conclusions.**

Using the CALPHAD method, we have described the Co - Fe -Sb phase diagrams and shown the usefulness of this kind of study for the fabrication processes. We have modelled the Co-Sb and Fe-Sb phase diagrams that are the first step of the constitution of our database. Three sections of the ternary have been determined and particularly the $CoX_3$ section. The ternary Co-Fe-Sb is experimentally determined and the modelling is presently obtained and lead us to explain the problems expected in the materials synthesis.

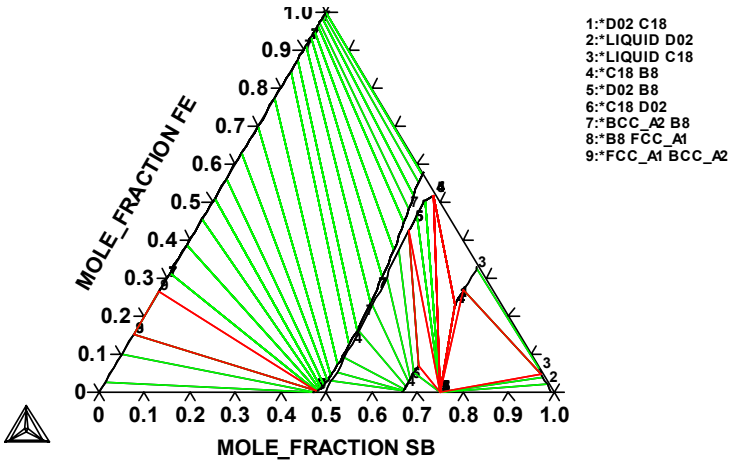



Figure 6. Calculated isothermal section at 1000 K showing the phase fields and the tie-lines.

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