

Conditions for the Electrochemical Synthesis of the $CoPn_3$ (Pn = P, As, Sb) Skutterudites

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The binary pnictide skutterudites, $CoPn_3$ (Pn = P, As, Sb), have been successfully synthesized for the first time by molten salt electrolysis. The melt for depositing CoP_3 contained CoO and $(NaPO_3)_3$, and graphite rods were used for both anode and cathode. All experiments were run in a flowing N_2 gas atmosphere. By adjusting the melt composition, single phase CoP_3 could be prepared. Attempts were also made to deposit CoP_3 using platinum and silver strip electrodes. Although CoP_3 powder was obtained in the crucible, no CoP_3 deposit was found on the Pt cathode, which was attacked by the phosphorus present in the melt and produced platinum phosphide (PtP₂). A low deposition rate was observed for Ag cathodes, and as a result, a very small amount of material was deposited. This made it difficult to determine the type and number of phases formed. Using graphite electrodes, two other cobalt skutterudites were prepared. CoAs₃ was synthesized from a CoO + NaAsO₂ melt and CoSb₃ from a CoO + Na₂CO₃ + Sb₂O₃ melt. While the skutterudite phase were formed in these systems, the optimal melt compositions and other experimental conditions necessary to prepare single phase deposits still need to be determined. $(0 \ 2001)$ The Electrochemical Society. [DOI: 10.1149/1.1389342] All rights reserved.

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Skutterudite compounds have been identified as potential candidates for thermoelectric applications.^{1,2} One of the target materials within this class is CoPn₃ (Pn = P, As, Sb) and its derivative compounds obtained by cation and/or anion substitution. The common methods for synthesizing bulk quantities of the cobalt skutterudites are either direct synthesis from the elements (reaction temperature range ~600 to 1000°C)³⁻⁸ or solution growth, usually from molten tin for cobalt triphosphide or antimony for cobalt triantimonide (processing temperature range ~780 to 1000°C).⁸⁻¹⁰ Both of these techniques require extended reaction time (up to 2 weeks) and in the case of the phosphides and arsenides involve high vapor pressure of group V components. The tin solution process requires acid etching to remove the tin. In addition, the presence of tin in the skutterudite lattice and its role in the thermoelectric performance of the material is not known.

A possible alternative to direct synthesis or solution growth of the pnictide skutterudites is electrochemical synthesis. Chene¹¹ electrochemically synthesized a series of cobalt-phosphorous compounds from melts containing cobalt oxide and sodium metaphosphate. However, he did not report synthesizing CoP₃. Other investigators have reported on the electrochemical synthesis of some technologically important materials such as GaP^{12,13} and GaAs.¹⁴ These earlier results led to the current investigation.

Electrochemical synthesis offers several advantages over direct synthesis and solution growth techniques. First, it is a relatively low temperature technique and thus avoids problems of thermal decomposition and excessive vapor pressure. Second, it is relatively unaffected by small changes in temperature. Third, the technique does not require that either the starting material or the final product be congruently melting. (CoPn₃ compounds are peritectics.^{15,16}) Fourth, the total reaction time is 2 to 4 days. Finally, electrochemical synthesis is controlled by electrical parameters, which can be more precisely controlled than temperature.

This investigation represents the first electrochemical synthesis of the cobalt pnictide skutterudites. The conditions for the synthesis of these compounds are reported.

Experimental

All electrodepositions were performed in a closed Inconel 600 cylinder fitted with a removable cover sealed with an O-ring. The cover had fittings for two electrodes (anode and cathode), a gas inlet and outlet, a thermocouple, and a view port (Fig. 1). The cylinder was externally heated by a resistance furnace controlled by a proportional integral differential controller. The melts were contained in a graphite crucible fitted with a baffle to separate the anode and

cathode compartments. All experiments were conducted under a flowing nitrogen atmosphere at temperatures ranging from 650 to 700°C, depending on the type of melts under investigation. Current *vs.* voltage (I-V) plots were made before each deposition in order to be sure that the deposition potential was above the last plateau. The applied voltages ranged from 3 to 5 V with currents as high as 1 A. The products were recovered by dissolving the melts in a recirculating water stream.

The reactions taking place at the electrodes during electrolysis can be described by the equations

$$M^{+2} + 2e^- \rightarrow M$$
 cathode

 $PO_3^- + 5e^- \rightarrow P + 3 O^{-2}$ cathode

 $M^{+2} + 3PO_3^- + 17e^- \rightarrow MP_3 + 9 O^{-2}$ overall cathode

 $\begin{array}{rl} {\rm O}^{-2} \rightarrow \ 1/2 \ \ {\rm O}_2 \ + \ 2e^- & anode \\ \\ 2\,{\rm M}^{+2} \ + \ 6{\rm PO}_3^- \rightarrow \ 2{\rm MP}_3 \ + \ 17/2 \ \ {\rm O}_2 \ + \ {\rm O}^{-2} & overall \end{array}$

The potential (E) for driving the overall reaction can be expressed by the Nernst equation

$$E = \Delta E^0 - (RT/34F) \ln([O_2]^{8.5}[O^{-2}]/[M^{+2}]^2[PO_3^{-1}]^6)$$

where ΔE^0 is the difference in standard electrode potentials and the oxygen is included since its partial pressure (or more properly fugacity) is less than 1 atm. Unfortunately, the standard elec-



Figure 1. Schematic drawing of the experimental setup for electrochemical synthesis of $CoPn_3$ (Pn = P, As, and Sb) skutterudites.



Figure 2. Experimental I-V curves for the $CoO + Na(PO_3)_3$ melt using different cathode/anode pairs for the synthesis of CoP_3 .

trode potentials for the molten salt systems used for skutterudite deposition were not known and, therefore, the Nernst equation could not be used to determine either the reactant concentrations for a given potential or the potential to apply for a given concentration of reactant species. As a result, the proper metal to metaphosphate ratio must be determined empirically. This is one of the few disadvantages of the molten salt electrochemical synthesis method.

The following are the experimental conditions for each of binary pnictide skutterudites.

 CoP_3 .—The results of Chene's investigations¹¹ were used to plot the ratio of PO₃ (metaphosphate) to Co⁺² in the melt *vs.* the ratio of P to Co in the product. This was then extrapolated to a P:Co ratio of 3:1 which gave a starting point for a melt composition of 93.6:1.0 $(PO_3^-:Co^{+2})$. Electrolysis was carried out using a graphite anode and cathode in a melt containing CoO and $(NaPO_3)_3$ (sodium trimetaphosphate). The initial result was a mixture of cobalt phosphide compounds. A systematic study of the effects of melt composition on the number and stoichiometry of the phases present in the synthesized product was used to find the optimum melt composition for the production of single phase CoP₃. Attempts were also made to deposit CoP₃ on platinum and silver strip electrodes using the same melt composition. In these experiments, a Pt anode was used. Figure 2 shows experimental I-V plots for these melts with different electrode materials.

 $CoAs_3$.—There is no commercially available metaarsenate, but experience with GaAs¹⁴ demonstrated that arsenides can be electrodeposited from melts containing sodium metaarsenite (NaAsO₂). The only melt that was tried for the synthesis of CoAs₃ contained 95 mol % metaarsenite. An I-V curve for this melt system with graphite electrodes is shown in Fig. 3.

 $CoSb_3$.—Initially, we were not able to find any commercially available metaantimonate or metaantimonite so the melt was prepared from sodium carbonate (Na₂CO₃) and antimony oxide (Sb₂O₃) which would react to form the antimonite. The melt was nominally 95% metaantimonite and, like the CoAs₃ experiment, was electrolyzed using graphite electrodes. The I-V characteristics for the deposition of CoSb₃ are plotted in Fig. 3 along with that of CoP₃ and CoAs₃ experiments.

Results and Discussion

 CoP_3 .—The synthesized materials did not adhere well to the graphite electrodes and the products were recovered from the solidified melts in the form of a black powder and tiny crystalline particles. Table I shows the results of the systematic melt composition



Figure 3. Experimental I-V curves for deposition of CoAs₃ and CoSb₃ using graphite electrodes. An I-V curve for CoP₃ is also shown for comparison.

changes that lead to the formation of CoP₃. When a lower concentration of sodium trimetaphosphate was used, the phases present in the products were Co₂P and CoP. Increasing the amount of sodium trimetaphosphate resulted in mixtures containing various ratios of CoP₃ and CoP. The final melt composition used was 99.7 mol % metaphosphate and 0.3 mol % Co⁺². Electrolysis of this melt composition yielded phase pure CoP₃ with slight traces of graphite contamination. An X-ray diffraction (XRD) pattern of the electrochemically synthesized CoP₃ is shown in Fig. 4a.

Preliminary studies of the deposition of a CoP_3 film on platinum sheet yielded a dark gray deposit on both sides of the cathode. These areas were very brittle, and X-ray analysis showed that they consisted mostly of the compound platinum phosphide (PtP₂). No sign of CoP_3 was observed on the cathode. A portion of the material retrieved from the crucible, however, contained the skutterudite phase. It seems that Pt, similar to graphite, does not provide a good surface for cobalt triphosphide adhesion. When the Ag cathode was used, a very small amount of material was deposited. The low deposition rate corresponds to the low current observed in the I-V curve (Fig. 2). Preliminary energy dispersive X-ray analysis indicated that there were different Co and P ratios in the deposits but the actual phases formed have yet to be determined.

The results with CoP_3 are rather interesting in light of Chene's work.¹¹ He reported obtaining CoP_2 as one of the products of his electrochemical studies and there is also an XRD pattern for this compound from another source. Even though compounds ranging from Co_2P to CoP_3 were electrochemically synthesized in the current experiments, there was no evidence for the formation of the CoP_2 phase. There are several reasons that may explain these discrepancies. First, the voltage and current used in Chene's work were much higher than those in our experiments, and such a large driving force may shift the experimental conditions very far from equilibrium conditions, thereby leading to metastable phase formation. Second, Chene used chemical analysis rather than XRD to determine

Table I. Products vs. melt composition for the Co-P system.

Melt composition (mol % PO_3^-)	Products	Amount (%, estimated from X-ray)	Average P content (atom %)
97.6	Co ₂ P	5	48.8
	CoP	95	
99.0	CoP	50	66.7
	CoP ₃	50	
99.3	CoP	12	73.4
	CoP ₃	88	
99.7	CoP ₃	100	75.0



Figure 4. XRD patterns of electrochemically synthesized skutterudites: (a) CoP_3 , (b) $CoAs_3$, and (c) $CoSb_3$.

the composition of the synthesis products. Since the former technique only gives the relative amount of elemental constituents, it could not have been used to distinguish between the pure CoP_2 phase or a 50:50 mixture of CoP_3 and CoP. In our experiments, the XRD patterns did not reveal any sign of CoP_2 formation and it is possible that this phase may not form under normal experimental conditions.

The difficulty in obtaining CoP_2 was also mentioned by Donohue¹⁷ who reported the presence of CoP_2 phase only when prepared at high pressure. Since the data in the Co-P phase diagram¹⁸ are incomplete, especially in the high phosphorus region, it cannot be precisely determined whether CoP_2 is a thermodynamically stable phase. It is possible, however, that this compound may form peritectically under certain conditions, similar to the behavior of the di- and tripnictides compounds in Co-As¹⁵ and Co-Sb¹⁶ systems

 $CoAs_3$.—The product of the electrolysis of the 95 mol % metaarsenite melt contained approximately 90% CoAs₃ and 10% CoAs₂ as estimated from the XRD pattern (Fig. 4b). There was evidence that most of the metaarsenate had evaporated from the melt during the two day experiment. Although there have been no further attempts to synthesize phase pure CoAs₃, it is clear in which direction the melt composition must be modified. Not only will the ratio of metaarsenite to cobalt ion have to be changed, but other components will have to be added to reduce the melting temperature of the charge and therefore its vapor pressure. This was done with the melts for the electrochemical synthesis of GaAs.¹⁴

 $CoSb_3$.—The products of the electrolysis of the nominally 95 mol % metaantimonate were metallic antimony (70%) and $CoSb_3$ (29%). Again, the melt composition needs to be adjusted to produce phase pure material. Changing to another source of antimony, such as potassium hexahydroxyantimonate, may also be useful.

The above results show that all three pnictide skutterudites can be synthesized by molten salt electrolysis. While cobalt triphosphide was obtained as a single phase, the arsenide and antimonide have not yet been obtained in pure form. The principal barrier to obtaining these materials as a single phase is the adjustment of the melt composition.

Conclusions

It was demonstrated for the first time that the binary skutterudite compounds, $CoPn_3$, could be synthesized electrochemically. However, there is some anomalous behavior in the electrodeposition of the phosphorous compounds that remains to be understood. Using platinum metal as electrodes for the electrodeposition of CoP_3 did not work well because it reacted with phosphorous to form a platinum phosphide phase. Ag cathodes gave poor deposition rates under the experimental condition investigated, and resulted in a very small amount of the synthesis products. Running more experiments at longer time will be useful to determine whether Ag is a suitable electrode material. In the case of $CoAs_3$ and $CoSb_3$, the optimum melt compositions for the synthesis of phase pure compounds need to be determined.

There are other interesting areas of research that may follow from these results. These include the synthesis of pure or doped mixed pnictide skutterudites, and the electrodeposition of thin films on suitable substrates. The latter would greatly facilitate the study of their thermoelectric properties.

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