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The Electrochemically Assisted Synthesis of $ZnSiP_2$

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Efforts directed toward the electrochemical synthesis of the ternary chalcopyrite $ZnSiP_2$ are discussed. In all cases reported here, the zinc source was a molten zinc cathode. Electrolysis current densities and temperatures are found to be important variables in determining whether the predominant products are ternary or binary phosphides. The binary phosphides are formed at temperatures below the boiling point of the zinc cathode (906°C). Above 1000°C, transport of zinc and silicon sources occurs readily. In the atmosphere of nearly pure elemental phosphorus maintained by the electrochemical reduction of the phosphorous source onto the cathode, the ternary phosphide is formed by the direct combination of the elements on the walls of the cell. The chemical nature of the silicon source is also found to be a critical factor influencing the formation, purity, and silicon content of the ternary phosphides. Silicon sources studied included: Mg_2Si, Na_2SiF_6, and SiO_2. The characteristics of $ZnSiP_2$ samples prepared in this fashion using a variety of silicon sources are described.

Introduction

This effort is directed toward exploring new routes to the synthesis of chalcopyrite structure ternary phosphides, $ZnSiP_2$ and $ZnGeP_2$. The chalcopyrite structure (ABC_2) belongs to the tetrahedral $E1_1$ structure type, space group $I\bar{4}2d$, with four formula units per cell (*1*).

Previous syntheses of the $ZnSiP_2$ and $ZnGeP_2$ ternary phosphides have involved reaction of the elements, typically using either a halide chemical vapor transport scheme or a tin flux (*2, 3*). In all previously reported syntheses, the ternary phosphides are reported to form only at temperatures above 1100°C. Synthesis from the elements in a tin flux requires several weeks to produce a small sample with fair yields (*3*). Because these synthetic techniques are unlikely to prove feasible for producing large quantities of window quality materials, other synthetic routes to the ternary phosphides are clearly desirable. This paper will describe studies of possible electrochemical routes to $ZnSiP_2$.

Electrochemical methods of synthesis in molten metaphosphates are well known for the preparation of simple transition metal binary phosphides (*4–10*). In most instances, the product of the production of a metaphosphate melt and a transition metal oxide or halide at high current density and temperatures (between 600 and 800°C) is the binary phosphide. The stoichiometry of the binary phosphide produced and the pu-

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rity of the phosphide phase have been found to depend not only on the melt stoichiometry but also on the conditions of the electrolysis. For example, the electrochemical preparation of iron phosphides is a case where the stoichiometry of the product phosphide can be varied simply by changing the rate of electrolysis and temperature (*7, 8*).

There have been few reported electrochemical syntheses of nontransition metal phosphides to date. Elwell *et al.* (*6*) reported the electrochemical deposition of InP, Cuomo *et al.* (*11*) grew GaP electrochemically and we have found no reports of the electrochemical synthesis of ternary (or higher) phosphides. The electrochemistry of the group IV components of the ternary compounds that we desire are difficult to control. Silicon and germanium are semiconductors that undergo surface oxidation readily in oxidizing media, particularly at elevated temperatures. In nonoxidizing media (like molten chlorides or fluorides), no such passivation occurs and silicon deposition has been reported. Unfortunately, melts which show the desired electrochemical behavior of the *M*(IV) species generally have an unfavorable phosphorous chemistry. Conversely, melts which show favorable phosphorous chemistry are generally oxide rich and tend to passivate metal surfaces and precipitate the *M*(IV) species as a nearly insoluble oxide.

Experimental

Electrolytic apparatus. All chemicals used in this study were reagent grade or higher purity. $NaPO_3$ was heated to 400–500°C in air before use to ensure that the salts were as anhydrous as possible. Despite this drying procedure, some "ultraphosphoric acid" reflux was frequently noted on the walls of the cell, particularly during the initial heating of experiments to temperatures over 900–1000°C. The azeotropic H_2O–P_2O_5 acid has a reported composition of 0.69 H_2O/P_2O_5 ratio and a reported boiling point of 864°C (*12*). KPO_3 was formed by dehydrating KH_2PO_4 at 500–600°C.

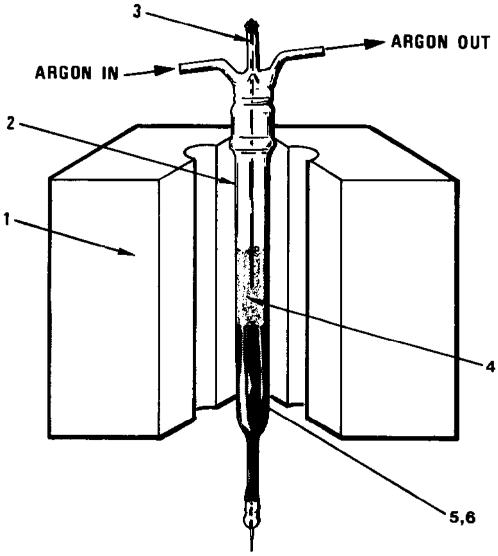

FIG. 1. Electrochemical cell. (1) Furnace. (2) Thick wall quartz vessel, 0.75 in. (3) Anode carbon rod, 0.25 in. (4) Electrolyte, $NaPO_3$, $NaPO_3/KPO_3$. (5) Silicon source (Mg_2Si, Na_2SiF_6, SiO_2). (6) Cathode (molten zinc or molten zinc–tin alloy).

The electrochemical cell for the liquid cathode studies consisted of a thick well quartz vessel, 0.75-in. internal diameter. As shown in Fig. 1, the cell cathode was a molten pool of zinc, a zinc–tin alloy, or pure tin, roughly 2.85 cm^2 centered in the hot zone of a thermostated furnace. The silicon containing source (Mg_2Si, Na_2SiF_6, or SiO_2) was mixed intimately with the elemental zinc cathode. Cathode prefusion occurred during the initial heating and was generally complete before the melting point of either the pure $NaPO_3$ electrolyte or an electrolyte of equimolar $NaPO_3$–KPO_3. The anode was a carbon rod, 0.25-in. diameter, immersed 1–2 in. into the melt. Cells were normally loaded with electrolyte then purged with argon for 30 to 45 min. All experiments reported here used a quartz cell that was placed in a preheated furnace. Reaction times range from 2 to 16 hr. When long reaction times were attempted, cells short-circuited and, therefore, reactions were self-terminating. Argon flow continued throughout the experiment to prevent the buildup of significant quantities of oxygen formed by the anodic reaction. Because oxygen is formed at the anode through the oxidation of metaphosphate (*13*), more stringent precautions for the exclusion of oxygen from the cell were not considered necessary.

One significant disadvantage to the use of a quartz electrochemical cell is that the quartz is chemically attacked, particularly at elevated temperatures. Therefore, all of our samples are silica and silicate contaminated. However, the relatively simple electrical connections made possible by the electrically insulating nature of quartz at these temperatures outweighed the other experimental considerations.

In the present synthetic studies, the cells were run at a constant 5-V potential. Geometric considerations prevented the use of a reference electrode in the molten zinc cathode studies. These experiments normally ran at initial current densities over 2 A cm^{-2} (cathode area). This high rate reduction of the melt on the zinc cathode serves gradually to coat the cathode with binary phosphide. The current is observed to diminish as the overpotential for the melt reduction reaction increases because the electrode surface changes from liquid metallic zinc to solid semiconductive binary phosphide. At elevated temperatures (over 1000°C), the binary phosphides chemically decompose and stable electrolysis current densities near 500 mA cm^{-2} are observed.

At the conclusion of the synthesis, the cell was first disconnected from the electronics and then air quenched to room temperature while maintaining the carbon electrode in the melt. The irregular single crystals of ternary phosphide were recovered by breaking the electrochemical cell. The crystals of ternary phosphide product were found as a deposit on the cell walls and on the carbon anode above the melt level. It should be noted that large quantities of the white (pyrophoric) allotrope of phosphorus are formed and care is necessary when breaking the electrochemical cell. Further, the presence of trace amounts of the P_2O_5–H_2O azeotrope, unstable binary phosphides, and reactive finely divided white phosphorus leads to the production of insignificant quantities of the highly toxic gas phosphine (observed on GC–MS analysis of the argon flush gas and present in sufficient quantities to produce the characteristic unpleasant odor of that gas).

X-ray analysis. The samples prepared by the above procedures have been analyzed by X-ray diffraction. Diffractometer scans of powders and Gandolfi data on single crystals were collected for a variety of samples using nickel-filtered Cu$K\alpha$ radiation. A Philips diffractometer with a theta-compensating slit, diffracted beam monochromator, scintillator with pulse-height discrimination and a copper source were used (Cu$K\alpha$ = 1.5418 Å, Cu$K\alpha_1$ = 1.5405 Å, Cu$K\alpha_2$ = 1.544 Å).

Diffuse reflectance infrared spectra. A Nicolet model 7199 FTIR spectrometer was used to measure the diffuse reflectance spectra of bulk $ZnSiP_2$ that was synthesized by using a tin flux route and a 10- to 20-mol% $ZnSiP_2$ for KBr for the electrochemically synthesized compounds.

X-ray photoelectron spectroscopy (*XPS*). Particle size distribution was performed on an Amray 1400 with a 40 Å lateral resolution. Electron microprobe analyses were performed on a Tracor-northern TN 2000 energy dispersive X-ray analyzer with an incident beam energy of 25–35 kV.

Scanning auger microprobe spectroscopy (*SAM*). SAM spectroscopy was performed on a PHI 600 scanning auger spectrometer with beam currents from 10–15 nA and incident beam currents of 3–10 kV.

Results and Discussion

The only phosphides previously synthesized electrochemically have been those materials with reduction potentials more positive than the −0.9 V (versus carbon) reduction potential of metaphosphate (*13–15*). The electrochemical characteristics of the reduction of metaphosphates have been well explored by earlier researchers (*13–15*). One can speculate on a mechanism in which the reduction of a solution of transition metal ions in the metaphosphate melt has metal deposition as the first cathodic process with subsequent melt reduction and production of elemental phosphorus. A case where this mechanism for the formation of the phosphides is the reduction of WO_3 solutions in metaphosphates can produce both elemental tungsten and the phosphide (*4*). The second electrochemical process (melt reduction) is the chemical equivalent of adding pure white phosphorus to the newly deposited transition metal surface. Similar studies resulting in the deposition of GaP and InP have been performed (*11, 6*). The production of binary phosphides and elemental phosphorus predominates the Faradaic processes. In all cases discussed here, the crystalline ternary phosphide products were formed as a result of chemical processes obscured by the efficiency of binary phosphide and elemental phosphorus reactions. We have discussed the electrochemical production of binary phosphides elsewhere (*16*). Furthermore, no elemental analysis was performed on any of these samples.

The production of silicon containing crystalline ternary phosphides presents a particularly difficult challenge since the use of a pure silicon cathode is made impractical because of its high electrochemical resistance. The choice of the silicon source for the synthesis of a ternary phosphide from molten metaphosphates is a critical factor in determining the products that are produced and the yield of those products. The high melting point of silicon and the fact that the silicon is nearly insoluble in molten tin or molten zinc makes the design of a practical silicon source for these reactions more difficult. No zinc silicides are known. All of the research reported here used the liquid zinc cathode as the zinc source while elemental silicon, silica, silicides, and hexafluorosilicates were tested as possible silicon sources.

Elemental silicon segregates from the molten zinc cathode and no ternary phosphide has been observed using elemental silicon as the silicon source. Amorphous SiO_2 is only sparingly soluble in molten metaphosphates. However, the formation of the ternary $ZnSiP_2$ has been observed from silica added as either quartz (from the cell walls), or quartz wool, but not as amorphous silica, in molten metaphosphates. Unfortunately, the product is frequently not well formed crystal, and nonstoichiometric crystals produced are full of defects. Undoubtedly, one factor that influences this is the fact that SiO_2 and polymeric silicon–oxygen anions (e.g., $Si_2O_7^{6-}$) are virtually impossible to obtain in an anhydrous state. The precise role of adsorbed water on the chemical reactions at the silica surface is unknown. The production of the ternary phosphide was not observed at the cathode. Rather, binary phosphide formation occurs at the cathode and ternary phosphide productions occurs by a chemical (*not* electrochemical) reaction in the body of the cell, presumably by the reaction of the elements. Further, high current densities are necessary to form the product, and after brief electrolysis (several hours), yields are uniformly small. These observations may be explained by the need to get adequate amounts of vapor-phase zinc phosphorus, zinc, and silicon into the reaction zone in the body of the cell.

It has been found that the fluorosilicates decompose in the molten metaphosphates but that decomposition is reasonably slow and some crystalline ternary products were noted. One interesting observation is that the fluorosilicates decompose in these melts with the evolution of SiF_4,

$$Na_2SiF_6 \xrightarrow{\Delta} 2NaF + SiF_4 \uparrow \qquad (1)$$

This decomposition is observed by a vigorous foaming of the melt as the electrolyte fuses. In general, the yield produced using Na_2SiF_6 as the silicon source is poor and the majority of the silicon originally present as the fluorosilicate escapes from the cell.

The use of Mg_2Si as a silicon source has produced crystalline material of good chemical quality and near stoichiometry. Like the fluorosilicates, the Mg_2Si has a tendency to decompose in the metaphosphate melt to form silane on reaction with the trace quantities of azeotropic "ultraphosphoric acid" mentioned earlier. The silane then decomposes on the walls of the vessel by the reaction

$$SiH_4 \xrightarrow{1100°C} Si + 2H_2 \uparrow \qquad (2)$$

As with the experiments using fluorosilicate silicon donors, the production of the ternary phosphide does not occur at the cathode. Again, ternary phosphide production occurs on the cell walls. Yields are uniformly poor and high current densities are again necessary to maintain a phosphorus rich atmosphere above the melt. Inclusion of Mg in the $ZnSiP_2$ product was not a problem when Mg_2Si was used as the silicon source. Auger and SEM analysis of the $ZnSiP_2$ showed no sign of magnesium impurities.

X-ray diffraction analysis of the polycrystalline ternary phosphide shows the presence of some Mg_2Si in the melt even after several hours at 1100°C. This suggests that the reaction of the melt with the silicide may be limited by the quantity of protons (as H_2O contamination) present in the melt.

Using either fluorosilicate or silicide as the silicon donors, the ternary phosphide may be deposited on the walls of the cell through the reaction of the reduced forms of the elemental constituents at 1100°C. Table I shows the observed X-ray diffraction lines for the ternary phosphide formed using Na_2SiF_6 and Mg_2Si as silicon sources compared to the calculated diffraction pattern using a tetragonal cell with $a = 5.400$ Å and $c = 10.440$ Å (space group $I\bar{4}2d$). In both cases, the other major impurity phases present were ZnP_2 and Zn_3P_4. This X-ray data should only be used as a fingerprinting tool, since no internal standard was used. Furthermore, relative intensities of diffrac-

TABLE I

GANDALFI CAMERA DATA FOR THE PRODUCTS FORMED BY THE ELECTROCHEMICALLY ASSISTED SYNTHESIS OF $ZnSiP_2$ USING Na_2SiF_6 AND Mg_2Si AS SILICON DONORS

Na_2SiF_6 source *d* spacing	Mg_2Si source *d* spacing	$ZnSiP_2$	
		h k l	*d* spacing
4.55	—	1 0 1	4.796
3.086	3.103	1 1 2	3.08
2.977	3.001	1 0 3	2.925
2.753	2.681	2 0 0	2.70
2.514	2.500	0 0 4	2.61
2.340	2.334	2 2 1	2.354
—	2.314	1 0 0 of Mg_2Si	(2.25 calc)
2.216	2.193	3 0 0 of SiP	(2.2 calc)
2.160	2.112	2 1 3	2.20
2.082	2.024	2 2 0	1.909
2.005	1.940	1 0 5	1.947
1.909	1.790	2 0 4	1.877
1.833	1.758	3 0 1	1.774
—	1.706	3 1 1 of SiP_2	(1.71 calc)
1.660	1.666	2 2 2 of SiP_2	(1.64 calc)
—	1.642	3 1 2	1.623
1.586	1.599	1 1 6	1.583
—	1.585	2 1 5	1.579
1.548	1.541	2 2 4	1.5409
1.506	1.477	3 2 1	1.496

tion lines changed from one synthesis to the next suggesting that different syntheses created products with varying degree of crystallinity.

A parallel between present results and those reported in the literature for syntheses of other ternary phosphides is quite evident, particularly in the case of solution growth from a tin flux. With flux growth, the product is slow to form and always highly crystalline. Experiments performed here suggest that during flux growth the rate of crystal growth may be a function of the rate of silicon dissolution in the flux rather than the rate of reaction, nucleation, and crystallization. This conclusion is supported by the observation that this electrochemically assisted synthesis of the ternary zinc silicon phosphide has been demonstrated with the production of the crystalline product after electrolysis times as short as several hours. Our samples are frequently quite small and silicon poor about the edges, suggesting crystal nucleation on silicon deposited by either the decomposition of SiF_4 or SiH_4 on the cell walls, at 1100°C.

Supporting experiments using a twofold excess of silicon in a tin flux reaction of zinc, silicon, and phosphorus produce a small increase in yield than corresponding experiments using a stoichiometric amount of silicon. In all syntheses from the elements in a sealed ampoule, significant quantities of undissolved silicon remain segregated from the melt. Similarly, the samples synthesized using the electrochemically assisted route form product on the wall of the electrochemical cell, probably at silicon sites. There are, no doubt, many more silicon sites present than ternary phosphide sites. These results strongly suggest that the rate determining step in the synthesis of the ternary phosphide using either route is the dissolution and migration of the silicon rather than a kinetic barrier to crystallization.

Diffuse reflectance infrared spectra of $ZnSiP_2$ synthesized using traditional tin flux route and the electrochemically assisted route are shown in Figs. 2 and 3, respectively. The diffuse reflectance spectra of the sample synthesized using tin flux route had only minor impurity bands due to the presence of anionic impurities. The sample synthesized using the electrochemically assisted route has significantly higher concentrations of anionic impurities bands in the

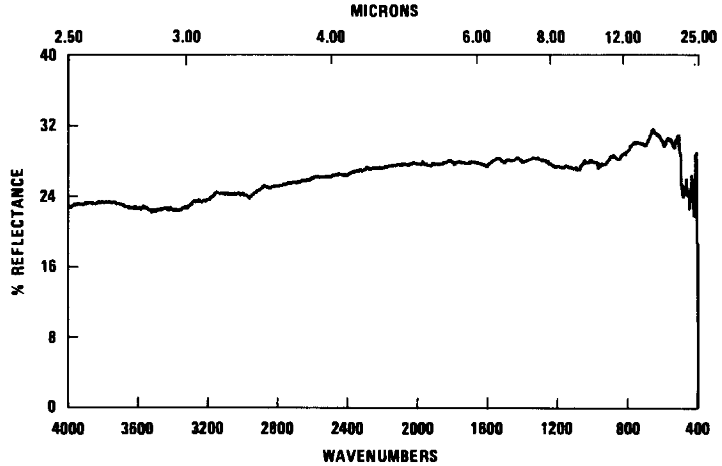

FIG. 2. Diffuse reflectance spectrum of $ZnSiP_2$ crystals synthesized by tin flux procedure.

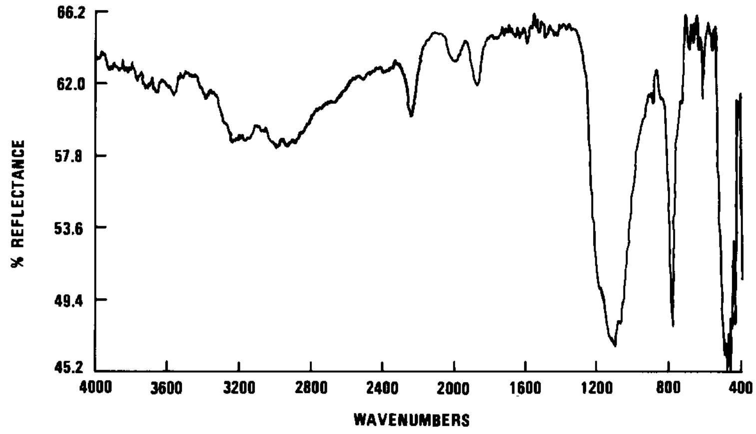

FIG. 3. Diffuse reflectance spectrum of $ZnSiP_2$ crystals synthesized by the electrochemically assisted route.

region from 1200–400 cm^{-2}. These bands can be attributed to PO_3^{-1}, PO_4^{-3}, $H_2PO_2^{-2}$, HPO_3^{-2}, and $P_2O_7^{-4}$. These impurities have very strong, broad infrared allowed (ν_3) bands from 1000 to 200 cm^{-1} and moderately strong bands (ν_4) from 500 to 650 cm^{-1}.

Figure 4 shows a secondary electron image of the electrochemically assisted synthesized $ZnSiP_2$ (fluorosilicate silicon donor). The samples, although crystalline, are badly etched and have many defect sites. The surface composition of these crystals showed a Zn/P ratio near 1/2 with no sili-

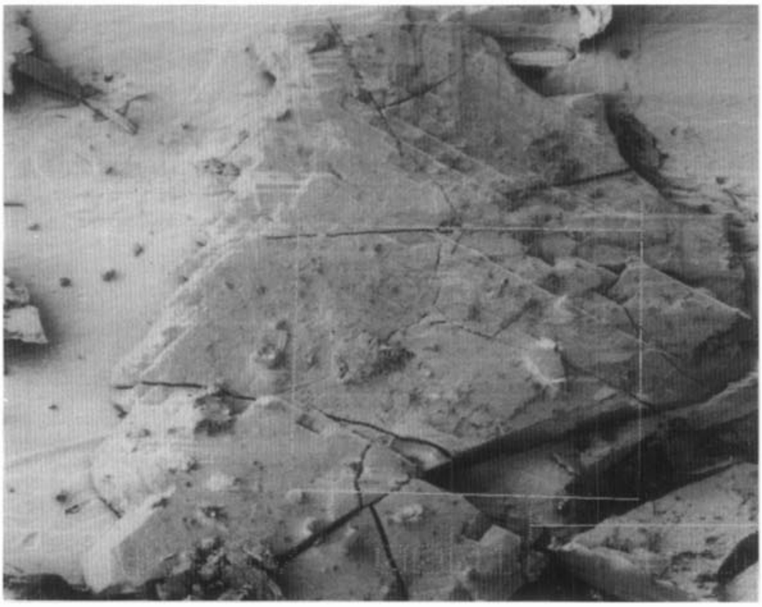

FIG. 4. Secondary electron image of the electrochemically assisted synthesized $ZnSiP_2$ (fluorosilicate silicon donor). 3 kV, 100 μm.

con present. After argon ion sputtering of 20 Å in depth, noticeable quantities of silicon were present, but the crystals remained silicon deficient. This seems to contradict the X-ray data that identifies the product as $ZnSiP_2$ and suggests the possibility of preferential sputtering (*17*). Auger data also shows that oxygen is present only on the surface of the sample shown in Fig. 3. Auger electron spectroscopy of the samples indicated a rough stoichiometry of $Zn_{0.77}Si_{1.07}P_2$. The samples synthesized by the use of the silicide donor gave an approximate stoichiometry of $Zn_{1.22}Si_{0.2\text{-}0.86}P_2$. The silicon concentration varied drastically from 0.2 to 0.86 depending on what part of the sample analyzed. This range of stoichiometries for silicon was often noted even in microscopically similar crystals or in different locations on the same crystal, again suggesting that preferential sputtering and/or crystalline inhomogeneity were present. The "$ZnSiP_2$" products formed by using either silicon source was a brilliant red color and was crystalline. In both cases, the amount of ternary product formed was quite small, even after overnight electrolysis. The crystalline ternary $ZnSiP_2$ formed in this fashion always forms above the electrolyte. The ternary phosphide thus formed is frequently silicon poor around the edges of the samples but generally becomes closer to being stoichiometric in the bulk of the crystal.

Conclusions

In the electrochemically assisted synthesis of $ZnSiP_2$, the crystalline products formed are frequently small, silicon deficient at the edges and have significant contamination with phosphate oxyanions. The only significant electrochemical step appears to be the reduction of the metaphosphate to gas phase phosphorus which then condenses to the white allotrope of elemental phosphorus. The chemical nature of the silicon donor is an important factor influencing the production of the ternary phosphides. The best product yield was obtained with Mg_2Si and hexafluorosilicate silicon sources. The only phosphorus source used in this study was the metaphosphate. Electrolysis rate and temperature are found to be important variables in determining whether the predominant products are ternary or binary phosphides. The binary phosphides are formed at temperatures below the boiling point of the zinc cathode, 906°C. Above 1000°C, transport of zinc and silicon sources occurs readily, and in the atmosphere of nearly pure elemental phosphorus maintained by the reduction of the phosphorus source onto the cathode, the polycrystalline ternary phosphide product is formed on the walls of the cell above the melt.

Acknowledgments

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