Preparation of zinc phosphide

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Zn_3P_2 has recently gained importance owing to its possible use in photovoltaic devices [1, 2]. All previous investigations have been on materials synthesized by direct reaction of zinc and phosphorus. These materials exhibited p-type conductivity which has been attributed to the presence of native defects (phosphorous interstitials).

In our laboratory Zn_3P_2 was prepared by the carbon reduction of pure zinc orthophosphate. Two varieties of $Zn_3(PO_4)_2$ were used as the starting chemical. In one case, zinc dust and orthophosphoric acid, both of Analar grade quality, were used. In the other case, Analar grade ZnO and H_3PO_4 were used. Using both these materials, Zn_3P_2 was prepared by a carbon reduction process (using specpure carbon) at temperatures around 600° C. Whereas the yield of Zn_3P_2 was poor for firing temperatures lower than 600° C,

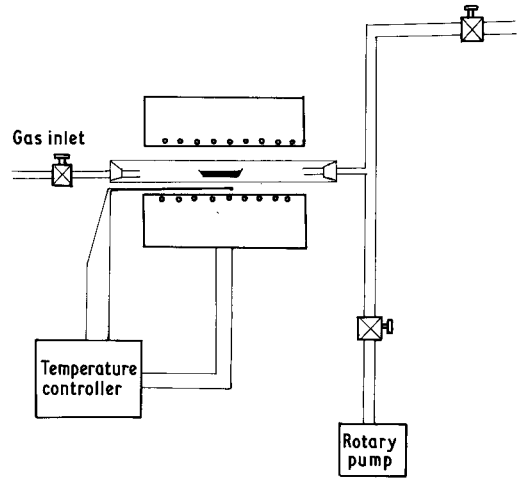

Figure 1 Schematic diagram of the vacuum furnace.

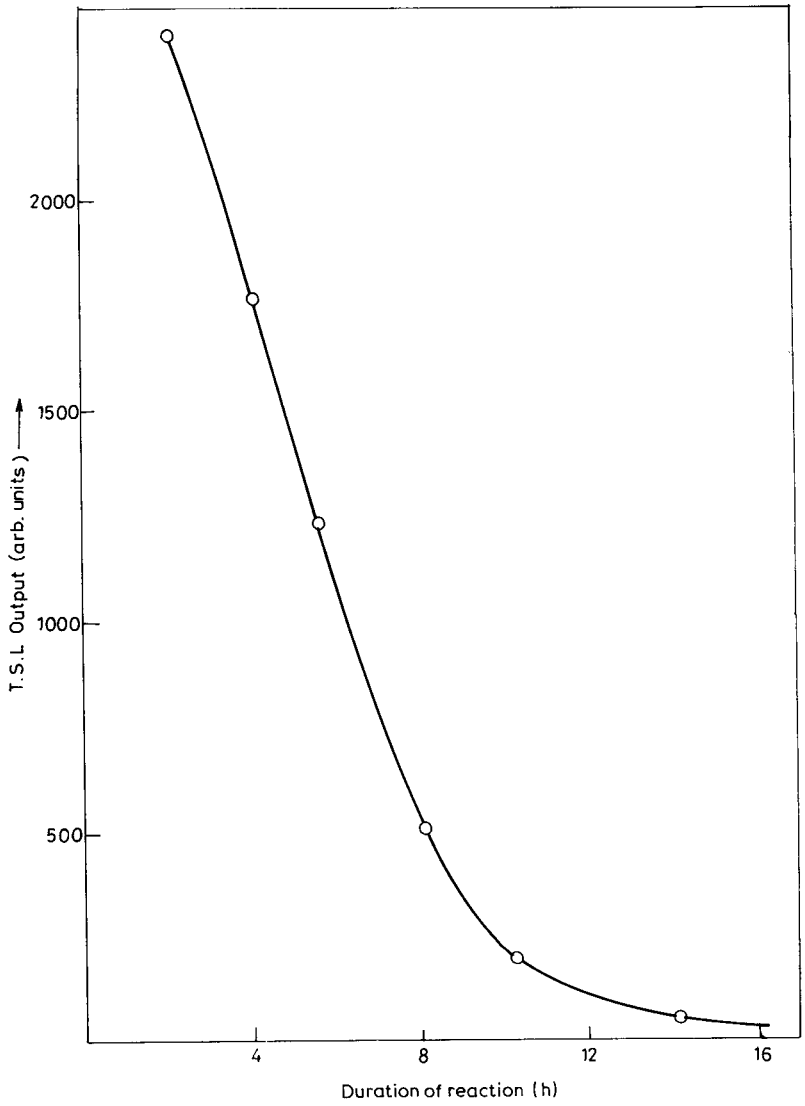

Figure 2 TSL output plotted against reaction time.

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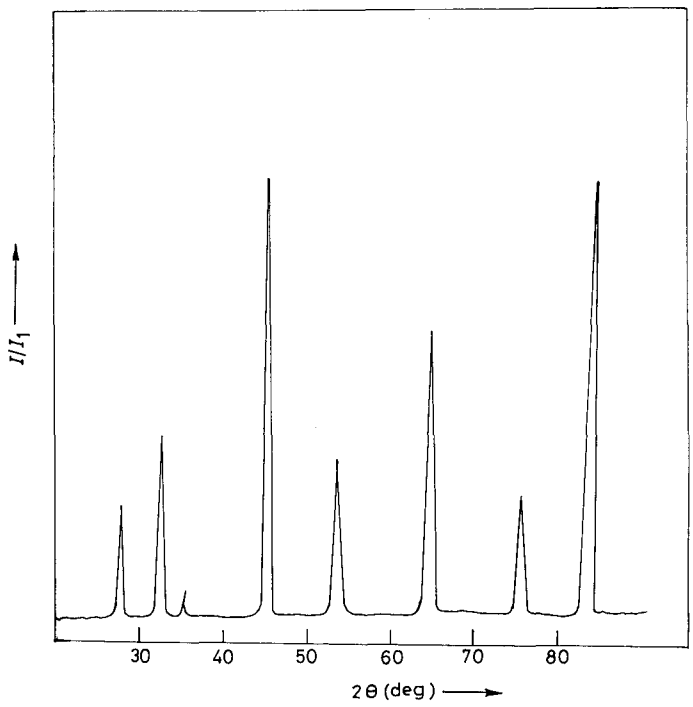

Figure 3 X-ray diffractogram of Zn_3P_2.

material loss occurred above 600° C in a vacuum (10^{-3} torr) furnace for different times between 2 and 16. The product obtained from both types of $Zn_3(PO_4)_2$ exhibited similar properties.

The material studied in this investigation was prepared by thoroughly grinding a mixture of 3.8 g pure $Zn_3(PO_4)_2$ and 1.6 g specpure carbon in a pulverizer. The powder was then transferred to an alumina boat which was subsequently heated in a vacuum furnace. After completion of the heat treatment the samples were quenched to room temperature by blowing cold air over them for about 5 min. A schematic diagram of the tubular vacuum furnace designed for this purpose is shown in Fig. 1. A facility has been provided in the furnace for heating the samples under vacuum, as well as in an inert atmosphere.

Materials obtained by this method after continuing the reaction for 16 h in vacuum have exhibited only the prominent lines of Zn_3P_2. Zn_3P_2 was also prepared by carbon reduction of $Zn_3(PO_4)_2$ in air and the yield of Zn_3P_2 was very poor; it also contained some unreacted $Zn_3(PO_4)_2$, and so only the material prepared under vacuum/inert atmosphere was used as starting material for crystal growth and film preparation.

We have established the duration of the reaction by studying the thermally stimulated luminescence (TSL) of samples taken from the furnace after different reaction times. These samples were exposed to X rays (30 kV, 10 mA, 10 min) and their TSL glow curves were compared with those of pure $Zn_3(PO_4)_2$. The glow curves exhibited glow peaks in almost the same temperature regions for durations less than 8 h because of the presence of unreduced $Zn_3(PO_4)_2$ and Zn_3P_2.

As the reaction proceeds beyond 8 h the TSL output also decreases. The TSL output proportional to the area under the glow curve is plotted against time of reaction in Fig. 2. For the material (Zn_3P_2) obtained after allowing the reduction process to continue for periods greater than 15 h no TSL output could be detected, even after operating the detector in the very high sensitivity range.

The X-ray diffractogram obtained using Cu$K\alpha$ radiation on materials obtained after continuing the reduction process beyond 15 h indicated only the sharp lines assignable to α–Zn_3P_2. The X-ray diffractograms are shown in Fig. 3.

The material obtained by the above process was finally ground to a uniform particle size of 75 μm and was then used as starting material for obtaining thin films of Zn_3P_2 on glass substrates by thermal evaporation. Some of the results on electrical properties have already been published [3–5]. Further work on the preparation of crystals and epitaxial films is in progress.

References

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Received 28 February
and accepted 17 April 1986