# I. GENERAL INTRODUCTION

## 1.1 General :

A study of the optoelectronic properties of semiconducting materials helps a great deal in the general understanding of the electronic processes involved in the different related phenomena. As real crystalline solids are never ideally perfect and pure, the effect of imperfections (related with trace impurities as well as intrinsic native defects) on the different opto-electronic properties like electrical conductivity has to be systematically investigated before the materials are considered for device applications. Such investigations on III-V compound semiconductors (44,45) have been made extensively while such informations of similar studies on II-V group materials are limited (39-43). Some papers (39-41) have recently appeared on the electrical properties of $\alpha$-$Zn_3P_2$, the material least studied previously amongst the II-V semiconducting compounds, and the different properties of these materials are also very well reviewed by Zdanowicz et al (1). In view of the interesting properties exhibited by $Zn_3P_2$, both in the form of single crystals and films, it has attracted the attention of several research workers who feel that it may find promising applications in energy devices (39,40). All the investigations on this material, made till to-day, are on single crystals grown by direct synthesis and they have all exhibited p-type conductivity at R.T. Attempts to prepare (by doping with impurities) n-type

$\alpha$-$Zn_3P_2$ crystals have all been unsuccessful till date; the nature of the native defects responsible for the p-type behaviour of this material has also not been unambigously established.

## 1.2 Scope of the present work :

In spite of the few recent publications on $\alpha$-$Zn_3P_2$, the electronic processes involved and responsible for the p-type behaviour of this material has not been understood properly. This material, unlike using the methods adopted by the earlier workers in this field, has been prepared in this investigation by the reduction process of $\alpha$-$Zn_3(PO_4)_2$ using specpure carbon. In this way the results (reported in the latter chapters) on the electrical and optical properties of $\alpha$-$Zn_3P_2$, both in the form of pellets and thin films are of the first kind and new. Thus a comprehensive program has been undertaken in our laboratory to prepare and study some aspects on opto-electronic properties of $\alpha$-$Zn_3P_2$ with a view to understand further the various properties. Since the method of preparation utilises $Zn_3(PO_4)_2$ as starting chemical, the energy storage properties of this system (both undoped and doped) have also been studied by exciting with UV and X-rays at R.T. Radiation induced traps, both electron and hole type, play a significant role in the light emission phenomena and their presence and distribution in the material modify to a greater extent the luminescence properties (44,45,54-56). The different aspects (nature, kinetics of recombination etc., ) of the associated traps and emitting centres are conventionally studied by using experimental techniques like TSC (Thermally stimulated conductivity) (57-59), photocaoacitance (60,61), decay and thermoluminescence (TL) glow curve method (62,63). Thus, the materials $\alpha$-$Zn_3(PO_4)_2$ and $\alpha$-$Zn_3P_2$ (undoped and doped) have been studied in the present investigation. It may also be added here that using $Zn_3P_2$ powder GaP has been prepared and its conductivity in the form of pellets as well as thin films have been studied. These results indicate properties (well discussed by others) similar to those reported earlier in such materials and these preliminary results, though included, are not discussed. In the following and the general informations one can derive from the different experiments conducted in the study of the opto-electronic properties, are briefly discussed.

## 1.3 Optical absorption :

The absorption coefficient of a transparent material is generally calculated by measuring the optical density log $I_o/I$, where $I_o$ and $I$ are respectively the intensities of the incident and transmitted monochromatic light. In the case of powders, the extent of absorption can be estimated from their reflection spectra. From the study of the optical absorption of a single crystal or thin films at different temperatures as a function of the wavelength of the incident light, different processes like (i) band to band transitions related to the fundamental absorption band (ii) edge absorption and excitons and (iii) absorption associated with impurities and imperfections, involved in optical excitation can be understood. The major contribution to the absorption coefficient in a semiconductor is usually from the excitation of electrons from the valence to the conduction band which may occur via either a direct or indirect transitions. It is also possible to obtain the free electron absorption characteristics similar to that observed in metals, provided the electron concentration or holes in the conduction / and valence bands is sufficiently large; the absorption coefficient, in this case is proportional to the free carrier density and the square of the wavelength in the case of free electrons while for holes, it depends also on the type of involved scattering. For allowed transitions in a direct band gap semiconductor, the absorption coefficient varies as $(h\nu - E_g)^{\frac{1}{2}}$ where '$E_g$' is the minimum band gap value in eV, while for forbidden transitions it varies as $(h\nu - E_g)^{3/2}/h\nu$. In the case of indirect band gap semiconductors, the optical transitions also involve participation of phonons. Thus, information regarding the band structure of a semiconducting material can be broadly obtained from the optical absorption studies where the absorption coefficient is normally larger for semiconductors having a direct gap than indirect band gap values. Indication of sharp line spectra near the band edge is due to exciton absorption which becomes broader in the case of indirect band gap semiconductors.

Further, in the field of color centres which constitute an important class of point defects in ionic solids, the identification of absorption bands makes a significant