CHAPTER I

GENERAL INTRODUCTION AND SCOPE OF THE PRESENT WORK

1.1. INTRODUCTION :

Studies on luminescence, electrical conductivity and related properties of Zn/Cd sulfides belonging to $II^{B}-VI^{A}$ compounds have been extensive in the past and are still being studied actively for various applications in optoelectronic devices (1-9). Such systematic investigations have not been carried out on materials like CaS, SrS, BaS and their mixed systems which belong to alkaline earth sulfide (AES), $II^{A}-VI^{A}$ group of phosphors. These AE sulfides have received greater attention, in recent years in view of their versatile applications as phosphor materials in display screens, multicolored fluorescent lamps, luminescent pigments etc. These sulfides which are traditionally known as Lenard Phosphors and posses NaCl (F.C.C.) crystal structure, have not received due attention, in the past, because of their poor reproducibility and chemical instability under normal conditions. The results of the extensive investigations of Lehmann and his group (10,11,47,48) later on AES have given a great hope to continue investigations on AES for many potential applications in display devices. Methods of preparation and modern technology of fabrication of devices utilising AES system of phosphors are now well established and these phosphors are found to exhibit fairly reproducible optoelectronic properties. Further, Japanese group (12, 13) has recently demonstrated the application of the combination of the three phosphors namely CaS, SrS and BaS doped with impurities like Cu, Ag, Sb, Pb, Bi, Mn, Ce in the application of large area thin film EL screens.

Research activity on the studies of IR stimulable (IRS) properties of AES phosphors had started as early as 1945 and at that time IRS phosphors prepared with SrS (doped with RE impurities like Ce, Eu and Sm) were only investigated extensively (14,15,39). Practically the work on BaS was meagre. These AE sulfides doped with RE impurities have exhibited emission bands in the wavelength region extending from UV to NIR region (16,17,38,57,71,72). In our laboratory, studies on the photoluminescence (PL), thermally stimulated luminescence (TSL), thermally Stimulated conductivity (TSC) and infrared stimulability (IRS) of BaS system of phorphors doped with impurities like Cu, Bi, Ce, Eu and Sm have started way back in 1977, and these results have already been published (18-27). As compared to the vast existing literature on luminescent properties, the corresponding information on the energy storage phenomena of AES phosphors is scarce. Further, to our knowledge no attempts have been made to carry out a systematic study of TSL and TSC of these phosphors.

Amongst the various experimental techniques employed to study the energy storage properties of phosphors, TSL and TSC have been widely used to investigate the nature and distribution of traps. The storage capability and related luminescence phenomena which involve trapping and radiative recombination respectively can be reasonably understood by considering the various results on PL, TSL, TSC, after-glow characteristics etc. All these different properties get significantly modified by the presence of impurities and the role of native defects also has to be considered, in this regard, for a satisfactory understanding of the involved electronic processes.

The results of the previous study on the BaS system of phosphors (from our laboratory) have guided us to undertake the present program of work on the PL, energy storage and dielectric studies of Ce and Sm doped AES system of phosphors namely CaS, SrS and BaS individually as well as in combinations (CaS-SrS, SrS-BaS, BaS-CaS, CaS-BaS-SrS). The general information, that one can derive from the different experiments conducted to study the various aspects as mentioned above, are briefly discussed in the following sections.

1.2 PHOTOLUMINESCENCE (PL) :

Photoluminescence (PL) is a phenomenon in which the phosphor/luminescent material excited by photons (usually UV) emits light in the wavelength region (usually in the visible) different from that of the exciting electromagnetic radiation. When absorption and emission is caused to take place within a single luminescence centre such as a foreign atom or molecule in a substance, the photoluminescence produced is associated with localized centres of the lattice.

Whereas the radiative recombination during excitation occurs between the electrons and holes generated in the crystalline lattice, the phenomenon of light emission is called intrinsic/recombination luminescence. The spectral composition of the emitted light gives the PL spectrum of the substance which provides useful information regarding the different optical transitions leading to radiative recombination processes, in general. A schematic diagram indicating the different radiative recombination transitions is shown in Fig.1.1. The photoluminescence efficiency which is controlled by the radiative transition probability (P_r), decreases with increase of temperature because of the increasing role of the competing non-radiative transitions, the general relation between the luminescence efficiency (η) and the two transition probabilities P_r and P_{nr} is

$$\eta = P_r/(P_r + P_{nr})$$

Phosphor materials which are used in conventional display devices are generally prepared by doping with suitable activator impurities into the pure phosphor matrix which otherwise behave as non-photoluminescent materials. The PL spectrum of such activated phosphors exhibits the characteristic emission bands related to the electronic levels of the activator ion. Depending upon the valence state of the activator impurity differing from the constituents of the phosphor, the host crystal (phosphor) develop lattice defects which may also effectively participate in the phenomenon of photoluminescence particularly when they form