PREFACE

Highly dispersed particles termed microclusters, fine particles, small particles microcrystals or colloidal particles represent a new class of materials particles expected to have chemical and physical properties that span the range from molecules to bulk and as such are of intrinsic interest in their own right. The evolution of the structural, electronic and other properties as atoms form progressively larger clusters leading to a macroscopic solid has long been a challenging problem for solid state and theoretical physicists. An enormous amount of experimental and theoretical work has been conducted to resolve how these various properties of the solid state evolve. These efforts opened new horizons in micro-cluster research. Many long standing problems related to small particles have been solved, but many new ones emerged.

An important problem in cluster physics is the production of clusters of desired materials in the desired size range. Many methods have been developed for the production of clusters. Some methods of preparation are condensation methods, matrix isolation technique, vapour deposition and dispersion methods. The system of particles so far studied include metallic, ionic, covalent and van der Waal's clusters. This thesis consists of a systematic study
of the properties of highly dispersed particles of silver, sulphur, arsenious trisulphide, silver iodide and mercuric iodide. The ease of preparation of fine particles of these materials was the main consideration in choosing them for the present study. For the preparation of particles in this study, dispersion by electrical disintegration and chemical preparation methods are used. The crystallinity of these fine particles and the deviation of their crystal structure from those of the bulk, the phenomenon of cluster aggregation and interaction between clusters have been studied using TEM and electron diffraction. The peculiar vibrational properties of these clusters were investigated using laser Raman spectroscopy. The phenomenon of nucleation of macroscopic deposits and pattern formation when clusters of different materials interact through a diffusion controlled process were systematically investigated. Finally ultrasonic measurements are carried out in suspensions of particles of some of the materials to investigate the adiabatic compressibility of the particles and the interaction of particles with the suspension medium.

The thesis is divided into five parts. In part 1 chapter 1 gives a general introduction with recent developments in the field of fine particles. Chapter 2 deals with the experimental techniques used for the present study and chapter 3 discusses the methods of preparation of
suspension of fine particles, their stability and aggregation.

The study of crystal structure of microclusters and the deviation from the bulk structure are fundamental problems in microcluster research. In part 2, chapter 4 discusses the TEM and electron diffraction studies of finely dispersed particles of silver, arsenious trisulphide, silver iodide and mercuric iodide. The TEM pictures are used to determine the size of the particles and the electron diffraction patterns are used in judging the crystallinity and to have an idea about lattice contraction where ever possible. The TEM images are also used to study the phenomenon of cluster aggregation which is discussed in chapter 5. The mechanism of cluster aggregation can be described by two universal regimes called diffusion limited aggregation (DLA) and reaction limited aggregation (RLA). The TEM micrographs together with electron diffraction pattern have been made use of in studying the nature and extent of aggregation of the microclusters.

Interaction of the clusters with other atoms or molecules will provide a useful probe into the structural make up of the clusters and also will yield informations regarding the mechanism of breaking and making of chemical bonds on cluster surfaces. Although the formation of surface
adsorbate bonds by the interaction of clusters with gases have been studied in detail by many workers, there has not been much effort focusing on the possibility of interaction of clusters of different materials resulting in a rearrangement of existing chemical bonds and establishment of new ones. Chapter 6 describes the electron microscopy study of the feasibility of interaction between microclusters of silver and arsenious trisulphide. The product of interaction has been analysed using electron diffraction and X-ray diffraction analysis to understand its crystallinity and the nature and extent of interaction. This chapter also contains the report of the investigation of interaction between microclusters of silver iodide and mercuric iodide, using electron diffraction, EDAX and X-ray diffraction.

The lattice vibrational properties of highly dispersed particles are very much different from those of the bulk. One reason for this change in properties is the finite size effect which causes the breakdown of vibrational selection rule $K \neq 0$ forbidden and as a result the vibrational lines may become broad and frequency shifted compared to those of the bulk crystals. A second reason is the surface effect arising from the peculiar behaviour of surface atoms. As the size of the microclusters decreases the surface effects are expected to become more and more
important, since the surface-to-volume ratio increases. Laser Raman spectroscopy (LRS) may be used as an efficient tool to investigate the peculiar vibrational properties of highly dispersed particles as well as the nature and extent of interactions between small particles of different materials. In part 3 of the thesis, chapter 7 deals with the laser Raman study of microclusters of sulphur dispersed in water-methanol mixture. The effect of finite size of the sulphur particles, the influence of the particle being a cluster rather than a finite crystallite and the role of other molecules attached on the surface of the size limited sulphur particles on the Raman frequencies are discussed. Chapter 8 consists of laser Raman study of highly dispersed particles of silver iodide and mercuric iodide. The observed decrease in intensity and shift in the frequencies of the Raman lines corresponding to silver iodide and mercuric iodide have been discussed in the light of existing theories of size effect and surface amorphousness of the particles. The effect of large internal pressure of highly dispersed particles in influencing the Raman lines is also discussed. Chapter 9 deals with the study of interaction between microclusters of silver iodide and mercuric iodide using laser Raman spectroscopy. The LRS of the product of interaction shows most of the characteristic lines of single crystals of $\text{Ag}_2\text{HgI}_4$, but in a frequency shifted manner. It is attempted to establish that LRS can be effectively used for the investigation of interaction between microclusters.
A study of the effect of allowing suspensions of highly dispersed particles of different materials to interact by direct mixing as well as through a diffusion controlled process will be of interest in problems of nucleation and growth of crystalline phases. Though pattern formation in initially uniform suspensions of fine particles of materials has been studied in detail by many workers, investigation of pattern formation in systems of interacting clusters of different materials has not been reported so far. Chapter 10 of part 4 gives a review of the existing theories of nucleation and pattern formation. Chapter 11 discusses the observation of macroscopic deposits and pattern formation, when clusters of silver and arsenious trisulphide are allowed to interact through a diffusion controlled process. The production of periodic bands and macroscopic deposits of the product of interaction may be explained on the basis of a chemical instability of autocatalytic reaction mechanism of colloid growth and nucleation. Chapter 12 deals with the study of growth and morphology of composite clusters of \( \text{Ag}_2\text{HgI}_4 \) produced through the interaction between microclusters of \( \text{AgI} \) and \( \text{HgI}_2 \).

The measurement of ultrasonic velocity in suspensions of a solid phase in a liquid medium can yield significant results regarding the physical properties of the system. Ultrasonic attenuation observed in a medium of
highly dispersed particles is an important parameter representing the interaction between the suspended particles and the suspension medium. In part 5 chapter 13 discusses ultrasonic velocity measurements in colloidal dispersions of sulphur in water-methanol mixture. For very low volume fractions, much less than 1% of the dispersed phase, the velocity in the suspension is found to be appreciably different from that of the dispersion medium. The measured ultrasonic velocities are used to calculate the adiabatic compressibility of the dispersed sulphur particles. In chapter 14, study of ultrasonic velocity and attenuation and the temperature dependence of these quantities in dilute suspensions of AgI in water is reported. It is found that the ultrasonic velocity in dilute suspensions do not appreciably vary with concentration of suspended particles, but attenuation changes appreciably. The ultrasonic velocity is found to increase with temperature whereas attenuation remains fairly constant.
A major part of the work included in this thesis has been published and presented in the following journals and conferences.

Research Papers Published/ Accepted for Publication/ Communicated


6. Study of Interaction Between Microclusters of Silver and Arsenious Trisulphide, Proceedings of the Indian Academy of Sciences - Chemical Sciences (accepted for publication)


9. Laser Raman Study of Interaction Between Microclusters of AgI and HgI₂, Solid State Commun. (communicated)

10. Study of Growth and Aggregation of Microclusters of AgI and HgI₂, Nanophase Materials (communicated)


12. Study of interaction between microclusters of AgI and HgI₂, Nanophase Materials (communicated).

Research Papers Presented/ Accepted for Presentation in National/ International Seminars and Conferences.


7. Study of Growth and Aggregation of Microclusters of AgI and HgI$_2$, 10th International Conference on Crystal Growth, San Diego, U.S.A, 1992.