Optical & Morphological Properties of Zinc Sulphide-Strontium Chloride Doped Polymer Nanocomposites

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Abstract: Strontium Chloride doped with Zinc Sulphide (ZnS: SrCl$_2$) is well studied, due to its promising luminescence characteristics. Though there are numerous publications related to Strontium and chloride doped zinc sulphide, there are no reports on the growth of free standing and stable nanocomposite films of ZnS: SrCl$_2$ with a polymer. The search for freestanding, flexible, mechanically and thermally stable films endowed with the excellent luminescent properties of doped zinc sulphide is the motivation behind the present studies. Poly (vinylidene difluoride) (PVDF) is a fluoro polymer with impressive piezoelectric, ferroelectric and pyroelectric properties and at the same time highly flexible and processable. When PVDF/ doped ZnS nanocomposite film is placed in UV light, bright yellow orange luminescence is observed for the Strontium chloride doped film and blue luminescence, for the chloride doped film. These nanocomposite films offer high prospects of wide range of applications in field emission displays, plasma displays and electroluminescent devices. By combining the yellow orange emission of ZnS: SrCl$_2$ and the blue emission of ZnS: SrCl$_2$ in the required optimised ratio, it is possible to develop white light emitting, freestanding, stable and flexible nanocomposite films of PVDF/doped ZnS. So in the present’s work we have prepared polymer nanocomposites of PVDF and doped (ZnS/SrCl$_2$) in the different ratio of ZnS/SrCl$_2$ and characterized these polymer nanocomposites with UV-visible, FTIR and SEM to studies the morphological behaviors & optical properties.

Keywords: Nanocomposites, photoluminescence, free standing films, co-precipitation method, solution casting, surface passivation effects.

1. Introduction

Poly (vinylidene difluoride) (PVDF) is a semi crystalline polymer with a repeat unit of CH$_2$-CF$_2$. It is an attractive material for use in various applications, because of its promising piezoelectric, ferroelectric and pyroelectric behavior and finds widespread applications in two sensors, infra-red detectors, transducers, energy harvesters, actuators, super capacitors and MEMS$^{[1,3]}$. The advantageous properties of PVDF can be attributed to its crystalline structures for which five different polymorphs have been observed and are referred to as α, β, γ, ε and δ. The first two are the most common crystalline structures observed in PVDF$^{[4,5]}$. It is chemically, thermally and mechanically very stable and is a highly flexible and Process able material. Because of its excellent film forming properties, it is ideal as a polymer matrix for obtaining a variety of polymer nanocomposite films$^{[6]}$. Inorganic particles often exhibit novel physical properties as their size approaches nanometer scale dimensions. For example, the unique electronic and optical properties of Nanocrystalline quantum dots may lead to future applications in electro optic devices and biomedical imaging. For many advanced and diverse applications, ranging from chemical sensing to magnetic recording, current research is increasingly focused on exploiting the high surface-to-volume ratios of nanoparticles as a framework for the assembly of complex nonmaterial’s$^{[7]}$. The development of highly uniform and biocompatible
inorganic nanoparticles with optimized functional properties is critical. In the past decades, various inorganic nanoparticles have been successfully prepared by many different synthetic methods. One is the precipitation of salts in aqueous media\cite{8,9}. In the past decades, considerable attention has been paid to the use of inorganic nanoparticles in various technological fields, particularly in bio nanotechnology. The main advantage of inorganic nanoparticles is attributed to their intrinsic properties such as optical and super paramagnetic properties as well as some biological activities\cite{10}. Inorganic nanoparticles are formed by the crystallization of inorganic salts, forming a three-dimensional arrangement with linked atoms. The nature of the binding atoms is mainly covalent or metallic. These particles are highly ordered and rigid with little influence by the body. Organic nanoparticles, on the other hand, are mainly formed by spontaneous aggregation, as with micelles or vesicles. These systems are dynamic due to the weak nature of the cohesive interactions. Therefore, the size and geometry of organic aggregates are difficult to maintain below a certain size threshold, particularly in living systems\cite{11}. In some cases, it is possible to produce anisotropic inorganic particles by taking advantage of some of the material properties. For instance, performing the synthesis of magnetic materials in the presence of a magnetic field or producing some metal nanowires under an electric field\cite{12,13}. The specific optical or magnetic features of the inorganic nanoparticles are sometimes exploited and integrated in Microsystems in order to elaborate medical devices providing fast analysis with high sensitivity for low volume analytee, similar to that existing in large-scale analysis equipment. Such systems are called micro-Total Analysis Systems (m-TAS) in which all steps are concentrated in one device\cite{14}. Many metal and metalloid elements are able to form nano-scale structures. Some of the better known nanoparticles currently being investigated include those based on silver, which are known for their anti-microbial and anti-inflammatory properties\cite{15}. Alkaline earth metals refer to a group of elements in the periodic table. They include beryllium, magnesium, calcium, strontium, barium, and radium. Here we will focus on metallic nanoparticles of strontium chloride. Strontium chloride is a salt of strontium and chloride. It is a typical salt, forming neutral aqueous solutions. Like all compounds of Strontium chloride, this salt emits a bright red color in a flame. In fact it is used as a source of redness in fireworks. Its chemical properties are intermediate between those for barium chloride, which is more toxic, and calcium chloride\cite{16}. Compounds are widely used in fireworks and flares for the red color they produce when burnt. Strontium carbonate is used as a glass additive. Strontium hydroxide is used for refining beet sugar. A highly abstracted metallic ‘mushroom cloud’. It alludes to the presence of strontium in nuclear fallout. A soft silvery metal that burns in air and reacts with water. Strontium is best known for the brilliant reds its salts give to fireworks and flares. It is also used in producing ferrite magnets and refining zinc. Modern ‘glow-in-the-dark’ paints and plastics contain strontium aluminates. They absorb light during the day and release it slowly for hours afterwards. Strontium-90, a radioactive isotope, is a by-product of nuclear reactors and present in nuclear fallout. It has a half-life of 28 years. It is absorbed by bone tissue instead of calcium and can destroy bone marrow and cause cancer. However, it is also useful as it is one of the best high-energy beta-emitters known. It can be used to generate electricity for space vehicles, remote weather stations and navigation buoys. It can also be used for thickness gauges and to remove static charges from machinery handling paper or plastic. Strontium chloride hex hydrate is an ingredient in toothpaste for sensitive teeth. Strontium is incorporated into the shells of some deep sea creatures and is essential to some stony corals. It has no biological role in humans and is non-toxic. Because it is similar to calcium, it can mimic its way into our bodies, ending up in our bones\cite{17}.

Synthesis of nanoparticles to have a better control over particles size distribution, morphology, purity, quantity and quality, by employing environment friendly economical processes has always been a challenge for the researchers\cite{18}. The choice of synthesis technique can be a key factor in determining the effectiveness of the photovoltaic as studies. There are many methods of synthesizing metallic nanoparticles such as co-precipitation process, hydrothermal\cite{19,20} combustion synthesis\cite{21}, Micro Emulsion, Microwave, Microwave synthesis and sol-gel processing etc\cite{22,24}.

In the present work, chemical co-precipitation method was used to synthesize nanostructures, SrCl2 doped ZnS. The nanocomposite of doped ZnS with PVDF was obtained by solution mixing and the corresponding nanocomposite films were grown in a Petri-dish using solution casting. Detailed studies were
carried out on the structural, morphological properties of the free standing, nanocomposite films of PVDF/doped ZnS and the application prospects of these films in display devices and solid state lighting technology were assessed.

So in the present’s work we have prepared polymer nanocomposites of PVDF and doped (ZnS/SrCl$_2$) in the different ratio of ZnS/SrCl$_2$ and characterized these polymer nanocomposites with UV-visible, FTIR and SEM to studies the morphological behaviors & optical properties.

2. Material and method

All the required materials and solvents are commercially available and were without further purification. Zinc acetate [Zn (CH$_3$COO)$_2$.2H$_2$O] (purity > 98 %), strontium chloride [SrCl$_2$] (purity > 98-100 %) and sodium sulphide [Na$_2$S.9H$_2$O] (purity > 50 %) were purchased from Merck limited Mumbai. Poly (vinylidene diflouride) PVDF, [-(&#x2591;C$_2$H$_2$F$_2$) n-] powder (purity > 99%) was purchased from Sigma Aldrich, Mumbai and N, N-Dimethylformamide (DMF) [C$_3$H$_7$NO$_7$] (purity > 99%) was purchased from Sisco Chem. Industry Bombay. Methanol [CH$_3$OH] (purity > 99%) was purchased from Fisher Scientific, Mumbai.

2.1 Sample preparation

2.2 Synthesis of strontium chloride doped ZnS

Strontium chloride doped, nanocomposite ZnS, (ZnS: SrCl$_2$), was synthesized using the simple technique of chemical co-precipitation method. Freshly prepared aqueous solution of zinc acetate, strontium chloride and sodium sulphide were used for the synthesis. In this reaction, 10 mL of 0.02 mol. solution of zinc acetate was mixed with 10 mL of strontium chloride 0.02 mol solutions in a conical flask. To this solution 10 mL of 0.02 mol sodium sulphide solutions was added drop by drop from a burette with vigorous stirring for 2 hours at 60 °C. After stirring then filtered the solution and the precipitate was washed several time with distilled water and methanol and dried in an oven at 50 °C. Thoroughly ground in a mortar. The experiment was repeated with 0.02 mol, 0.04 mol, and 0.08 mol.

2.3 Casting of Pvdf/ ZnS: SrCl$_2$ Nanocomposite films

The solution mixing technique was employed for casting of film. 1gm of PVDF powder was dissolved in 10 ml of N, N-Dimethylformamide (DMF) and 10% of 0.02 mol ZnS: SrCl$_2$ was dissolved in 5 ml DMF and stirred for 15 minute after that mixed both of solution and stirred vigorously for 7 hours at 50 °C. This solution was poured into a petri-dish and kept in an oven at 100 °C for 2 hours. It was found that the nanocomposite film formed could be easily peeled off from the petri-dish to get film.

3. Results and discussion

3.1 Observation

FTIR studied were carried out in appropriate sample using Bruker alpha FTIR Spectrophotometer within a range of 4000-400cm$^{-1}$ using of 4cm$^{-1}$. An average of 16 scans was performed for each sample. FTIR spectroscopy was employed to characterize the formation of doped metallic nanoparticles.

The FTIR spectra for PVDF and PVDF/ZnS: SrCl$_2$ films are shown in figures (1a) (1b) & (1c). The peaks of $\alpha$-phase PVDF appear at 528, 679, 880, 1078, 1536, 1691 and 2312 cm$^{-1}$, whereas the absorption band at 840 cm$^{-1}$ is characteristic of $\beta$-phase. The peak at 466 cm$^{-1}$ corresponds to asymmetric bending and those at 601cm$^{-1}$ and 764cm$^{-1}$ to stretching vibrations in ZnS. Bands around 1100 and 1200 cm$^{-1}$ are due to the characteristic frequency of inorganic ions. Weak bands observed at 975 cm$^{-1}$ indicate the presence of resonance interaction between vibrational modes of sulphide ions in ZnS. Since there is no shift or change in intensity for the FTIR peaks of ZnS, after getting dispersed in the PVDF matrix, so there is no possibility for any bond formation between PVDF and ZnS: SrCl$_2$ in the nanocomposite.
FTIR spectra of PVDF films baked at different temperatures are taken. The spectra of films prepared from all three solutions are found to be similar. Representative spectra for 0.02 mol., 0.04 mol., and 0.08 mol., solution are shown in Figure 5. It can be seen that FTIR peaks at 434, 445, 511, 532, 615, 763, 795, 812, 855, 975, 1000 cm\(^{-1}\) are observed in these films. These are attributed to various molecular bonding available in PVDF structure. Further the FTIR peaks at 1000 and 511 cm\(^{-1}\) are attributed to TTTT conformation of molecular dipoles i.e. \(\beta\) phase and peaks at 615, 763, 795, 855 and 975 cm\(^{-1}\) indicate presence of TGTG' (T = Trans, G = Gauche) conformation of molecular dipoles i.e. \(\alpha\) phase in the films. Very small peaks at 812, and 434 cm\(^{-1}\) are attributed to TTTG' confirmation of molecular dipoles i.e. \(\gamma\) phase. The peaks are compared with standard FTIR peak data available in the literature and are in agreement with the same.

3.2 Ultra violet visible spectroscopy (UV)

3.2.1 Observation

The optical absorption of the samples was recorded using Lab India UV 3200+ from Department of Chemistry, Institute of Basic Sciences, Dr. Bhimrao Ambedkar University (Khandari) Agra. Lab India UV 3200+ spectro photometer over the range 200nm - 700nm and the absorption spectra of nano-structured ZnS: SrCl\(_2\) and PVDF/ ZnS: SrCl\(_2\) films are given respectively in figures 8 and 9. The absorption peak for nano-structured ZnS: SrCl\(_2\) appears around 214nm which is fairly blue shifted from that of the bulk (280nm). The band-gap energy is increased from 230 to 245 which is an indication of strong quantum confinement effects. From the absorption spectrum of ZnS: SrCl\(_2\), it is seen that there is a red shift in the absorption peak, when the molarity of ZnS: SrCl\(_2\) is increased from 230 to 245. The same red shift in the absorption peak is observed in the case of PVDF/ZnS: SrCl\(_2\) nanocomposite films also, which confirms the good dispersion of ZnS: SrCl\(_2\) in the polymer matrix.
Figure 2. 3.2 UV Visible Spectrum of 0.08 mol PVDF/ZnS: SrCl$_2$ nanocomposite films.

Figure 3. 3.3 UV Visible Spectrum of 0.04 mol PVDF/ZnS: SrCl$_2$ nanocomposite films.

3.3 Structural analysis

3.4 Scanning electron microscopy

3.4.1 Observation

SEM micrograph of ZnS/SrCl$_2$ is shown in figure 3.4 the average grain size of ZnS/SrCl$_2$ was to be found to be 6.7 micrometer. This is actually not the size of ZnS/SrCl$_2$ nanoparticles; but this showing cluster of nanoparticles.

The image of ZnS/SrCl$_2$ nanoparticles at magnification 75.27 kX, 44.76kX, 18.30kX is shown in figure 3.4 and for different variations 0.02 mol, 0.04mol, 0.08mol. Powder nanocomposites images shown size of particle Pa2=77.40nm, Pb2=3400°, Pa1=174.7nm, Pb1=347.9°, Pa3=44.40nm, Pb3=15.9°.

The SEM morphology of prepared polymer is presented in figure: 12. It can be seen that nanoparticles are embedded in the PVDF matrix as the loading percent of ZnS: SrCl$_2$ up increasing in PVDF matrix then the connectivity of particle with matrix is increases. Property dispersed nanoparticles in PVDF matrix has been synthesized and confirm from the SEM analysis. The lighter region in SEM show ferroelectric ceramic and darker region show polymer matrix.
Figure 4. 3.4 Strontium chloride nanoparticles at 1500x.

Figure 5. 3.5 Strontium Chloride Nano Polymers composite.
4. Conclusion and future scope

In the present work, attempts were made to develop, free standing and stable nanocomposite films of strontium chloride doped ZnS in PVDF matrix. The present results offer sample scope for developing free standing nanocomposite films based on PVDF and suitably doped ZnS: SrCl$_2$. The present work deals with novelty, since the synthesis of the nanocomposite films of doped ZnS: SrCl$_2$ in PVDF matrix have not been reported earlier. The freestanding, flexible, stable and eco-friendly nature constitute the most advantageous aspects of these nanocomposite films of thickness around 6.7 micrometers. The highlight of the present investigations is the development of these luminescent, stable in packaging and freestanding nanocomposite films for the first time, with high application potentials in the present day display device technology and the day by day progressing solid state lighting technology.

ZnS: SrCl$_2$/PVDF Poly (vinylidene fluoride) composites with different morphologies were synthesized by combining several appropriate techniques: co-precipitation and solution mixing technique (solution casting). Different connectivity was obtained by the use of ZnS: SrCl$_2$ nanoparticles and nanofibers in PVDF films and nanofibers. We demonstrated the suitability of such techniques to synthesize polymeric nanocomposites. ZnS: SrCl$_2$ PVDF crystallite size was 4.4 and 6.7 nm. The fraction of beta phase present in the polymer was higher than the raw material, as revealed by FTIR analysis. Electrospun samples of the system ZnS: SrCl$_2$/PVDF presented an electric behavior from linear dielectric to lossy ferroelectric when the amount of ZnS: SrCl$_2$ nanoparticles increased. Sample with a ZnS: SrCl$_2$/PVDF peaks of α-phase PVDF appear at 528 to 2312 cm$^{-1}$ whereas the absorption band at 840 cm$^{-1}$ is characteristic of β-phase. Bands around 1100 and 1200 cm$^{-1}$ are due to the characteristic frequency of inorganic ions. Weak additional bands observed at 975 cm$^{-1}$ indicate the presence of resonance interaction between vibrational modes of sulphide ions in ZnS. And in the UV visible the absorption peak for nano-structured ZnS: SrCl$_2$/PVDF appears around 214nm which is fairly blue shifted from that of the bulk (280nm). From the absorption spectrum of ZnS: SrCl$_2$, it can be revealed that there is a red shift in the absorption peak from 230 to 245nm, when the molarity of ZnS: SrCl$_2$ is increased. The same red shift in the absorption peak is observed in the case of PVDF/ZnS: SrCl$_2$ nanocomposite films also, which confirms the good dispersion of ZnS: SrCl$_2$ in the polymer matrix. Particle size determination is very essential and important while working with nonmaterial.

There are a few good experimental techniques, which are currently used by the researchers worldwide, for particle size determination. XRD, SEM, TEM, SPM, and particle size analyzers are some of the efficient and reliable techniques which can precisely determine particle size of the nonmaterial depending on the type of the material. In the present work, SEM techniques have been employed to determine the particle size of the materials prepared, the average grain size of ZnS/SrCl$_2$ was to be found to be 6.7 micrometer. This is actually not the size of ZnS/SrCl$_2$ nanoparticles; but this showing cluster of nanoparticles due to doping. ZnS/SrCl$_2$ nanoparticles at magnification 75.27 kx, 44.76kx, 18.30kx. Shown for different variations 0.02 mol, 0.04mol, and 0.08mol. Powder nanocomposites images shown size of particle Pa2=77.40nm, Pb2=3400°, Pa1=174.7nm, Pb1=347.9°, Pa3=44.40nm, Pb3=15.9° and The PVDF matrix as the loading percent of ZnS: SrCl$_2$ up increasing in PVDF matrix then the connectivity of particle with matrix is increases.

Strontium titanate ZnS: SrCl$_2$ fine powder and PVDF polymer by using a co-precipitation method. Dried powder of PVDF/ZnS: SrCl$_2$ exhibited a large total mass loss. Three peaks originated from cubic–tetragonal, tetragonal–orthorhombic, and orthorhombic–rhombohedral phase. Values of the dielectric constant and dielectric loss factor increases with increasing of the temperature to next decreasing. In the low temperature range, the dielectric response of the composites is determined by the anomaly characteristic in the glass transition of the polymer, whereas in the high temperature range the relaxation related to the wide angle oscillation of the polymer polar groups followed by their rotation with main chain co-operation is dominant.

The sample of ZnS: SrCl$_2$ nanocomposites have been successfully synthesized by co-precipitation. The SEM image of samples shown good surface morphology and average grain size of ZnS: SrCl$_2$ nanocomposites have found to be 6.7 micrometer. The ZnS: SrCl$_2$/PVDF composite have been synthesized by solution casting. The SEM Studies shows nanoparticles are embedded in the PVDF matrix. Connecting decreases
with increases in weight percent of ZnS: SrCl₂ in PVDF.

4.1 Future scope

The studies consisting in this research, for future suggests need of some studies which are very important from academic scientific and technical Point of view. They are as follows:

The dielectric behavior of PVDF ZnS: SrCl₂ nanocomposite need to be investigated. This will provide the information about dielectric relaxation and percolation threshold. The capacitive behavior of metal insulator. In the material could be developed for the use of packaging, sensor and for coating industries.

References