Synthesis and Photoluminescence Characteristics of $Zn_xCd_{1-x}S$ Thick Films Prepared by Flux Technique

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Abstract: **All feasible compositions of $Zn_xCd_{1-x}S$ [0≤x<1] were prepared by flux method using Na_2S as a flux. With the basic source materials, the optimum conditions for preparing good quality screen-printed thick films have been found. The optical band gap (Eg) of the films has been studied by using reflection spectra in wavelength range 350–600 nm. Increasing $[Zn^{2+}]/[Cd^{2+}]$ led to films with higher band gap (Eg). Pure CdS has the least photoluminescence intensity, whereas pure ZnS has the highest. The high transmittance, widened band gap and low resistivity obtained for ZnCdS thick films make them promising candidate for photoluminiscent applications.**

Index Terms: **Flux technique, thick films, screen printing, band gap, phosluminiscent materials.**

I. INTRODUCTION

Semiconductor nano-crystals have recently received much interest due to their unique size dependent structural, electrical, and optical characteristics. Researchers are particularly interested in II-VI chalcogenide compound semiconductors nano crystals (SNCs) because they have potential uses in solar cells, optical sensors, light emitting diodes, and biological labeling, among other things (Zia, R., et al.,2010; Jaiswal, J. et al.,2003; Jang, E. et al.,2003; Jr, M.B, et al.1998).

The study of solid-state luminescence yields information on the band structure and energy levels of impurities and defects, as well as crucial steps in the photoconductivity mechanism. In general, photoconductivity will be higher in phosphorescent luminescent materials than in non-phosphorescent luminescent materials (Gobrecht et al.,1953).

Becquerel's work in the nineteenth century marked the beginning of the scientific study of luminescence. He recognized two forms of phosphorescence decay processes: exponential and hyperbolic, which he ascribed to monomolecular and bimolecular decay mechanisms, respectively. When impurities occupy substitutional positions, the integration of either IB and VB or IIIB and VIIB elements into IIB-VIB compounds is considered as creating an activator or donor state, respectively (Bequerel E. et al.,1867) Investigators have suggested many models for the luminescence transition in ZnS type phosphors, including the Schon-Klasens model (Schon M. et al.,1942). Lambe-Klick model (Lambe J., et al.,1955) and Williams-Prener model (Williams F., et al., Prener 1956). It's crucial to remember that the properties of this sort of luminescence are highly complex, and these basic models aren't always accurate enough to grasp the nature of luminescence centers and radiative transitions.

Zinc and cadmium are two II-VI SNCs with appropriate nanocrystals for solar applications due to their straight band gap. The most widely researched substance for use as a window layer is cadmium Sulphide (CdS). By combining CdS with ZnS, the band gap of CdS may be widened. Because the band gap and lattice characteristics of the $Zn_xCd_{1-x}S$ alloy combination may be adjusted, it has a lot of potential (Olaseni I.et al.,2000). Yunchao et al. used a novel method to create tunable $Zn_xCd_{1-x}S$ alloyed SNCs with composition-dependent structural and optical characteristics at low temperatures. As a result, it's a viable option for usage in nano devices as light-emitting materials (Kumar P., et al.,2000).Vacuum evaporation (Singhal S.et al.,2009), chemical bath deposition (Khare, A., et al.,2009) spray pyrolysis (Ilican, S., et al.,2007), thermal evaporation (Sebastian, P., at al.,2004), dip-coating technique (Rafea, M.et al.,2009), molecular beam epitaxial growth (Telfer S., et al.,2000), e-beam evaporation (Kumar, P., et al., 1998) have previously been used to create $Zn_xCd_{1-x}S$ thick

films. However, there are just a few publications on the flux technique of forming $Zn_xCd_{1-x}S$ thick films.

The flux method is a straightforward approach for producing high-quality homogenous solid solutions with up scaling potential. The flux approach allows solid solutions to be synthesized much below the melting point of the material (Mughal M.,et al.,1996; Bidnaya D.,et al.,1962; Scheel H.et al.,1974; Patil L.,et al., 998; Patil L.,et al., 2001; Amalnerkar, D.,1980). The use of Na_2S_2 liquids as fluxes to manufacture metallic sulphides has been described. The existence of a common anion and little sodium incorporation into the substance to be synthesized are two benefits of Na_2S_2 solvents. The needed equipment is basic and within most laboratories economic capability.

To explore the photoluminescence characteristics of thick films for functional applications, our efforts have been undertaken to synthesize $Zn_xCd_{1-x}S$ solid solutions.

II.   MATERIALS AND METHODS

Preparation of Zn_xCd_{1-x} Solid Solutions by Flux Method

Starting materials contained hydrated sodium Sulphide ($Na_2S.9H.O$), with high quality, and a suitable weight percent of coarse zinc and cadmium powders. The following is the process for preparing one of the compositions (x = 0.1).

Preparation of $Zn_{0.1}Cd_{0.9}S$

The 0.1 weight percent Zn, 0.9 weight percent Cd, and an adequate amount of sulphur and $Na_2S.9H_2O$ were carefully mixed together. The solution was poured into a platinum crucible. In a kanthol wrapped muffle furnace, the crucible was put. Corundum powder was used to fill the area surrounding and above the crucible. The temperature of the furnace was raised to 600°C. After then, the temperature was kept constant for an hour. After that, the furnace was brought to normal temperature. Excess sulphur evaporated, leaving behind residual oxygen and water in the form of S02 and H2S. Double distilled water was used to wash the product in the crucible. Sodium polysulphides dissolved in water and were easily separated. The finished product has to be dried. The additional components (x = 0.2 to 0.9) were synthesized using the same technique. The same technique was used to make CDs and ZnS granules.

Preparation of $Zn_xCd_{1-x}S$ Thick Films

Screen printing was used to create thick films of each mixture. To ensure adequately fine particle size, the powder of a particular composition produced using the procedure described above was ball milled in ethanol for 24 hours. Fine solid solution powder was mixed with a solution of ethyl cellulose (a temporary binder) in a combination of organic solvents such as butyl cellulose, butyl carbitol acetate, and terpineol to make the thixotropic paste [29]. When making the paste, the ratio of inorganic to organic parts was

maintained at 75:25. The paste was screen printed in a pattern appropriate for measurements on glass and alumina substrate. The films were burned in air for 10 minutes at 550°C.

Structural Analysis of the Films

X-ray diffraction patterns of the films corresponding to each composition were recorded using CuK radiations with a Ni filter on a Phillips X-ray diffractometer Model PW-1730 (A 1.5418 A). For comparison, all of the compositions' X-ray patterns were grouped in a single figure. The lattice constants of each mixture were calculated and visually displayed [30].

III.   RESULTS

Photoluminescence measurement

Photoluminescence properties of thick films of $Zn_xCd_{1-x}S$ ($0 \leq x \leq 1$) were studied using Perkin-Elmers luminescence spectrometer.

Luminescence spectrometer

The model LS 50 luminescence spectrometer measures the fluorescence, phosphorescence and chemical or bioluminescence of samples either in a continuous scan over the wavelength range of the instrument (or part of the range) or at pre-selected points within the range. The excitation source is triggered at line frequency (50 or 60 Hz) to produce an intense, short duration excitation pulse of radiation. The optical system consists of two reflection grating monochromators (excitation and emission), a series of mirrors, the reference and sample, photo-multiplier detectors. The signals from the detectors are processed by the instrumental electronics, and can be displayed on a PC screen.

1. Excitation of phosphors

Phosphor under test was excited using excitation wavelengths 365nm. Excitation wavelength gave its own luminescence spectrum for a particular sample.

2. Photoluminescence of $Zn_xCd_{1-x}S$ ($0 \leq x \leq 1$) thick films

The photoluminescence of CdS, $Zn_xCd_{1-x}S$ ($0.1 \leq x \leq 0.9$), ZnS thick films are shown in the Fig.2.1 to Fig.2.11 respectively.
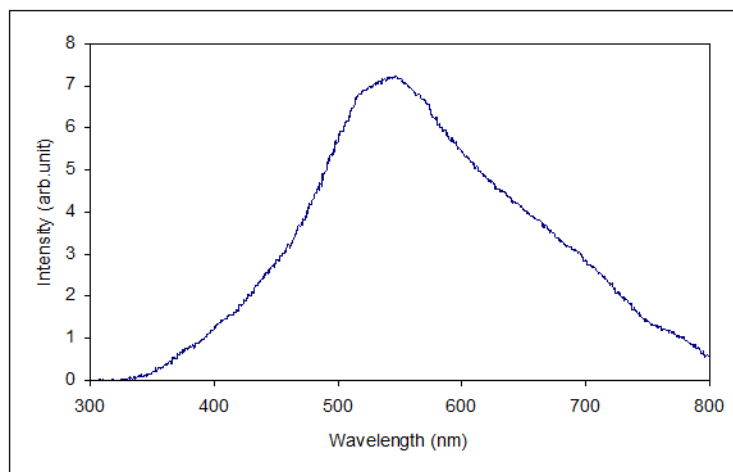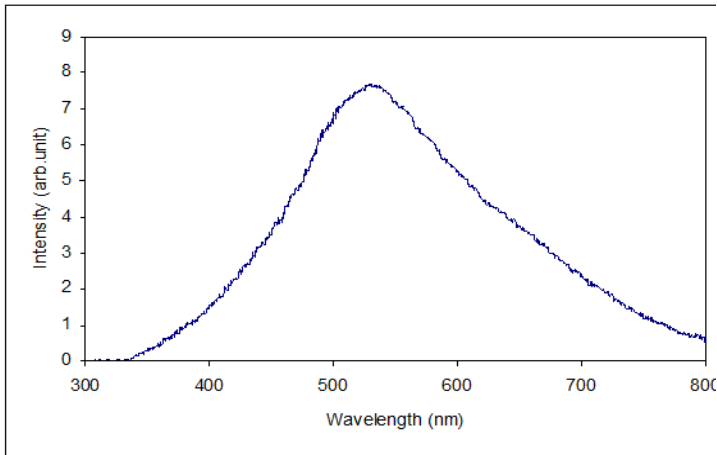

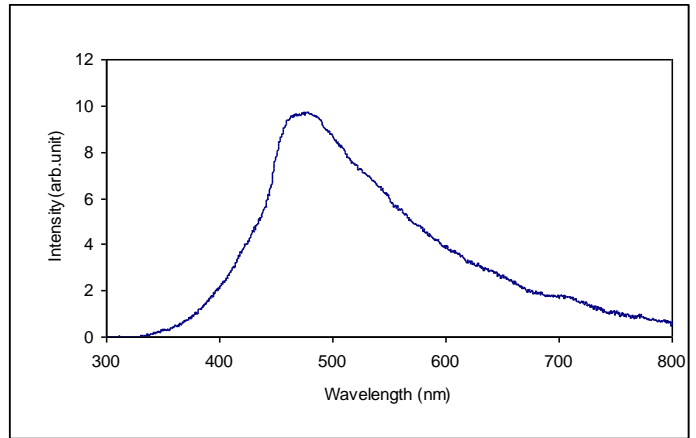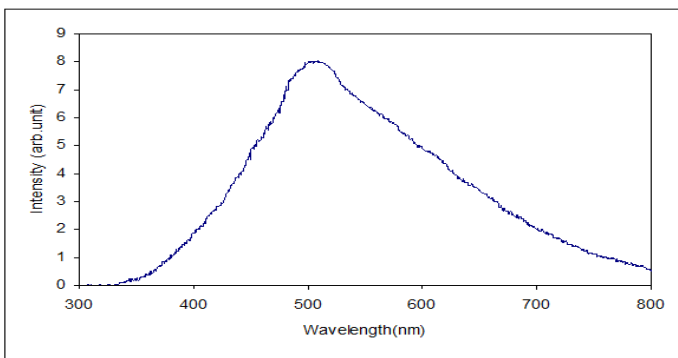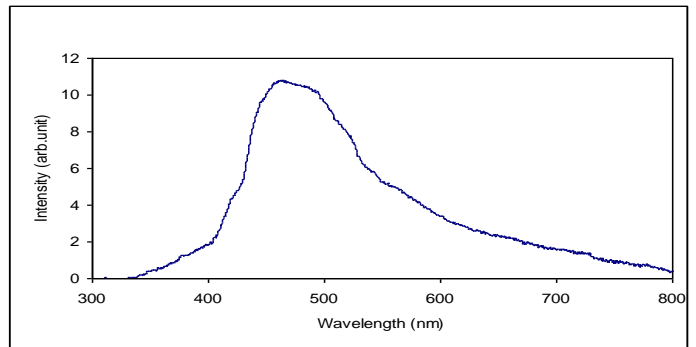Fig. 2.1: PL of CdS

Fig. 2.2: PL of $Zn_{0.1}Cd_{0.9}S$

Fig. 2.3: PL of $Zn_{0.2}Cd_{0.8}S$

Fig. 2.4: PL of $Zn_{0.3}Cd_{0.7}S$
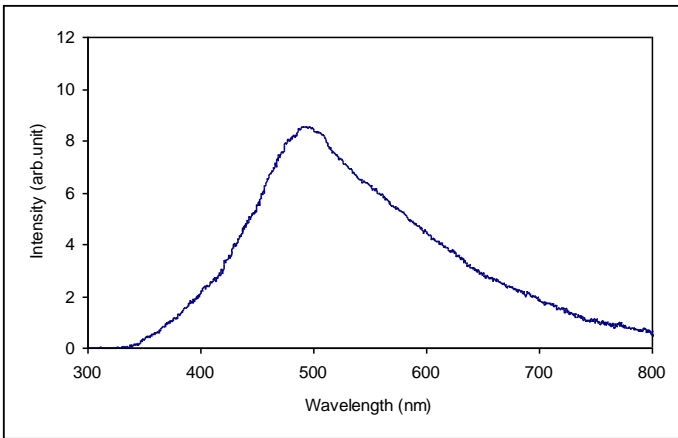

Fig. 2.5: PL of $Zn_{0.4}Cd_{0.6}S$

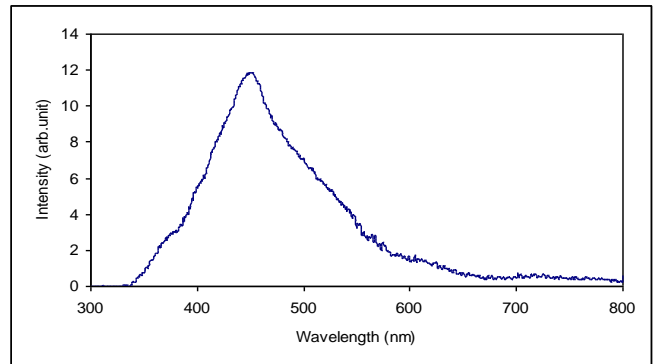Fig. 2.6: PL of $Zn_{0.5}Cd_{0.5}S$

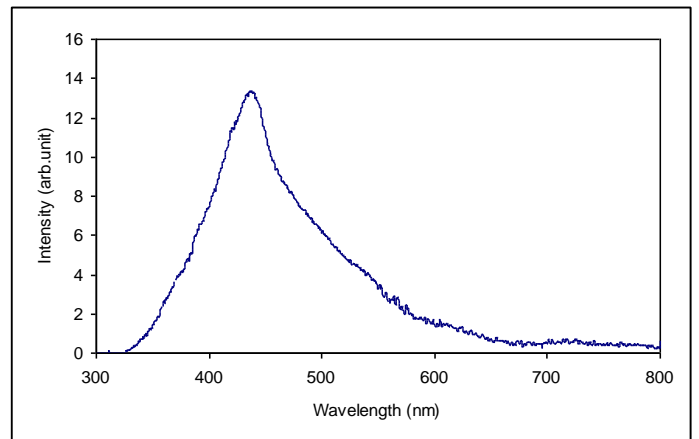Fig. 2.7: PL of $Zn_{0.6}Cd_{0.4}S$
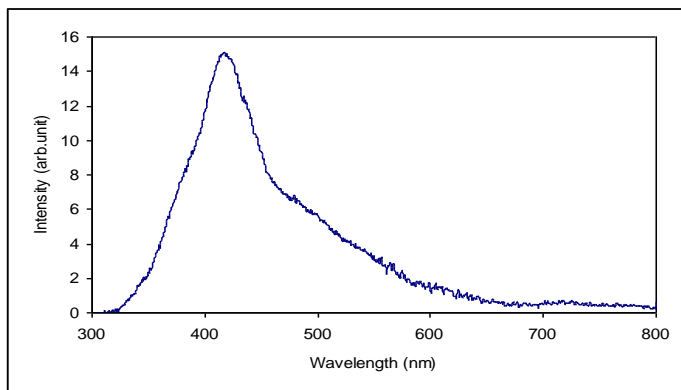
Fig. 2.8: PL of $Zn_{0.7}Cd_{0.3}S$

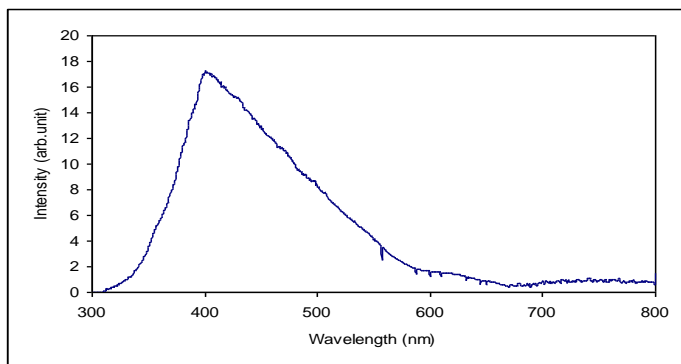Fig. 2.9: PL of $Zn_{0.8}Cd_{0.2}S$

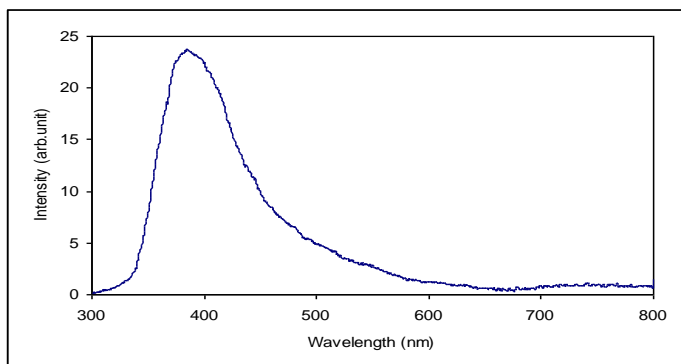Fig. 2.10: PL of $Zn_{0.9}Cd_{0.1}S$

Fig. 2.11: PL of ZnS

The photoluminescence spectra of $Zn_xCd_{1-x}S$ thick films display a wide range of photoluminescence colors, ranging from blue owing to ZnS to red due to CdS. These findings also show that the energy gap between the emission center and the conduction band changes depending on the energy gap of the different $Zn_xCd_{1-x}S$ thick films. Intensity diminishes as CdS rises in ZnS.

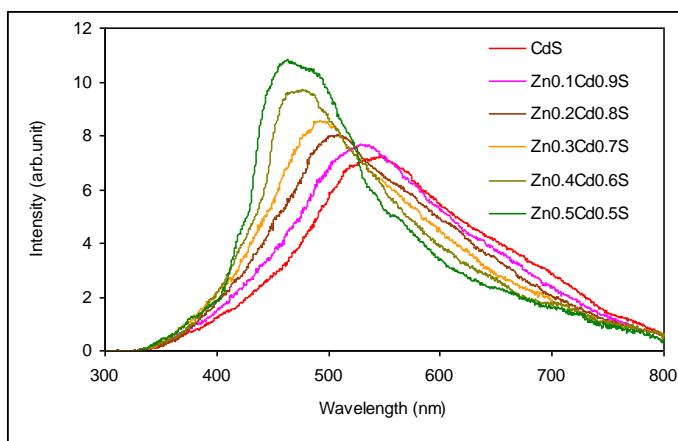*3. Superimposition of PL of $Zn_xCd_{1-x}S$ (0≤x≤0.5)*

Fig. 3a: PL of $Zn_xCd_{1-x}S$ (0≤x≤0.5)

Superimposition of PL of $Zn_xCd_{1-x}S$ (0.6≤x≤1)
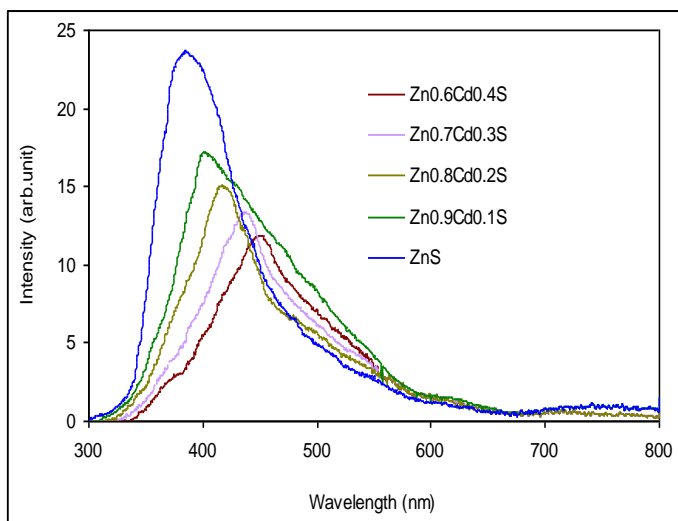
Fig. 3b: PL of $Zn_xCd_{1-x}S$ (0.6≤x≤1)

4. The variation of peak intensity with wt % of Zn in $Zn_xCd_{1-x}S$ (0≤x≤1) as shown in Fig.4. The Figure shows as wt % of Zn increases its peak intensity also increases.

Fig.4: The variation of peak intensity with wt % of Zn

IV.   DISCUSSION

Photoconductivity and photoluminescence were detected in all $Zn_xCd_{1-x}S$ (0≤x<1) compositions. Rapid recombination is required for good luminous materials, whereas delayed

recombination is required for good photoconductors. The typical material would satisfy these opposing demands if (i) both luminescence and photoc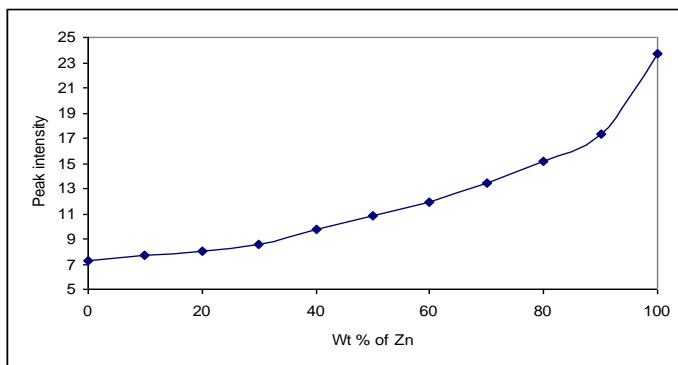onductivity are associated with the capture of the same type of carrier, either electron or hole, and (ii) luminescence is associated with one type of carrier but photoconductivity is associated with the capture of the other type of carrier. In instance (i) the existence of excellent luminescence emission indicates photoconductivity-friendly centres.

The existence of light emission might be due to a reduced density of "large-cross-section centres." As a result, free charge carriers will live for a long period before recombination. For example, in instance (ii), a suitable luminous material requires centres with a large cross section for minority carriers, which produce emission, and a small cross section for the majority carrier, which produces extended free life time for majority carriers, which produce photoconductivity. In this paper, the materials examined are n-type materials ($Zn_xCd_{1-x}S$ ($0 \leq x < 1$). These compounds should have photo sensing and photoluminescent characteristics for the reasons stated above.

V.   CONCLUSION

Thick films of $Zn_xCd_{1-x}S$ having large band gap (compared to 2.42 for CdS) have been created by flux method using distinct formulations. The band gap of the film and the ratio Zn/Cd in the film initially rise when the ratio $[Zn^{2+}]/[Cd^{2+}]$ is increased. The photoluminescence peaks of pure CdS and pure ZnS are 547 nm and 385 nm, respectively. These peaks would be ascribed to the individual materials edge emissions. The intensity of photoluminescence increases as the wt. percent of Zn in $Zn_xCd_{1-x}S$ increases. In the case of pure CdS and compositions with a higher wt. percent of CdS, the rates of rise and decay of photoluminescence intensity are nearly symmetrical.

In compositions with wt. percent CdS ranging between 50 and 70 wt. percent CdS, the rate of rise in photoluminescence intensity is considerably faster than the rate of decay. In the case of greater ZnS compositions, the rate of rise in photoluminescence intensity is quite fast compared to the rate of decay. In the case of pure ZnS, the rate of growth of photoluminescence intensity is the fastest, while the rate of decay (photoluminescence intensity) is the slowest. As the wt percent of Zn in the $Zn_xCd_{1-x}S$ compositions increases, the peaks of the spectra shift towards shorter wavelengths (blue shifts).

VI.   REFERENCES

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