The theoretical optoelectronic properties of chalcogenide perovskites (e.g., BaZrS$_3$) are as good as those of halide perovskites (e.g., CH$_3$NH$_3$PbI$_3$). But the fabrication of optoelectronic devices is rarely reported, mainly because researchers still do not know how to prepare good quality thin films of chalcogenide perovskites. Here, we report colloidal BaZrS$_3$ nanocrystals (NCs, 40–60 nm) and their solution processed thin film transistors. BaZrS$_3$ NCs are first prepared using a solid-state synthesis route, and the subsequent surface modifications lead to a colloidal dispersion of NCs in both polar N-methyl-2-pyrrolidinone and non-polar chloroform solvents. The NCs exhibit good thermal (15–673 K) and aqueous stability. Colloidal BaZrS$_3$ NCs in chloroform are then used to make field effect transistors showing ambipolar properties with a hole mobility of 0.059 cm$^2$ V$^{-1}$ s$^{-1}$ and an electron mobility of 0.017 cm$^2$ V$^{-1}$ s$^{-1}$. This report of solution processed chalcogenide perovskite thin films with reasonable carrier mobility and optical absorption and emission is expected to pave the way for future optoelectronic devices of chalcogenide perovskites.

Oxide perovskites have long been exhibiting amazing properties including colossal magnetoresistance, ferroelectricity and multiferroicity. But oxide perovskites are often not good semiconductors with a wide band gap in the UV region, mainly because of the high electronegativity of oxygen. On the other hand, Pb-halide perovskites have been recently proven to be excellent solution processed semiconductors with high efficiency and other exciting optoelectronic properties. But Pb toxicity and moisture/thermal instability remain major challenges to overcome for this class of materials. Can chalcogenide (sulfide, selenide, and telluride) perovskites combine the good semiconducting properties of halide perovskites with the high stability and non-toxicity of oxide perovskites? This question re-ignited the study of chalcogenide perovskites, with the first theoretical report of the optoelectronic properties of chalcogenide perovskites appearing in the year 2015. Subsequently, there are other theoretical studies suggesting high solar cell efficiency and photoelectrochemical water splitting of certain compositions of chalcogenide perovskites. Some of the suggested chalcogenide perovskite compositions such as BaZrS$_3$, SrZrS$_3$ and SrHfS$_3$ are experimentally synthesized in the form of their bulk powder. Also, 2D Ruddlesden–Popper and Dion–Jacobson type phases of chalcogenide perovskites are reported. Optical properties in terms of strong light absorption and reasonable photoluminescence (PL) are also encouraging for their optoelectronic applications. But unfortunately, fabrication of thin films of chalcogenide perovskites, which is a prerequisite for a typical optoelectronic device, remains very challenging to date. The major problem of material design is that the formation of BaZrS$_3$ and other chalcogenide compositions requires a temperature >600 °C. Physical methods such as sputtering and pulsed laser deposition (PLD) or chemical sulfurization of BaZrO$_3$ thin films require multiple steps at temperatures ≈900 °C or above, to achieve films of complex ternary chalcogenide compositions. In this process, non-stoichiometric compositions and also sometimes impurity phases are observed. For example, PLD grown (at 1150 °C) BaZrS$_3$ films suffer from a high level of sulfur vacancies resulting in high carrier density ($10^{19}$–$10^{20}$ cm$^{-3}$) that is undesired for optoelectronic applications. Furthermore, it will be very challenging to incorporate such complex processes requiring a temperature of ~900 °C for manufacturing the desired interfaces in optoelectronic devices such as solar cells. Until now, there is no chemical method reported for solution processed thin films of BaZrS$_3$. The obvious reason for this failure is that no solvent can...
survive the high synthesis temperature of BaZrS₃. In contrast, colloidal NCs of ternary and quaternary metal chalcogenides are well reported in the literature which makes them suitable for thin film fabrication.⁴⁴

To overcome this difficulty, we have employed a two-step process to achieve solution processed thin films (~50 nm thick) of BaZrS₃. In the first step, cube-shaped (edge length ∼50 nm) BaZrS₃ NCs are synthesized at 600 °C using a solid-state synthesis route. In the second step, we functionalized the surface of BaZrS₃ NCs to achieve their colloidal dispersions either in polar solvents such as N-methyl-2-pyrrolidinone or in non-polar solvents such as chloroform. Then field effect transistors (FETs) are fabricated to explore the charge transport characteristics of BaZrS₃ NC films. FETs are fabricated with the solution processed thin films of BaZrS₃ NCs at room temperature. High thermal stability and aqueous stability of BaZrS₃ NCs are ensured, along with the preliminary results of good photocatalytic activity of the NCs towards degradation of methylene blue dye.

**Synthesis, morphology, structure and stability**

BaZrS₃ NC powders are prepared using a slightly modified solid-state synthesis method reported by Niu et al.⁴³ The details of the synthesis methodology are given in the ESL†. Stoichiometric amounts of BaS, Zr and S powders are reacted at 600 °C for 60 hours in the presence of an I₂ catalyst, inside a sealed quartz tube. The schematic of the reaction pathway is given in Fig. S1 in the ESL†. We noted that our efforts to synthesize BaZrS₃ NCs using direct colloidal synthesis conditions were unsuccessful (see the ESL†). Taking a clue from the prior literature,⁴⁵ it appears that more reactive precursors are required for the direct colloidal synthesis of BaZrS₃ NCs. The existing precursors do not react under the milder conditions of colloidal synthesis, requiring us to use the harsh conditions of solid-state synthesis. Fig. 1a shows the powder X-ray diffraction (PXRD) pattern of the product confirming the formation of phase pure BaZrS₃ NCs with an orthorhombic crystal structure (distorted perovskite) with the space group Pnma (62). The lattice constants are calculated from the PXRD pattern and found to be: a = 7.021 Å, b = 9.894 Å and c = 6.908 Å. The schematic crystal structure of BaZrS₃ is shown in Fig. 1b. The UV-visible-near infrared (NIR) diffuse reflectance spectrum of BaZrS₃ NC powder is recorded, which is then converted to absorbance spectra by using the Kubelka-Munk equation.⁴⁶

Interestingly, the PXRD peaks of BaZrS₃ powder in Fig. 1a show small broadening suggesting the possibility of the formation of NCs. Indeed, the transmission electron microscopy (TEM) image in Fig. 2a shows the formation of NCs with cubic morphology. The edge lengths of the cubic NCs are around 40 to 60 nm. However, it is to be noted that the size distribution is wide and some of the NCs agglomerate on the TEM grid as shown Fig. S3 in the ESL†. Also note that the sample does not form a homogeneous colloidal dispersion in any typical liquid solvents. So, we drop-casted the sample on the TEM grid using an inhomogeneous suspension of BaZrS₃ NCs in n-butanol. Since the smaller sized NCs tend to form a better suspension, the TEM grid will also have a relatively more contribution from smaller sized NCs. The high resolution TEM (HRTEM) image in Fig. 2b shows lattice fringes with interplanar distances of 2.98 Å and 2.69 Å corresponding to the (004) and (220) planes of BaZrS₃ NCs, respectively. Fig. S4 in the ESL† shows the magnified HRTEM image of the same NC, with the assignment of interplanar distances and the corresponding planes. The selected area electron diffraction (SAED) pattern of the NC in the inset of Fig. 2b demonstrates the single crystallinity of the sample. The diffraction spots can be assigned to the orthorhombic phase of BaZrS₃, similar to the PXRD patterns in Fig. 1a. These TEM results are interesting because there is no prior report on the synthesis of BaZrS₃ NCs or any other chalcogenide perovskite NCs. More importantly, the formation of NCs gives us the hope to make the first ever solution processed thin films of chalcogenide perovskites.

To assess the thermal stability of BaZrS₃ NCs, PXRD patterns are recorded at different temperatures. As shown in

![Fig. 1](image-url) (a) Comparison of the PXRD pattern of BaZrS₃ NC powder with that of the reference pattern (00-015-0327) for the orthorhombic phase of bulk BaZrS₃. (b) Schematic crystal structure of the BaZrS₃ chalcogenide perovskite. The unit cell is shown by a dashed black rectangular box.
Fig. 2 Characterization and stability (thermal and aqueous) of BaZrS$_3$ NCs. (a) TEM image of cube-shaped BaZrS$_3$ NCs with edge lengths in the range of 40–60 nm. The inset shows the magnified image of NCs. (b) HRTEM image of a single BaZrS$_3$ NC showing lattice fringes. The inset shows the SAED pattern recorded on a different BaZrS$_3$ NC. (c) Variable temperature (298–673 K) PXRD patterns of BaZrS$_3$ NCs. The orthorhombic phase is maintained without any sign of degradation in the entire range of temperatures. Peaks marked with an asterisk is due to the Pt substrate. EXAFS data showing (d) $k^2$ weighted $\chi(k)$ versus $k$ plots and (e) Fourier transformed $\chi(r)$ versus $r$ plots of the BaZrS$_3$ NCs at a few representative temperatures. (f) Testing the water stability of BaZrS$_3$ NCs by monitoring the photocatalytic degradation of an aqueous solution of methylene blue dye in their presence. $C_0$ and $C$ are the concentrations of methylene blue at time = 0 min and time = $t$ min, respectively.

Fig. 2c, the BaZrS$_3$ NCs remained in the orthorhombic phase throughout the temperature range, while heating up the sample from 298 K to 673 K. The PXRD patterns recorded during the cooling of samples also show similar data (Fig. S5 in the ESI†). These results show that BaZrS$_3$ NCs do not undergo any phase transition unlike lead halide-based perovskites where they transform from orthorhombic to tetragonal to cubic phases with increasing temperatures. Also, we have calculated the thermal volume expansion coefficient of BaZrS$_3$ NCs. The details are given in Fig. S6 in the ESI. We calculated the coefficient of volume expansion, $\alpha_{v,303\text{K}} = 9.97 \times 10^{-6}$ K$^{-1}$. The thermal expansion coefficient serves as a design parameter for materials having low thermal lattice conductivity, and hence has application in designing thermoelectric materials. This low thermal volume expansion of BaZrS$_3$ NCs gives an indication that they could have low thermal conductivity which has been recently reported.

To study the local structure of BaZrS$_3$ NCs, we have recorded the temperature-dependent X-ray absorption fine structure (XAFS) data of the samples at the Zr K-edge in the transmission mode at the Scanning EXAFS beamline (BL-09) at the Indus-2 synchrotron source (2.5 GeV, 200 mA) at the Raja Ramanna Centre for Advanced Technology (RRCAT), Indore, India. The details of the experimental methodology and data analysis are given in the ESI.† The X-ray absorption near-edge structure (XANES) in Fig. S7 in the ESI shows that there is no change in the Zr K edge position upon varying the temperature in the range of 15–673 K, indicating that there is no change in the oxidation state of Zr in the samples due to the increase in the temperature. There is a small but systematic decrease in the intensity of the peak-like feature just above the absorption edge with the increase in the temperature. This decrease is probably due to the reduction of unoccupied higher level states. The extended X-ray absorption fine structure (EXAFS) data in Fig. 2d show the $k^2$ weighted $\chi(k)$, where $\chi(k)$ has been defined in the ESI.† Fourier transformation of the $k^2\chi(k)$ data provided $\chi(r)$ in real space (Fig. S8 in the ESI), where $r$ is the distance from the centre of the absorbing Zr atom. Both $k^2\chi(k)$ and $\chi(r)$ plots of BaZrS$_3$ NCs remain similar in the entire temperature range of 15–673 K, apart from a systematic decrease in the intensity in the $\chi(r)$ plot with the temperature due to an increase in thermal disorder. The experimental data are fitted with the theoretically simulated $\chi(r)$ versus $r$ plots that are generated using the crystal structure of BaZrS$_3$ NCs obtained from our XRD data and are shown in Fig. 2e for a few representative temperatures. The experimental data are fitted from 1–2.5 Å assuming one Zr–S shell at 2.562(6) Å. The coordination number of this path ($N = 6$) is kept fixed during the fitting and the bond distances and disorder (Debye–Waller) factors ($\sigma^2$), which give the mean-square fluctuations in the distances, are used as fitting parameters. The best fit parameters are given in Table S1 in the ESI.† The Zr–S bond length obtained at 300 K is 2.527 ± 0.006 Å, with minor variations at other temperatures, whereas the disorder factor increases with increasing temperature, as expected. Thus, the temperature-dependent EXAFS results suggest that there is no major change in the local struc-
ture and the XANES data show no change in the Zr oxidation state of BaZrS₃ NCs in the temperature range of 15–673 K.

After confirming the thermal stability of BaZrS₃ NCs over a wide temperature range, now we will discuss their aqueous stability by testing the photocatalytic activity of BaZrS₃ NCs in water. We have studied the photocatalytic activity of BaZrS₃ NC powder by carrying out the degradation of methylene blue dye in distilled water, under sunlight. Fig. S9 in the ESI† shows the absorbance spectra of methylene blue at regular intervals after irradiation with sunlight. The decrease in the absorbance values shows the degradation of the dye. Fig. S10 in the ESI† shows the decrease in the concentration of methylene blue with time. We found that BaZrS₃ NCs degrade almost 98% of methylene blue within 50 min when exposed to sunlight. This preliminary photocatalytic activity of BaZrS₃ NCs is reasonably good compared to the prior literature.⁵⁰,⁵¹ Such photocatalytic performance probably arises from multiple factors such as the good solar light absorption capability of BaZrS₃ NCs, high surface to volume ratio of NCs and reasonably good water stability. Further mechanistic understanding of the dye degradation reaction is not the focus of this manuscript. To further check the water stability of BaZrS₃ NCs, we have investigated the recycling ability of the photocatalyst. Fig. 2f shows that the photocatalytic performance of BaZrS₃ NCs for the degradation of methylene blue is stable for at least 3 cycles, suggesting superior water stability of BaZrS₃ NCs compared to metal halide perovskites. However, we note that after several hours (10 to 12 hours), the BaZrS₃ NC sample starts to degrade in water as the water starts turning milky. In the dark, BaZrS₃ NC powder (not a colloidal dispersion) in water is stable for a few days, as confirmed by PXRD patterns recorded after the water treatment.

**Solution processability of BaZrS₃ NCs**

An important finding of the previous sub-section is that the BaZrS₃ powders are NCs of a size of around 40–60 nm. While the size is too large to observe the quantum confinement effect (the excitonic Bohr radius is expected to be ~2.8 nm, see the ESI†), the high surface to volume ratio could be utilized to make a colloidal dispersion of NCs. Traditionally, colloidal synthesis yields NCs with their surfaces decorated with long-chain organic ligands or charged inorganic ligands, facilitating solution processed film fabrication.⁵²,⁵³ Since our BaZrS₃ NCs are prepared by solid-state synthesis, the NCs do not have any such surface ligands. Therefore, we need to modify the surface of our pre-formed NCs to achieve solution processed BaZrS₃ NCs, which then can be utilized later to make thin film devices. The schematics in Fig. 3a illustrate our strategy to functionalize the surface of BaZrS₃ NCs. More details are provided in the ESI†.

The XRD pattern of the sample obtained by drop casting the dispersion in N-methyl-2-pyrrolidinone is compared with the XRD pattern of the synthesized BaZrS₃ NC powder in Fig. S11 in the ESI†. Both the XRD patterns correspond to BaZrS₃ NCs having an orthorhombic phase without any impurity phase. This result confirms that the colloidal dispersion is of BaZrS₃ NCs in N-methyl-2-pyrrolidinone. The dispersibility of the BaZrS₃ NCs is attributed to the coordination of N-methyl-2-pyrrolidinone to the BaZrS₃ NCs. N-Methyl-2-pyrrolidinone is known to coordinate to Lewis acidic sites and thus form coordination complexes with metals.⁵⁴,⁵⁵ N-Methyl-2-pyrrolidinone acts as a powerful coordinating solvent for ‘d block’ metal cations such as Fe and Mn.⁵⁶,⁵⁷ N-Methyl-2-pyrrolidinone has also been used to disperse transition metal dichalcogenides where it is believed that the interactions between the N-methyl-2-pyrrolidinone molecules and interactions between N-methyl-2-pyrrolidinone and transition metal dichalcogenides are of similar nature.⁵⁸

UV-visible absorbance and PL spectra of the colloidal BaZrS₃ NCs in N-methyl-2-pyrrolidinone are shown in Fig. 3b. The absorption data of the colloidal sample show an onset similar to the powder sample (Fig. S2 in the ESI†), but the onset is less clear for the dispersion because of the significantly reduced concentration of NCs in the dispersion. We have measured the extinction coefficient of colloidal BaZrS₃ NCs by using the Beer–Lambert law and absorption spectra shown in Fig. S12 in the ESI†. The absorbance varies linearly with the concentration of NCs. Using these data, we have calculated the extinction coefficient of BaZrS₃ NCs to be $0.44 \times 10^4$ m$^{-1}$ cm$^{-1}$ mL at 400 nm. For comparison, we note that the 11 nm sized CsPbI$_3$ NCs exhibit a similar extinction coefficient ($1.2 \times 10^4$ m$^{-1}$ cm$^{-1}$ mL) at 400 nm.⁵⁹ These results confirm the high absorption coefficient of the BaZrS₃ NCs, similar to Pb-halide perovskites, and agree with prior theore-
The PL signal is weak for BaZrS₃ NC powder (noisy data, not shown here), similar to the prior report.³³,³⁴ Interestingly, the PL intensity increases significantly by making the colloidal dispersion of BaZrS₃ NCs in N-methyl-2-pyrrolidinone. Comparison of the PL and absorption data suggests that the PL is due to band-edge (or excitonic) emission. The increase in the PL intensity for the dispersion is probably because of the reduction of both non-radiative energy transfer and radiative self-absorption processes in the dilute dispersion compared to the powder.⁵⁰ Since the PL quantum yield of our BaZrS₃ NCs is still rather low, such energy transfer from more to less emitting NCs is expected to quench the PL significantly. Also, there is a possibility that N-methyl-2-pyrrolidinone might passivate the surface of NCs, thus improving the PL intensity. The nature of surface defects plays an important role in determining the PL properties.⁶¹

While we could achieve the NC dispersion in N-methyl-2-pyrrolidinone, making thin films from this dispersion using standard techniques such as spin coating is difficult because of the high boiling point of N-methyl-2-pyrrolidinone. Therefore, we performed a second round of surface modification with oleylamine (OAm) to disperse BaZrS₃ NCs into low-boiling solvents like chloroform (CHCl₃). Fig. 3c shows the TEM image of the sample taken from the chloroform dispersion. Cube-shaped NCs are observed, implying that the treatment with N-methyl-2-pyrrolidinone and OAm does not significantly change the morphology and size of BaZrS₃ NCs.

**Thin films and FETs of BaZrS₃ NCs**

After achieving the colloidal dispersion of BaZrS₃ NCs in CHCl₃, now we can use it for making thin films. Fig. 4 shows the film morphology of spin-casted BaZrS₃ NC films as observed through scanning electron microscopy (SEM) images. To observe any possible morphological changes resulting from the thermal treatment of the BaZrS₃ NC film, an annealing process is carried out for 20 min in a N₂-filled glove box at 150, 200 and 250 °C. To confirm the thickness of the BaZrS₃ NC film in pristine and annealed states, atomic force microscopy (AFM) is used. The obtained thickness for the pristine film is 57.1 nm, and as the annealing temperature is increased, the thickness of the film is slightly decreased to 54.8 nm at 150 °C, 54.3 nm at 200 °C and noticeably decreased to 46.5 nm at 250 °C. As shown in Fig. 4(a–d), the SEM images show a gradual increase of surface roughness as the thermal annealing temperature increases, which can be related to the decomposition of OAm and any other residual molecular species, and thus the resulting rearrangement of BaZrS₃ NCs. In line with the noticeable thickness drop in the 250 °C annealed sample, an apparently rough surface was formed in the 250 °C annealed sample.

The BaZrS₃ NC FET is demonstrated with a bottom-gate top-contact geometry based on the solution process used for the film formation of a SEM specimen. A highly n-doped Si-wafer is used as the substrate and gate electrodes, and ZrOₓ with a high-k dielectric constant is introduced into the dielectric layer in order to enable low voltage drive and minimized interfacial trap. A ZrOₓ layer with a thickness of ca. 9 nm was prepared by sol–gel synthesis, and the areal capacitance value was 715 nF cm⁻² at 1 kHz.⁶² Source–drain gold electrodes with a channel length of 150 μm are deposited by thermal evaporation. The device geometry is schematically shown in Fig. S13a in the ESL.† For control measurements, the results of two other device geometries are also shown in Fig. S14 and 15 in the ESL.†

As shown in Fig. 5a and b, the BaZrS₃ NC FETs exhibit ambipolar properties. They are capable of both hole and electron transport. All samples showed a moderate on/off current modulation of ~10⁴ observed under both p- and n-type measurement conditions. To investigate the relationship between the surface morphology of the film and FET performances, we measured the transfer curves of devices under each annealing temperature condition. Then the FET mobility is obtained by using the linear regime equation of the FET which can be expressed as

\[ I_{DS} = \frac{W C}{L} \mu (V_G - V_{th}) V_{DS} \]

where \( W \) is the channel width, \( L \) is the channel length, \( C \) is the capacitance of the unit area of the dielectric layer and \( V_{th} \) is the FET turn-on voltage. With a drain–source voltage (\( V_{DS} \)) of \( ±0.1 \) V, it is found that the FET performances in terms of both mobility and threshold voltage (\( V_{th} \)) become worse at higher annealing temperatures of the film. We speculate that this decrease is due to the rough surface developed by the annealing process, which may hamper charge transport within the BaZrS₃ NC film. As shown in Fig. 5c and d, there are clear trends of decreasing mobility and increasing \( V_{th} \) when the annealing temperature is...
the present results confirm the significantly improved water stability of bare BaZrS₃ chalcogenide perovskite NCs, compared to their metal halide perovskite counterparts. The average size of the NCs is too big to observe the quantum confinement effect; however, the high surface to volume ratio is utilized not only for photocatalytic activity, but also more importantly for solution processability. We developed the desired surface chemistry for BaZrS₃ NCs making a stable colloidal dispersion in both the polar solvent N-methyl-2-pyrrolidinone and the non-polar solvent chloroform. The NC dispersion in low-boiling chloroform is then spin coated to make thin films with a thickness of ~50 nm. It is found that the formed NC thin film is not a monolayer with retained particles, as the particles are shrinked by the coalescence phenomenon that occurs during the solidification, so a continuous thin film with a thickness similar to that of the NC size could be realized. These solution processed thin films are then used to fabricate the FET device in the bottom-gate top-contact geometry. BaZrS₃ NCs show both p- and n-type ambipolar transistor behaviors with a hole mobility of 0.059 cm² V⁻¹ s⁻¹ and an electron mobility of 0.017 cm² V⁻¹ s⁻¹. To the best of our knowledge, this is the first report of (i) any chalcogenide perovskite NCs, (ii) solution processed chalcogenide perovskite thin films and (iii) the FET of any chalcogenide perovskite system. So, the early results of carrier mobility values, along with their light absorbing power and moderate band-edge PL, are encouraging for developing future optoelectronic devices of BaZrS₃ NCs and other related chalcogenide perovskite compositions.

Conflicts of interest

The authors declare no competing financial interest.

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