Structure, spectral, electrical, and second harmonic generation studies of Fe\(^{3+}\) doped MnS single crystals

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Abstract: In this present work, we report the growth, optical, and electrical studies of inorganic single crystals of manganese sulfate and FeCl₃-doped manganese sulfate grown by slow evaporation technique. Crystal structure and lattice parameters of the grown crystals were determined using powder X-ray diffraction and the studies confirm the formation of orthorhombic structure. The UV–vis spectroscopic measurement illustrates the grown crystals with good optical transparency in the visible region and less absorbance. Optical constants such as the band gap, refractive index, extinction coefficient, optical and electrical conductance reveals the good optical response of the material. The Fourier transform infrared spectroscopic analysis infers that there is a small change in the peak position and transmittance in the case of MnS:Fe³⁺ crystal which ensures the incorporation of Fe³⁺ ion to the host crystal. Second harmonic generation efficiency tested by Kurtz and Perry method showed the improvement in relative conversion efficiency compared with potassium dihydrogen phosphate.

Subjects: Bioscience; Physical Sciences; Engineering & Technology

Keywords: inorganic compounds; crystal growth; electron microscopy; electrical properties; optical properties

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PUBLIC INTEREST STATEMENT
The research on MnS-based nonlinear optical (NLO) materials is strongly motivated by the demand for higher data rates in future optical communication technologies which is great use for mankind for enhancement in optoelectronic applications. For high-speed second-order NLO applications, such as electro-optics (EO), second-harmonic generation (SHG), optical parametric oscillation (OPO), and optical rectification (OR), including terahertz (THz) wave generation, a highly asymmetric electronic response of the material to the external electric field is required. Single crystals have several advantages, they have a high chromophore packing density, and they are orientationally stable. Furthermore, organic crystals show a superior photochemical stability than polymer. On the other hand, highly polar molecules tend to aggregate in a centrosymmetric crystalline arrangement, and therefore, only certain specially designed chromophores like MnS can be used for the growth of NLO crystals. Also the processing of organic crystals, especially in thin films needed for integrated photonic structures, is generally much more challenging than for polymers.
1. Introduction

In recent times, single crystals with large optical susceptibility have gained immense research attention due to their ability to exhibit harmonic generation and optical modulation (Natarajan, Britto, & Ramachandran, 2006; Zhang, Li, Xi, Che, & Zheng, 2008). These properties of single crystals find use in various potential applications ranging from optical storage communications to signal communication and data storage to optical switching (Sun et al., 2009). Some of the other most promising applications of single crystal include laser printing, displays, photolithography, chemical and biological species detection (Chemla & Zyss, 1987; Sagadevan & Varatharajan, 2013; Suresh, Bahadur, & Athimoolam, 2016).

Based on the types of composition these single crystals can be classified in to organic, semi-organic, and inorganic single crystals. Large nonlinear figure of merit for frequency conversion, high laser damage threshold, fast optical response time, and ability to process into single crystals are the important advantages of organic and semi-organic single crystals. However, poor environmental stability, mechanical strength, performance at low and high temperatures limit their use in applications which need stable optical performance for longer duration in difficult conditions (Li, 2012; Nalwa & Miyata, 1996; Packiya Raj, Ravi Kumar, Srinivasan, & Ravisankar, 2015).

Inorganic single crystals are the best substitutions for organic single crystals because of their easy fabrication and non-centro symmetric structure to enable optical properties along with better environmental stability and mechanical properties (Papadopoulos, Sadlej, & Leszczynski, 2007). The most widely studied NLO crystal for SHG of Nd:YAG laser is KTP along with many other inorganic salts (Belt, Gashurov, & Liu, 1985; Bierlein & Vanherzeele, 1989). However, changes in the refractive, optical damage, and hygroscopic nature are the cause of concern in this single crystal for long durability (Arun Kumar, Arivanandhan, & Hayakawa, 2013). Hence, the search of other single crystals for opto-electronic applications is the need of hour to perform in all conditions.

Manganese sulfate is one among the best inorganic salt which excites many researchers because of it use in various applications (Sathiskumar, Balakrishnan, & Ramamurthi, 2016; Vijila Manonmoni, Bhagavannarayana, Ramasamy, Meenakshisundaram, & Amutha, 2014). The non-centro symmetric structure, availability, and low cost of manganese sulfate unlike organic materials make it as the suitable candidate to probe its optical behavior (Gandhimathi, Krishnan, & Selvarajan, 2015). However, the work on growth and characterization manganese single crystal is indeed limited. In order to know the influence of other impurities on the behavior of single crystal, doping is the most effective way to modify the behavior of the single crystal.

In this paper, we report the synthesis of pure manganese sulfate (MnS) single crystal by slow evaporation technique and its structural, optical, spectral, and second harmonic generation studies. The ability of MnS to form the single phase structure with FeCl₃ as dopent and its influence on MnS (MnS:Fe⁺³) structure along with other properties is reported here in detail.

2. Experimental procedure

2.1. Synthesis

Single crystals of manganese sulfate were synthesized by dissolving manganese Sulfate (MnSO₄·H₂O) in 25 ml of distilled water up to its saturation limit. The prepared solution was stirred continuously using magnetic stirrer for obtaining the homogeneous mixture of the synthesized compound. The solution was filtered successively by Whatman filter paper to remove the suspended impurities along with excess MnSO₄·H₂O and kept in the dust-free atmosphere. After the growth period of 15 days, well-defined single crystals of MnSO₄ were harvested. For the growth of single crystals of 10% FeCl₃-doped MnSO₄, 10% FeCl₃ is added to saturated solution of MnSO₄ separately and allowed to stir for more than 2 h using magnetic stirrer. The solution was filtered and allowed to evaporate at room temperature. A recrystallization process was carried out in order to eliminate impurities. The photographic images of single crystals grown using slow evaporation method is shown in Figure 1.
2.2. Characterizations

The phase identification of the as-grown single crystals were performed using powder X-ray diffraction (XRD) measurement using Bruker X-ray diffraction unit with CuKα-radiation and Ni-filter at room temperature, at the scanning rate of 2°/min. The lattice parameters and cell volume of the as-grown crystals were refined by the least squares fitting method-based software UNITCELL-97. The optical properties were studied using UV–visible spectrophotometer (Perkin Elmer Lambda-35 Spectrophotometer) in the range 200–1,100 nm with slit width 1 nm. In order to know the presence of functional groups present in single crystal and its variation after doping was studied using Fourier transform infrared spectroscoposc (Shimadzu FTIR-8700 Spectrometer). The spectrum was recorded for the powdered sample of the grown crystal in the frequency range 400–4,000 cm⁻¹.

The current–voltage relation of these single crystals was probed using precision source/measure unit [Keysight B2902A]. The second harmonic generation (SHG) conversion efficiency of grown crystals is measured by Kurtz and Perry powder technique. The crystals are grounded into a fine powder and densely packed between two transparent glass slides. A Q switched Nd: YAG laser emitting a fundamental wavelength of 1,064 nm with pulse energy of 1.1 mJ/pulse is allowed to strike the sample cell. The output was detected by the photomultiplier tube. KDP crystal, powdered to the identical size is used as reference material. The relative conversion efficiency was calculated from the output power with reference to KDP crystals.
3. Results and discussion

The room temperature XRD patterns of both the samples are shown in Figure 2. The patterns of MnS and MnS:Fe$^{3+}$ samples display clean patterns indicating highly crystalline phase with orthorhombic crystal structure. The XRD patterns of MnS and MnS:Fe$^{3+}$ showed three main diffraction peaks indexed at (0 2 1), (0 1 2), and (0 2 2) which correspond to the planes of orthorhombic structure. On the basis of least squares' fitting between observed and calculated inter-planar distance (d), we found that, the diffraction pattern reflects the formation of single phase structure with no other impurity phases. The lattice parameters of MnS crystal was $a = 5.2364$ Å, $b = 8.03391$ Å, $c = 6.82604$ Å with cell volume 287.766 Å$^3$, whereas for MnS:Fe$^{3+}$ crystal it was $a = 5.21935$ Å, $b = 8.04895$ Å, $c = 6.71694$ Å with cell volume 282.1804 Å$^3$. The presence of Fe ions influences the crystal structure with change in the cell parameters to a small extent due to its slight different ionic radii.

Figure 3 shows the SEM image of (a) MnS and (b) Fe ion-doped MnS. It is observed that the MnS single crystal grows in orthorhombic structure and its changes by doping into hexagonal structure.

The absorption spectrums of these samples have been recorded in the range of 200–800 nm as shown in Figure 4. The absorption peaks were observed around 210 and 220 nm corresponding to pure MnS and MnS:Fe$^{3+}$, respectively. This shift in absorption peak is due to the quantum size effect, representing a change in band gap along with excitation features resulting in more discrete energy spectrum of the individual particles. Here, the effect of the quantum confinement on impurity depends upon the size of the MnS crystal. As the size of the MnS crystal decreases, the degree of confinement and its effect increases. The grown crystals exhibit zero absorbance in entire visible region. This has an advantage in the field of optoelectronics applications like photo detectors. The lower cut-off wavelength indicates the wide optical transmission window favorable for second harmonic generation.

Optical band gap of both the single crystals were determined from the formula (Arumanayagam & Murugakoothanth, 2011):

$$E = \frac{1242.4}{\lambda} \text{ (in nm)}$$

where $\lambda$ is the wavelength. Figure 5 shows the electronic transition spectra of grown crystals. Optical band gap of Fe$^{3+}$:MnS is 5.85 eV higher than that of the MnS (5.65 eV). This result reveals that MnS:Fe$^{3+}$ has a good absorption for light in the wavelength range of 200–340 nm which refers the threshold energy above which a materials starts to absorb the light. The optical conductance ($\sigma_{op}$) and electrical conductance ($\sigma_{elec}$) of the crystals are calculated using the formulae (Akinlami & Olateju, 2012):
where α = absorption coefficient, n = refractive index, and c = velocity of light. Figure 6 shows the σ_{op} and σ_{elec} plot as a function of photon energy. The optical conductance of the crystals tends to increase at the higher photon energy values. Increase in the optical conductance at 6 eV can be attributed to increase in the absorption coefficient in this region. Nature of the curve remains same for both the single crystals but magnitude is found to be decrease with doping. The electrical conductivity decreases up to 3 eV and than exhibits the same behavior as optical conductance profile with increasing photon energy.
The deviation in refractive index \((n)\) with photon energy for both the single crystals was computed using the relation (Suresh & Arivuoli, 2011):

\[
n = -(R + 1) \pm 2 \frac{\sqrt{R}}{R - 1}
\]

where \(R\) is the reflectance. It can be observed that the \(n\) of both single crystals remains constant up to 5.8 eV and raises with increases in photon energy. The increase in \(n\) values with photon energy shows the interaction between photon and electrons. Thus, we can get the desired material for fabricating the optoelectronics devices by estimating the photon energy as internal energy of device depends on the photon energy (Weber, 1994).
Figure 7 shows the variation in extinction coefficient as a function of photon energy. The extinction coefficient shows the amount of absorption loss occurred during the propagation of electromagnetic wave through a material. The extinction coefficient is directly related to the absorption of material and is related to the absorption coefficient. Extinction coefficient ($K$) has been estimated by the relation (Sagar & Prathap, 2015):

$$K = -\frac{\alpha \lambda}{4\pi}$$
It can be seen from figure that the extinction coefficient remains constant like refractive index up to 5.8 eV and shows a steep rise thereafter. The rise in extinction coefficient with increase in photon energy represents the retention of light within the material. The increase in extinction coefficient and refractive index with the increase in photon energy is correlated with increase in absorption coefficient and decrease in the transmittance.

FTIR analysis was conducted to investigate the chemical structure of MnS before and after doping Fe$^{3+}$. From Figure 8, it appears that the FTIR spectra of MnS before and after doping Fe$^{3+}$ exhibit small change in spectral response. This signifies the change in chemical composition and structure of the single crystals after doping. The absorption bands at 3,180 cm$^{-1}$ that represent the hydroxyl (OH) group slightly shifted to 3,342 cm$^{-1}$ in the spectra of MnS:Fe$^{3+}$ whereas the peak corresponding to sulfonate stretching shifted from 2,181 and 1,633 cm$^{-1}$ to 2,225 and 1,673 cm$^{-1}$ respectively. The C–O stretching of both the single crystals were characterized by the presence of peaks at the frequency 1,068 and 1,078 cm$^{-1}$, whereas the SO stretching was probed by the presence of peaks at 812 and 840 cm$^{-1}$. The peaks present at 599 and 561 cm$^{-1}$ correspond to the metal oxide bonding. Also, the transmittance percentage in the case of MnS:Fe$^{3+}$ crystal found to be more than that of pure one. This slight change in all the standard peak values and transmittance with respect to MnS clearly indicates the successful doping of FeCl$_3$ in single crystal.

The second harmonic generation studies of as-grown single crystals were measured by Kurtz and Perry powder technique with KDP as reference materials. The relative conversion efficiency was calculated by the equation (Kurtz & Perry, 1968):

$$\eta = \frac{I^{2\omega}_{\text{sample}}}{I^{2\omega}_{\text{KDP}}}$$

where $\eta$ is relative conversion efficiency and $I^{2\omega}_{\text{sample}}$ and $I^{2\omega}_{\text{KDP}}$ is the output power of sample and KDP, respectively. The powder SHG efficiency output of MnS is found to be 0.87 times and MnS:Fe$^{3+}$ is found to be 0.68 times more than that of the reference KDP sample. The green radiation emitted from the sample confirms the second harmonic generation in the crystal. The intensity of the green light (532 nm) from various points on the powdered sample shows that the SHG signal intensity little high for MnS crystal as compared to MnS:Fe$^{3+}$ crystal. This may be due to central ion in metal sulfate which offers certain anisotropic field to keep NLO active centers which drastically vary the hyperpolarizibility value (Tokemoto, Ottenbrite, & Kamachi, 1997). Hence, these materials are advantageous for NLO and photonic devices.

Figure 9 shows the current v/s voltage curve of the both as-grown single crystals. From the characteristic curve it is clear that both the single crystals exhibit nonlinear electrical behavior along with switching behavior like faster rising and falling of current with positive and negative values. However, the rise and fall in the magnitude of MnS:Fe$^{3+}$ was more dominant over pure one. The reason for this switching and nonlinearity variation in current with respect to voltage is due to the ability of single crystal ability to respond for even small electric field that can influence the unit cell to polarize and switch (Jiang & Fang, 1999).

4. Conclusion

Single crystals of MnS and MnS:Fe$^{3+}$ with considerable size were grown at room temperature by slow evaporation method within 15 days. Powder XRD pattern of both the single crystals confirms the formation of orthorhombic crystal structure before and after doping. The SEM analysis reveals the existence of visible inclusions on the surface of the crystal. The optical studies of both the crystals show the zero absorbance in the entire visible region with lower cut-off wavelength which is an essential requirement for optoelectronic applications. The quantum size confinement was the reason behind increase in optical bandgap of MnS crystal after doping with Fe$^{3+}$. The small shift in the FTIR peak positions after doping Fe$^{3+}$ conforms the successful doping of Fe$^{3+}$ ions in MnS lattice. The electrical behavior of these single crystals reveals the nonlinear electrical behavior. Grown crystals also exhibit appreciable conversion efficiency because of non-centrosymmetric crystal structure which makes them most suitable for frequency doubling applications.
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Cover image
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