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Influence of Vo(II) doping on the thermal and optical properties of magnesium rubidium sulfate hexahydrate crystals

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Abstract We have prepared pure and divalent vanadyl ion-doped magnesium rubidium sulfate hexahydrate crystals by using slow evaporation solution growth technique. It is interesting to observe that Vo(II) doping influences the physical properties of MRSH. Presence of Vo(II) ions in the doped specimen was confirmed by energy dispersive spectroscopy and electron paramagnetic resonance spectroscopy. FTIR studies reveal that the doping of vanadium ion has not altered the basic structure of MRSH. Scanning electron microscope studies of doped sample reveals that structure defect centers are formed in the crystals. Gradual decomposition patterns were observed for pure and doped specimens in thermogravimetry and differential thermogravimetry. The grown crystals were also characterized by powder X-ray diffraction. The second harmonic generation efficiency tested using Kurtz powder technique is not influenced by the added dopant.

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Introduction

Tutton's salts have the general formula $M_1''M_2'(XPO_4)_2 \cdot 6H_2O$, where M'' is a divalent cation like Co, Cu, Ni, Mg; M' is a monovalent cation like K, Cs, Rb; and X is S or Se. These materials are double salts which mean that they contain two different cations M^+ and M^{2+}. They are named for Tutton [1], who identified and characterized a large range of these salts around 1900. Doping of divalent metal impurities on Tutton's salts has been studied for many years [2, 3]. The optical and magnetic properties of transition metal impurities in different solids are intimately connected with the electronic structure of the embedded ions [4, 5]. Paramagnetic ions have been used as impurity probes for understanding the defect, structural and orientational properties of the host lattices [6]. Vanadium is one of the transition group elements that has been studied in different experimental techniques [7, 8]. Only a few molecular paramagnetic ions are available for such studies. Vanadyl ion, Vo(II) is probably the most stable diatomic ion among the few molecular paramagnetic transition metal ions and hence is widely used as electron paramagnetic resonance (EPR) probe for such studies. The hexa-aqua coordinated vanadyl ion has been the subject of the many investigations [9, 10]. The ability to substitute vanadyl ion for spectroscopically silent divalent cations, such as Mg(II), Cd(II), and Zn(II) has led to the increased use of vanadyl ion Vo(II) as spectroscopic probe of biological systems using paramagnetic resonance EPR [11]. The Vo(II) effect on magnesium potassium Tutton salt has been carried out and the dopant has entered the crystal lattice

[6]. The vanadyl ions doped in cobalt ammonium sulfate hexahydrate (CASH) and ferrous ammonium sulfate hexahydrate (FASH) crystals showed reasonably sharp and well-resolved EPR spectra [12]. Absorption spectra of vanadyl ion doped in $MgNH_4PO_4{\cdot}6H_2O$ have been studied [13]. X-Band electron paramagnetic resonance (EPR) studies of Vo^{2+} ions in asparagine monohydrate indicated the presence of two magnetically in equivalent Vo^{2+} sites and also they occupied interstitial position [14]. Interstitial substitution of Vo(II) ion in hexaimidazole cobalt sulfate has been studied [15]. Vo^{2+} complexes have been of great interest for a number of workers in recent years [9, 16].

Recently, we have published the effect of Cu(II) on the thermal and optical properties of magnesium rubidium sulfate hexahydrate (MRSH) crystals [17]. In continuation of our work, in the present investigation, an attempt has been made to study the effect of Vo(II) doping on the thermal and optical properties of MRSH crystals. Although, EPR studies on Vo(II) doping has been extensively investigated [9, 12–16] a systematic investigation on the crystal growth, thermal properties, and spectral studies of Vo(II)-doped MRSH crystal has not been reported. Thermal, microscopic, X-ray, and spectral analysis are very important methods in material characterization [18–24] and they have been used in this study also.

Experimental

Synthesis and crystal growth

MRSH was prepared by mixing equimolar concentrations (1:1) of $MgSO_4$ (24.6 g) and Rb_2SO_4 (26.7 g). To this a small amount (about one molar percent) of transition metal impurity Vo(II) was added as dopant. The solution was stirred at 30 °C and slow evaporation solution growth technique (SEST) was used for the growth of the crystals from aqueous solution. Photograph of Vo(II)-doped MRSH crystals is shown in Fig. 1.

Fig. 1 Photograph of Vo(II)-doped MRSH crystal

Measurements

The FTIR spectra were obtained on an AVATAR 330 FTIR instrument using the KBr pellet technique in the range 500–4,000 cm^{-1}. The powder diffraction analysis was performed on a Philips Xpert Pro Triple-axis X-ray diffractometer. The surface morphology was observed on a JEOL JSM 5610 LV SEM. Energy dispersive spectroscopy (EDS) is a chemical microanalysis technique performed in conjunction with a scanning electron microscope (SEM). This method can detect elements from Na upward in the Periodic Table. Thermogravimetry (TG)–differential thermogravimetry (DTG) curves were recorded on a SDT Q600 (TA instrument) thermal analyzer. The EPR studies were carried out on a Bruker ELEXYS 580 Pulsed Spectrometer. Kurtz powder second harmonic generation (SHG) method [25] was used to reveal the SHG efficiency of the crystals.

Results and discussion

FTIR spectral analysis

FTIR spectrum of Vo(II)-doped MRSH crystal is shown in Fig. 2. The lattice band due to coordinated water molecules is slightly shifted when compared to Cu(II)-doped MRSH [17]. A band appeared at 1,703 cm^{-1} could be due to coordinated water molecules [26] present in the Vo(II)-doped MRSH. A strong intense band at 1,130–1,096 cm^{-1} shows the presence of sulfate.

X-ray diffraction (XRD) analysis

The powder XRD studies reveal that the growth promoting effect of metallic dopant is not connected with the additive entering into the crystal. Only slight intensity change was observed for the Vo(II)-doped MRSH (Fig. 3). Averaged

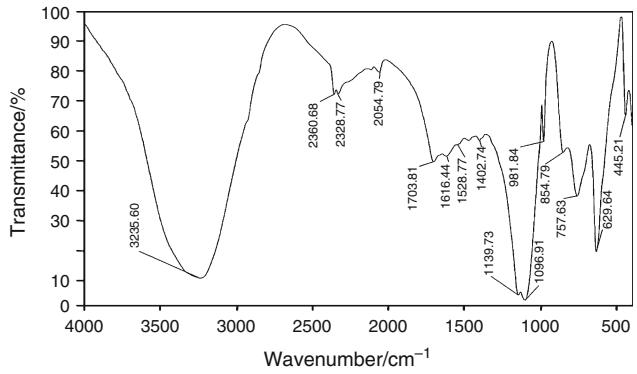

Fig. 2 FTIR spectrum of VO(II)-doped MRSH crystal

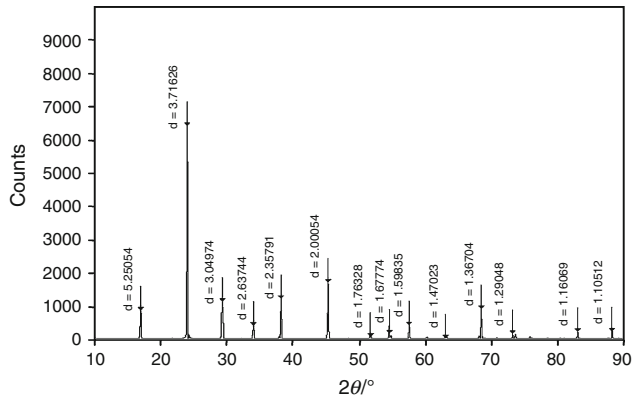

Fig. 3 Powder XRD of Vo(II)-doped MRSH crystal

dimension of crystals are calculated by using Scherrer equation [27],

$$t = \frac{K\lambda}{(\beta \ \mathrm{Cos}\theta)}$$

where K is Scherrer constant, λ is the wavelength of X-ray, θ is the peak position measured in radian, and β is the integral breadth of reflection (in radian 2θ) located at 2θ. The granularity of the Vo(II)-doped crystal calculated using this equation is found to be 42 nm.

Thermal analysis

The TG and DTG curves of pure MRSH (Fig. 4a) indicate that it is thermally stable up to 90 °C where the dehydration process commences. This is followed by an inflection at 129.6 °C with a mass loss of 22 %. This happened in the temperature range of 90–120 °C and again there is another drying between 1,000 and 1,100 °C with a total mass loss of 86 %. This could be due to the formation of MgS. The DTG shows sharp endothermic peak at 138.8 °C.

The TG and DTG curves for MRSH doped with Vo(II) (Fig. 4b) also stable up to the temperature range of 90–98 °C and the general observation is that there is slight increase of dissociation temperature when compared to the pure MRSH crystal. This could be due to the incorporation of vanadium into the crystalline matrix. This reveals that the increased strength of the material upon increasing concentration of dopant. The final residue was obtained at about 1,400 °C.

SEM and EDS studies

It has been reported that the effectiveness of different impurities in changing the surface morphology is different [28]. At low concentrations of dopant, the effects are reflected by changes in configuration of grown structures.

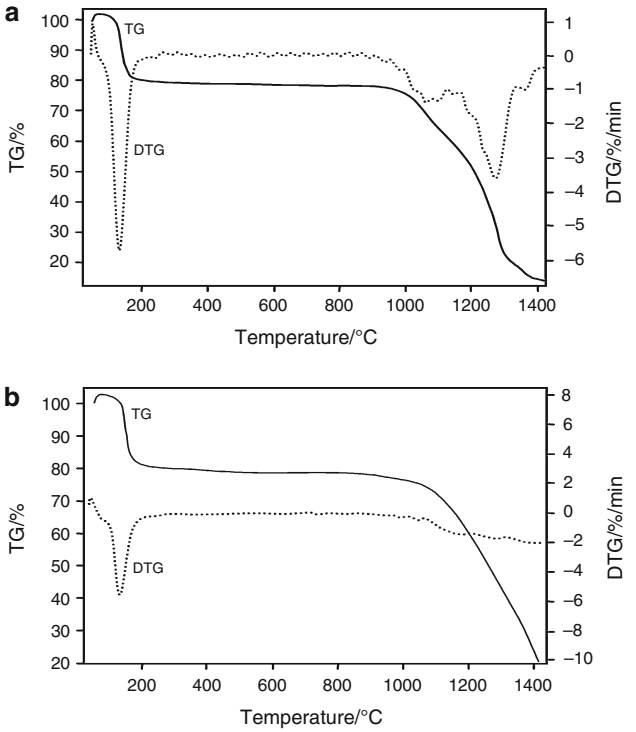

Fig. 4 TG-DTG curves of **a** pure and **b** Vo(II)-doped MRSH crystal

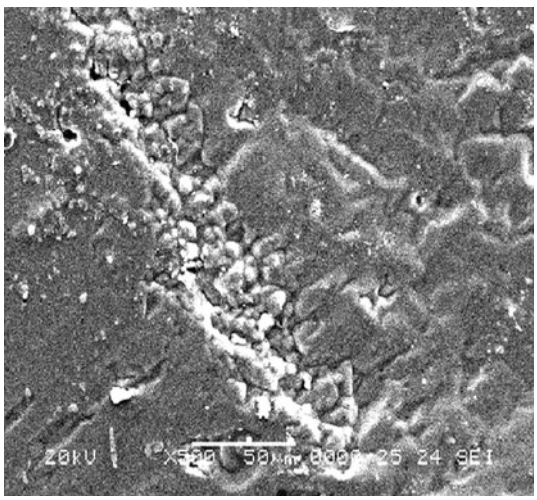

Fig. 5 SEM image of Vo(II)-doped MRSH crystal

The SEM image of doped MRSH is given in Fig. 5. In the case of doped sample, a layer with a rough surface morphology was obtained.

The presence of VO^{2+} ions in the doped specimen was confirmed by EDS. Bhagavannarayana et al. [28] has shown that ADP crystals grown in the presence of KCl contain K^{+} ions. The amount of Vo(II) incorporation into the MRSH lattice as revealed by EDS is shown in Fig. 6 and Table 1.

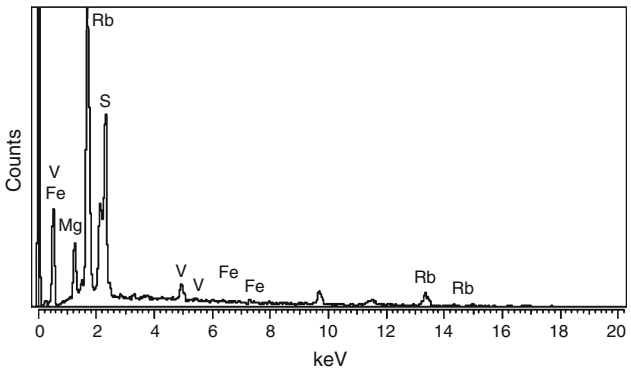

Fig. 6 EDS spectrum of Vo(II)-doped MRSH crystal

Table 1 EDS data of Vo(II)-doped MRSH crystal

Elements	Weight/%	Atomic/%
Mg	5.71	11.74
S	31.93	49.75
V	5.07	4.98
Fe	0.17	0.16
Rb	57.12	33.37
Total	100.00	100.00

It is evident from the Table 1 that magnesium rubidium sulfate has formed a lattice in which the doped Vo(II) has entered the crystal lattice.

EPR spectral analysis

Single crystals of optimum size with well-defined axes have been selected for crystal rotations, carried out in the three planes for every 10° of rotation. EPR spectra were recorded by rotating the crystal along the three mutually perpendicular axes, *a*, *b*, and *c**. Here, axes *a* and *b* are crystallographic axes, whereas axis *c** is perpendicular to the *ab* plane. In other words, single crystal rotations are done in the three mutually orthogonal planes namely *ab*, *be**, and *ac** to obtain spin Hamiltonian parameters.

Initially, the crystal is mounted along axis *b* and a typical EPR spectrum of Vo(II)/MRSH in *ac** plane is given in Fig. 7. This EPR spectrum consists of a number of overlapping angular-dependant eight line hyperfine patterns, each produced by ions located at specific site. This spectrum corresponds to the orientation, when the applied magnetic field (*B*) is making an angle of 10° with axis *c**. As the paramagnetic impurity is vanadyl ion, one can expects an octet spectrum due to the interaction of electron spin ($S = 1/2$). With 51 V nucleus ($I = 7/2$), two strong octets and a few octets of lower intensity were obtained. The approximate ratios of the intensities of the EPR lines corresponding to the Vo(II) sites for three octets are found to be approximately 12:6:1. This reveals the presence of

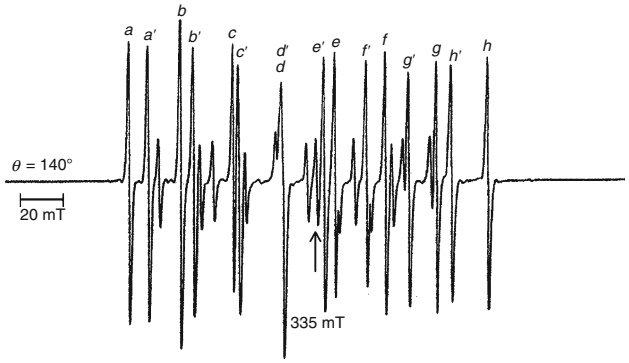

Fig. 7 Room temperature single crystal EPR spectrum of Vo(II)/MRSH in *ac** plane, where the applied magnetic field makes an angle of 140° with axis *c**

three vanadyl sites with different populations in the unit cell. The two strong octets are marked by *a*–*h* (represented as Site I) and *a*′–*h*′ (represented as Site II). Only these two sites are followed during crystal rotations, since others are having very weak resonance.

SHG efficiency

A Nd:YAG laser with a modulated radiation of wavelength 1,064 nm was used as the optical source and directed on the powdered sample through a filter. If the sample has SHG efficiency, the doubling of frequency is confirmed by the green radiation of wavelength 532 nm. Since Tutton's salts are centrosymmetric in nature one cannot expect any non-linear activity. The influence of dopant has not altered the centrosymmetric structure of MRSH and hence doping of Vo(II) has no effect on non-linear activity.

Conclusions

In the present investigation, the influence of transition metal vanadyl ion doping on MRSH crystals has been studied. EPR studies of the doped sample indicate the interstitial occupancy of dopant. EDS data confirms the presence of vanadium in the doped specimen. Thermal study of the Vo(II)-doped sample reveals slight change in the dissociation patterns when compared to pure MRSH. XRD and FTIR spectra of doped sample reveal some minor structural variations. The influence of dopant has not altered the centrosymmetric nature of MRSH, which is revealed in the SHG test.

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