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Growth, structure and spectral studies of a novel mixed crystal potassium zinc manganese sulphate

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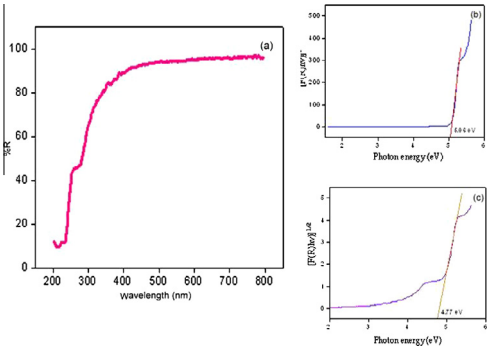
HIGHLIGHTS

- Mixed crystal $K_2Zn_{0.84}Mn_{0.16}(SO_4)_2{\cdot}6H_2O$ belongs to monoclinic system with P21/c space group.
- High-resolution XRD reveals the presence of vacancy type defects in the mixed crystal.
- Co-existence of Zn and Mg in the mixed crystal is confirmed by single crystal XRD, EDS and AAS.

GRAPHICAL ABSTRACT



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ABSTRACT

Mixed crystals of $K_2Zn_{0.84}Mn_{0.16}(SO_4)_2{\cdot}6H_2O$ were grown from an equimolar aqueous solution of Tutton's salt, $K_2Zn(SO_4)_2{\cdot}6H_2O$ and $MnSO_4$ by slow evaporation solution growth technique. The crystal composition as determined by single crystal XRD analysis reveals the co-existence of zinc and manganese in the mixed crystal. The surface morphological changes are observed by scanning electron microscopy. Small variations in cell parameter values, slight shifts in characteristic vibrational patterns in FT-IR and reduction in intensities observed in XRD confirm the crystal stress as a result of formation of mixed crystal. High resolution XRD diffraction estimates the crystalline perfection of the mixed crystal with predominantly vacancy type of defects. It belongs to $P2_1/c$ space group with cell parameter values, $a = 6.1530$ Å, $b = 12.2230$ Å, $c = 9.0430$ Å, $\alpha = \beta = \nu = 90°$, $V = 657.56$ Å^3, $Z = 4$. High transmittance in the visible region is observed.

Introduction

Tutton's salts are potential conductors due to the existence of comparatively strong hydrogen bonds. Zinc potassium sulphate hexahydrate $K_2Zn(SO_4)_2{\cdot}6H_2O$ belongs to a large number of isomorphic compounds with a general formula $Me'Me''(XO_4)_2{\cdot}6H_2O$ (Me' = K, NH_4^+, Rb, CS; Me'' = Mg, Mn, Co, Ni, Cu, Zn, X = (S, Se) [1,2]. It crystallizes in the monoclinic system with space group $P2_1/c$ [3]. Detailed studies on vibrational patterns of NH_4^+ and SO_4^{2-} ions in Tutton's salts have been carried out [4–8]. EPR studies on Mn(II) –, Cu(II) – and VO(II) – doped single crystal of $K_2Zn(SO_4)_2{\cdot}6H_2O$ [9–11] and other Tutton's salts [12–14] have been reported. The crystal chemistry, metal–water interaction and the system of hydrogen bonds in different series of the Tutton salts, Rb sulfates [15], Rb selenates [16] and Cs sulfates [17] by single crystal and powder diffraction have been discussed. Recently, we have reported the growth, structure and crystalline perfection of $Zn_{0.54}Mg_{0.46}(NH_4)_2SO_4{\cdot}6H_2O$ [18]. Although, extensive studies

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have been carried out on Tutton's salts, growth, characterization and structure of $K_2Zn_xMn_{(1-x)}(SO_4)_2{\cdot}6H_2O$ mixed crystals has not been reported so far. In the present work, we are reporting the growth and structure of the mixed crystal, $K_2Zn_xMn_{(1-x)}(SO_4)_2{\cdot}6H_2O$ ($x = 0.84$) (KZMS), characterized by FT-IR, XRD, HRXRD, SEM, EDS, AAS, UV–visible and thermal studies.

Experimental

Synthesis and crystal growth

Equimolar quantities of the component salts $K_2Zn(SO_4)_2{\cdot}6H_2O$ and $MnSO_4$ were dissolved in triply distilled water and thoroughly mixed for 3 h using a magnetic stirrer to ensure the homogeneity of the solution. The solution was covered with perforated paper and left undisturbed. The crystals were grown from slow evaporation solution growth technique. Good quality bulk crystals were harvested in a period of 3 weeks.

Characterization techniques

FT-IR spectra were recorded using AVATAR 330 FT-IR by KBr pellet technique. The powder XRD data were analyzed with the PAN analytical model X'pert pro analysis using graphite monochromated Cu Kα radiation. Single crystal XRD was done using Bruker AXS (kappa Apex II) X-ray diffractometer. The surface morphologies were observed by using a JEOL JSM 5610 LV SEM with the resolution of 3.0 nm, an accelerating voltage 20 kV and maximum magnification 3,00,000 times. AAS was recorded using VARIAN model SPECTRA 220 spectrometer in acetone-air flame. TG/DTA analysis was carried out between 25 and 600 °C, in the nitrogen atmosphere at a heating rate of 10 °C min^{-1}. The crystalline perfection of the grown single crystals was estimated by HRXRD by employing a multicrystal X-ray diffractometer developed at National physical laboratory. The well-collimated and monochromated Mo Kα1 beam obtained from the three monochromator Si crystals set in dispersive (+,−,−) configuration has been used as the exploring X-ray beam. The specimen crystal is aligned in the (+,−,−,+) configuration. The rocking or diffraction curves (DC) were recorded by changing the glancing angle (angle between the incident X-ray beam and the surface of the specimen) around the Bragg diffraction peak position θ_B (taken as zero for the sake of convenience). Before recording the DC, the specimen was first lapped and chemically etched in a non-preferential etchant of water and acetone mixture in 1:2 volume ratio.

Results and discussion

FT-IR analysis

Comparison of the characteristic vibrational patterns of mixed crystal with that of the parent Tutton's salt reveals small shifts in wave numbers of some of the characteristic vibrations (Fig. 1). It could be due to the lattice stress developed as a result of incorporation of Mn(II) – into the crystalline matrix.

SEM and EDS/AAS analysis

The influence of the incorporation of Mn(II) on the surface morphology of $K_2Zn(SO_4)_2{\cdot}6H_2O$ crystal faces reveals large scatter centers and imperfections. The surface roughness could be due to macrosteps as it is quite clear from the SEM micrograph. Presence of zinc and manganese in the crystal lattice is confirmed by EDS (Fig. 2). Atomic absorption spectroscopy studies reveal that quantity of incorporated Mn(II) – into the Tutton's crystal is 3.4 ppm.

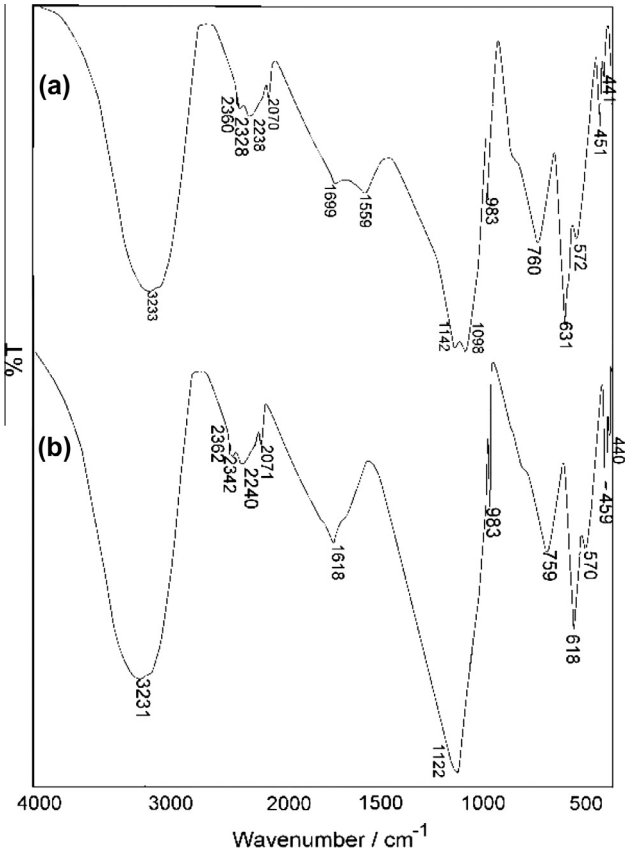

Fig. 1. FT-IR spectra of pure and KZMS.

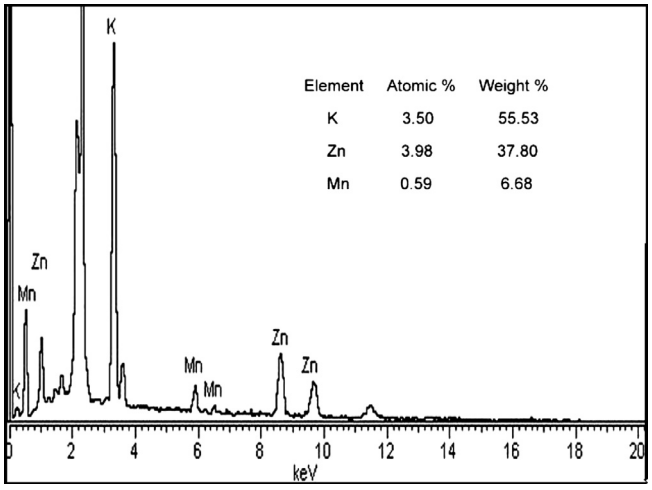

Fig. 2. EDS spectrum of KZMS.

It is clear that the amount of Mn(II) – into the crystalline matrix of Tutton's salt is not in tune with the amount of metal ion introduced in the growth process. The quantity of Mn(II) present in the Tutton's salt crystalline matrix is much less and it could be due to the limitations of the accommodating capability of the material. The incorporation is non- uniform over the surface.

Thermal analysis

The purity of the crystal is determined by thermogravimetry/differential thermal analysis (Fig. 3). A sharp endothermic peak