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CRYSTAL GROWTH, STRUCTURE AND CHARACTERIZATION OF TUTTON'S SALT MIXED CRYSTALS – POTASSIUM MAGNESIUM MANGANESE SULFATE HEXAHYDRATE

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ABSTRACT

New mixed crystals of $K_2Mg_{0.78}Mn_{0.22}(SO_4)_2.6H_2O$ (KMMS) were synthesized and grown from an equimolar mixture of the Tutton's salt $K_2Mg(SO_4)_2.6H_2O$ and $MnSO_4$ by slow evaporation of the aqueous solution at room temperature. Crystal composition as determined by single crystal XRD analysis reveals that it belongs to the monoclinic system with $P2_1/c$ space group and cell parameter values are, a= 6.1380⊕, β = 12.2740⊕, χ = 9.0940⊕, □ = ≀ = 90°, ® = 104.81°, ς = 662.33 ⊕^{3}, Z = 4. The coexistence of magnesium and manganese ions in the mixed crystal is confirmed by single crystal XRD analysis, atomic absorption spectroscopy, inductively coupled plasma and energy dispersive X-ray spectroscopy. Slight variations are observed in FT-IR and XRD of pure and mixed crystals. The surface morphology of the mixed crystal is studied by scanning electron microscopy. Thermogravimetric and differential thermal analysis curves show the purity of the substance. Large full width at half maximum value of diffraction curves in high resolution X-ray diffraction spectroscopy reveals the presence of misorientation in the lattice blocks because of the Mn(II)-incorporation.

Keywords: Crystal structure, HRXRD, FT-IR spectroscopy, Tutton salt, KMMS.

1. INTRODUCTION

The compound under study potassium magnesium sulphate hexahydrate $K_2Zn(SO_4)_2.6H_2O$ belongs to a large number of isomorphous compounds with a general formula Me'Me"$(XO_4)_2.6H_2O$ (Me'= K, NH_4^+, Rb, Cs; Me" = Mg, Mn, Co, Ni, Cu, Zn; X = S, Se) known as Tutton's salt[1,2]. These compounds are considered as potential conductors due to the existence of comparatively strong hydrogen bonds. They crystallize in the monoclinic system with space group $P2_1/c$. The synthesis and characterization of potassium magnesium sulfate hexahydrate crystals have been carried out by Dhandapani et. al.,[3] Recently, we have investigated the crystal structure and characterization of zinc magnesium ammonium sulphate hexahydrate mixed crystals, $Zn_{0.54}Mg_{0.46}(NH_4)_2(SO_4)_2.6H_2O$[4] crystallized from equimolar mixture of $Zn(NH_4)_2(SO_4)_2.6H_2O$ and $Mg(NH_4)_2(SO_4)_2.6H_2O$. We have also investigated the growth, structure and spectral studies of a novel mixed crystal potassium zinc manganese sulfate, $K_2Zn_{0.84}Mn_{0.16}(SO_4)_2.6H_2O$ (KZMS)[5]. Although extensive studies have been carried out on Tutton's salts, the growth, characterization and structure of $K_2Mg_xMn_{(1-x)}(SO_4)_2.6H_2O$ mixed crystals have not been reported so far. As a part of our investigation on the studies of mixed crystals of Tutton's slats[4,5] the present study was undertaken. The as-grown crystals have been characterized by FT-IR, XRD, HRXRD, SEM, EDS, AAS, UV- visible and thermal studies.

2. EXPERIMENTAL

2.1 Synthesis and crystal growth

Pure KMMS was prepared by mixing equimolar concentrations of $K_2Mg(SO_4)_2.6H_2O$ and $MnSO_4$ using deionized water as a solvent by the slow evaporation technique. Good quality crystals were harvested after 15 days. Photograph of mixed crystals is shown in Fig. 1.

2.2 Characterization techniques

The FT-IR spectra were recorded using AVATAR 330 FT-IR instrument using KBr pellet technique in the rang 400-4000cm^{-1}. The powder X-ray diffraction was performed by using Philips Xpert Pro Triple-axis X-ray diffractometer. The single crystal XRD was recorded using Bruker AXS (Kappa Apex II) X-ray diffractometer which emplys graphite monochromated MoKα. The structure was solved and refined by full matric least squares on F^2 with Wingx software package[6] utilizing SHELXS-97[7] and SHELXL-97[8] modules. The plots for the structures were created with DIAMOND Software[9]. The morphologies of the samples were recorded by using a JEOL JSM 5610 LV scanning electron microscope with a resolution of 3.0 nm, accelerating voltage 20 kV and maximum magnification x = 3,00.000 AAA, technique was recorded using VARIAN Model SPECTRA 220 Spectrometer in acetone – air flame. The molar proportions of the magnesium and zinc present in the mixed crystals are calculated using AAS and ICP studies.

To reveal the crystalline perfection of the grown crystals, a multicrystal X-ray diffraction (MCD) developed at National Physical Laboratory[10] has been used to record high-resolution rocking or diffraction curves. The well – collimated and monochromated Mo $K\alpha_1$ 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 around the Bragg diffraction peak position. The specimen can be rotated about a vertical axis, which is perpendicular to the plane of diffraction, with minimum angular interval of 0.5 arc s. The diffracted intensity is measured by using a scintillation counter. 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.

3. RESULTS AND DISCUSSION

3.1 FT-IR Spectral analysis

FT-IR spectrum of mixed crystal is shown in Fig. 2. A broadband appeared at 1,708-1,718 cm^{-1} indicates that it is due to the coordinated water molecules[11] in the mixed crystal (KMMS). A very slight shift in some of characteristic vibrational frequencies of pure $K_2Mg(SO_4)_2.7H_2O$ and the mixed crystal $K_2Zn_{0.84}Mn_{0.16}(SO_4)_2.6H_2O$ are observed because of lattice stress developed as a result of incorporation of Mn(II)- into the crystalline matrix. Important characteristic frequencies of the pure and studied mixed crystals are displayed in Table.1.

3.2 SEM, EDS and AAS analysis

The effect of the incorporation of Mn(II)- in the surface morphology of $K_2Mg(SO_4)_2.6H_2O$ crystal faces reveals the highest surface roughness which could be due to bunch steps or even macro steps (Fig. 3). The presence of manganese in the crystal lattice is confirmed by EDS (Fig. 4). The quantity of incorporated Mn(II)- into the Tutton's salt in estimated to be 2.5 ppm by atomic absorption spectroscopy. It appears that the accommodating capacity of the host crystal is limited and hence only a small quantity is incorporated into the crystalline matrix of $K_2Mg(SO_4)_2.7H_2O$.

3.3 Thermal analysis

The differential thermal analysis shows a sharp endothermic peak at 150^oC Thermogravimetry curve at a 600^oC shows the residual mass obtained is 75%. Thermogravimetry and differential thermal analysis reveals that no phase transitions between 150^oC to 460^oC. (Fig. 5).The endothermic peak around 150^oC could be due to dehydration of Tutton's salt. Another peak around 460^oC may be due to the decomposition of the residue.

3.4 UV - visible spectra

The UV-visible spectrum of the mixed crystal reveals high transmittance in the visible region and the lower cut - off wavelength is observed at ~370 nm. The concentration of absorbing species can be determined using the Kubelka-Munk equation[12], correlating reflectance and concentration,

$$F(R) = (1-R)^2 / 2R = \alpha/s = Ac/s \quad \ldots\ldots(1)$$

where *F(R)* is Kubelka-Munk function, R is the reflectance of the crystal and S is scattering coefficient, A is the absorbance and c is concentration of the absorbing species. The direct band gap energy obtained from the intercept of the resulting straight line with the

energy axis at $[F(R)hv]^2 = 0$ is deduced as 5.09 eV (Fig. 6).

3.5 Powder XRD analysis

The X-ray diffractogram shows many diffraction peaks. The experimental and simulated indexed powder XRD pattern of the mixed crystal KMMS are shown in fig. 7. It appears that there is a general agreement of the both XRDs with varied intensity patterns. The well defined Bragg's peaks at specific 2θ angles show good crystallinity of the materials.

3.6 Single crystal XRD analysis

Crystal composition of mixed crystal as determined by single crystal XRD is $K_2Mg_{0.78}Mn_{0.22}(SO_4)_2.6H_2O$. The structure of KMMS is found to be monoclinic and it belongs to $P2_1/c$ space group as that of the parent Tutton's salt. The ORTEP and packing diagrams are given in Fig. 8. These lattice parameters closely match the previous studies of structure determination of Tutton's salt mixed crystals[4,5] and the pure $K_2Mg(SO_4)_2.6H_2O$[13] (Table 2). The crystal data and structure refinement of KMMS are given in Table. 3. Slight changes are observed in the interatomic distances of the mixed crystal and pure $K_2Mg(SO_4)_2.6H_2O$[13]. The K-O bond distance is ~2.9 Å for the pure $K_2Mg(SO_4)_2.6H_2O$ and in KMMS it falls in between 2.7218 (13) and 3.2995 (17) Å. The Mg/Mn-O bond distance varies between 2.0508(13) and 2.1269(12) Å in KMMS mixed crystals. It is comparable with Zn/Mn-O bond distance in KZMS[5] and Zn/Mg-O bond distance in zinc magnesium ammonium sulfate hexahydrate[4] mixed crystals. The bond lengths and angles in the sulfate group of $K_2Mg(SO_4)_2.6H_2O$ are close to the tetrahedral pattern (S-O = 1.442 to 1.507 Å and O-S-O bond angle 107^o to 112^o) and in the new mixed crystal the corresponding values are 1.4727(12) Å and 108.10^o to 110.37^o respectively. The O-Mg-O bond angles for KMMS mixed crystal falls in the range from 89.13^o to 90.87^o which is comparable to that in $K_2Mg(SO_4)_2.6H_2O$ and $Zn_xMg_{(1-x)}(NH_4)_2(SO_4)_2$. The Mg-O and O-H bond lengths of KMMS mixed crystal lie between 2.0508 Å - 2.1269 Å and 0.810 Å - 0.859 Å respectively, whereas in $Zn_xMg_{(1-x)}(NH_4)_2(SO_4)_2.6H_2O$ mixed crystal it ranges from 2.0512 Å to 2.0904 Å and 0.858 Å to 0.862 Å respectively.

3.7 HRXRD

Fig. 9 shows the diffraction curve (DC) for a typical KMMS specimen single crystal recorded for (123) diffracting planes in symmetrical Bragg geometry using MoKα radiation. As seen in the figure, the curve is quite board with FWHM (Full width at half maximum) value 520 arc sec. The top of the diffraction curve is not smooth and indicates multiple peaks. The multiple peaks with large value of FWHM indicates that the specimen contains many mosaic blocks which are misoriented to each other with their adjacent regions by a few tens of arc sec as observed in benzimedazole single crystals grown by vertical Bridgman technique[14]. Impurities present in the raw material and thermal and/or mechanical fluctuations during the growth process may be responsible for such features of diffraction curve. However in the case of KZMS[5] the diffraction curve dose not contain any additional peak and indicates the absence of clustering of defects at microscopic level (FWHM is equal to 48 arc s) and fairly good crystalline perfection.

4. CONCLUSION

In the present study, the synthesis, characterisation and crystal structure of a new mixed crystal $K_2Mg_{0.78}Mn_{0.22}(SO_4)_2.6H_2O$ (KMMS), structurally similar to $K_2Mg(SO_4)_2.6H_2O$ have been studied. Single crystal XRD studies reveal that the bond lengths, and bond angles of the new mixed crystal KMMS are comparable with that of $Zn_{0.54}Mg_{0.46}(NH_4)_2(SO_4)_2.6H_2O$ and $K_2Zn_{0.84}Mn_{0.16}(SO_4)_2.6H_2O$. The incorporation of Mn(II)- in the crystalline matrix of $K_2Mg(SO_4)_2.6H_2O$ is confirmed by EDS and AAS. A slight shift in the vabrational patterns could be due to the incorporation of Mn(II)- in to the Tutton's salt crystal lattice. Highest surface roughness in the SEM micrographs of KMMS mixed crystal is due to the Mn(II)-incorporation. High resolution X-ray diffraction curve shows a broad single peak, revealing that the KMMS mixed crystal contains many mosaic blocks which are completely misoriented to each other.

Table 1: FT-IR Vibrational frequencies (cm^{-1})

System	SO_4^{2-} Symmetrical bending modes (cm^{-1})	SO_4^{2-} Asymmetric bending modes (cm^{-1})	SO_4^{2-} Symmetric stretching modes (cm^{-1})	SO_4^{2-} Asymmetric stretching modes (cm^{-1})	Reference
Tutton's salt	451	631	983	1098,1142	[13]
$K_2Zn_{0.84}Mn_{0.16}(SO_4)_2.6H_2O$	459	618	983	1096,1122	[5]
$K_2Mg_{0.78}Mn_{0.22}(SO_4)_2.6H_2O$	455	630	983	1096,1146	Present work
$Zn_{0.54}Mg_{0.46}(NH_4)_2(SO_4)_2.6H_2O$	460	621	980	1044,1138	[4]

Table 2: Cell parameters

System	a (Å)	b (Å)	c (Å)	V ($Å^3$)	Reference
$K_2Mg(SO_4)_2.6H_2O$	9.029	12.204	6.147	654.8	[13]
$K_2Zn_{0.84}Mn_{0.16}(SO_4)_2.6H_2O$	9.019	12.192	6.134	652.1	[5]
$K_2Mg_{0.78}Mn_{0.22}(SO_4)_2.6H_2O$	9.0940	12.2740	6.1380	662.3	Present work
$Zn_{0.54}Mg_{0.46}(NH_4)_2(SO_4)_2.6H_2O$	9.2557	12.534	6.221	690.6	[4]

Table 3: Crystal data and structure refinement for KMMS

Empirical formula Molecular formula	$H_6KMg_{0.39}Mn_{0.11}O_7S$ $K_2Mg_{0.78}Mn_{0.22}(SO_4)_2.6H_2O$
Formula weight	204.73
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, $P2_1/c$
Unit cell dimensions	a = 6.1530(2) Å, α = 90 ° b = 12.2740(3) Å, β= 104.8190(10) ° c = 9.0940(2) Å3, γ = 90 °
Volume	662.33(3) $Å^3$
Z, Calculated density	4, 2.053 Mg/m^3
Absorption coefficient	1.335 mm^{-1}
F(000)	418
Crystal size	0.30 x 0.30 x 0.20 mm
Theta range for data collection	2.85 to 24.99 deg
Limiting indices	-6<=h<=7, -14<=k<=14, -10<=l<=10
Reflections collected / unique	5448 / 1171 [R(int) = 0.0390]
Completeness to theta = 24.99	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7968 and 0.6486
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1171 / 10 / 115
Goodness-of-fit on F^2	1.090
Final R indices [I>2sigma(I)]	R1 = 0.0203, wR2 = 0.0561
R indices (all data)	R1 = 0.0220, wR2 = 0.0571
Extinction coefficient	0.128(5)
Largest diff. peak and hole	0.260 and -0.292 $e.A^{-3}$

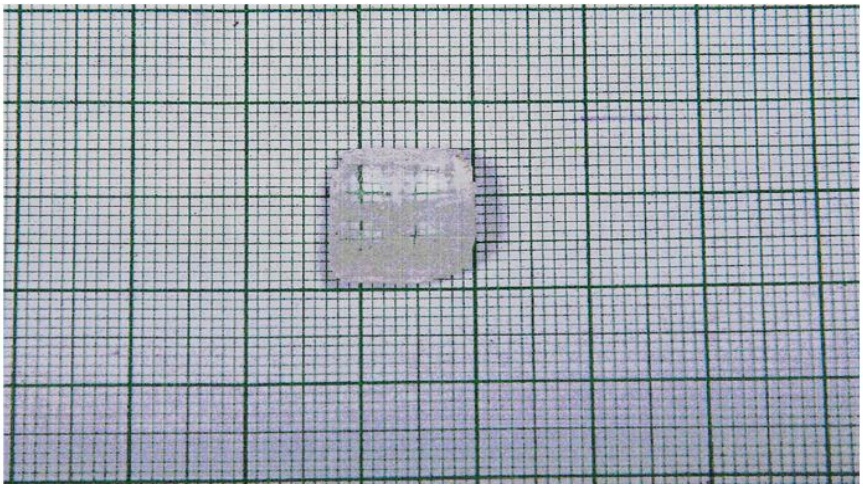

Fig. 1: Photograph of KMMS mixed crystal

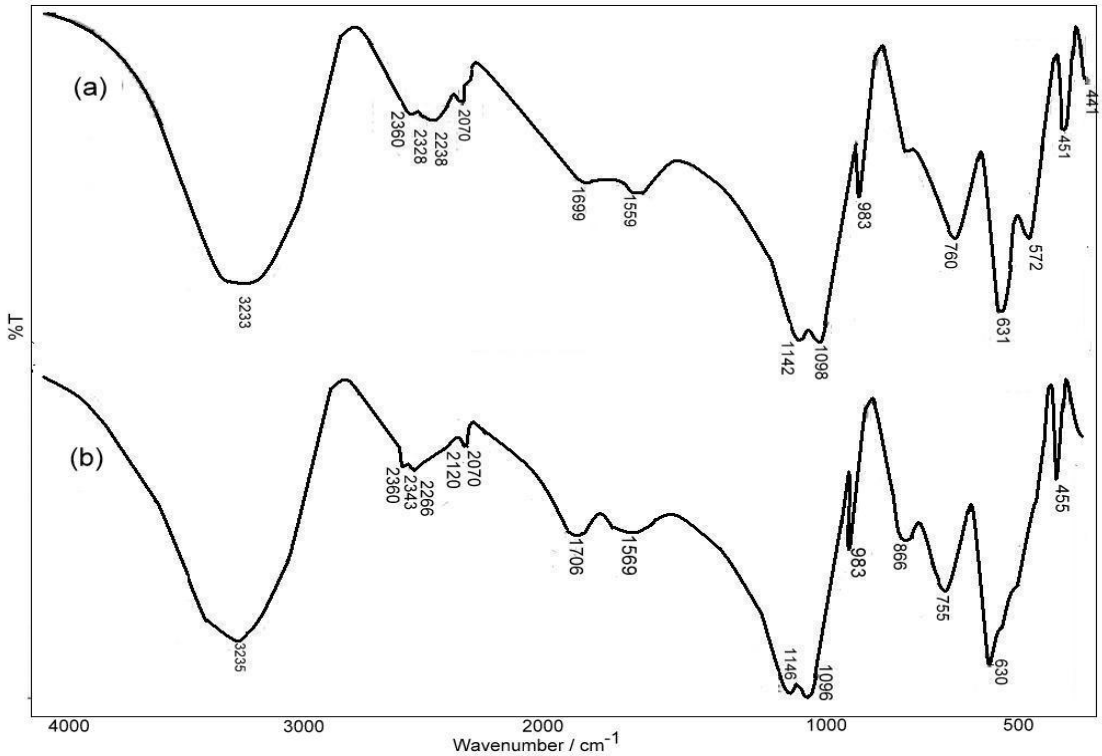

Fig. 2: FT-IR spectra of (a) Pure and (b) KMMS mixed crystal

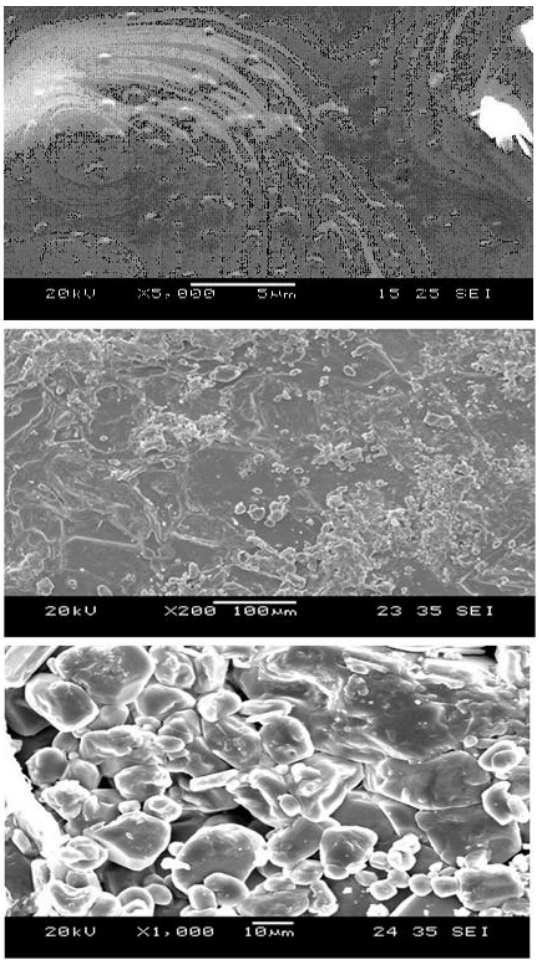

Fig. 3: SEM mircographs of KMMS mixed crystal

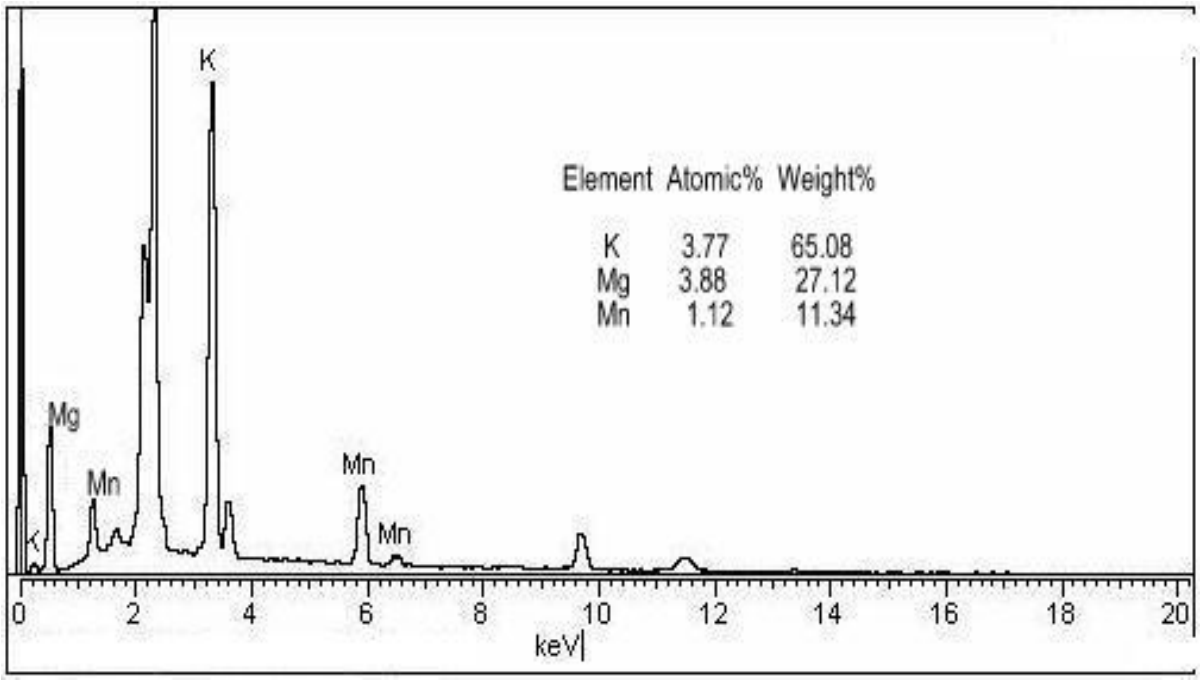

Fig. 4: EDS spectrum of KMMS mixed crystal

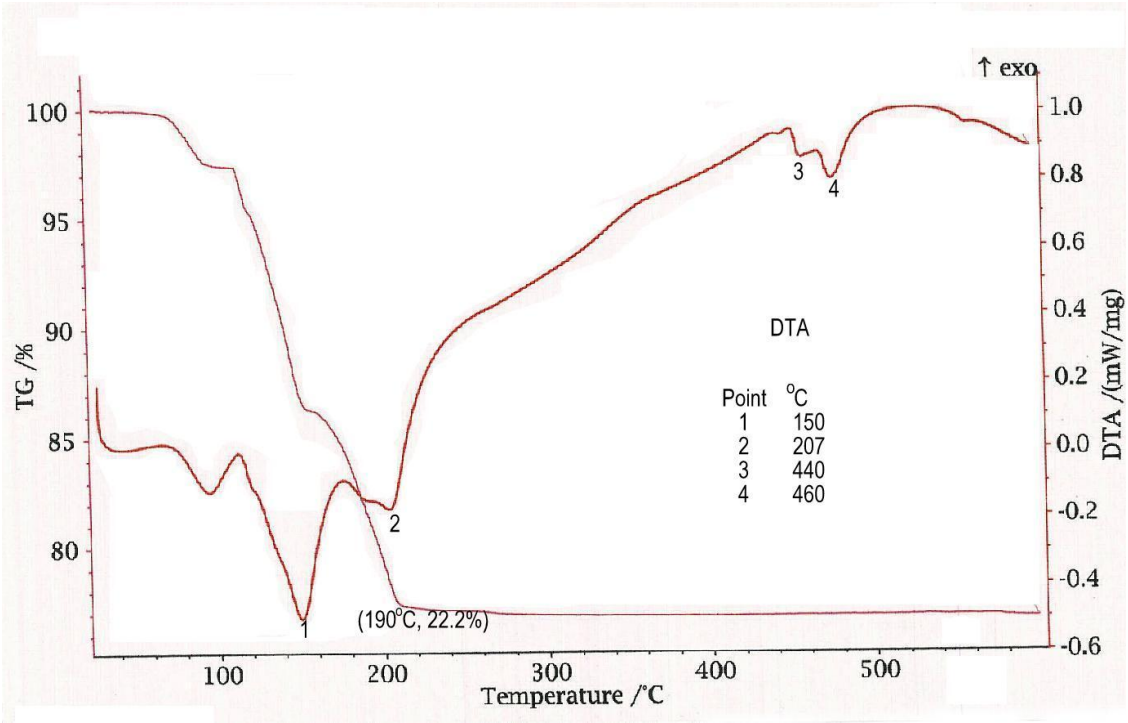

Fig. 5: TG/DTA curve of KMMS

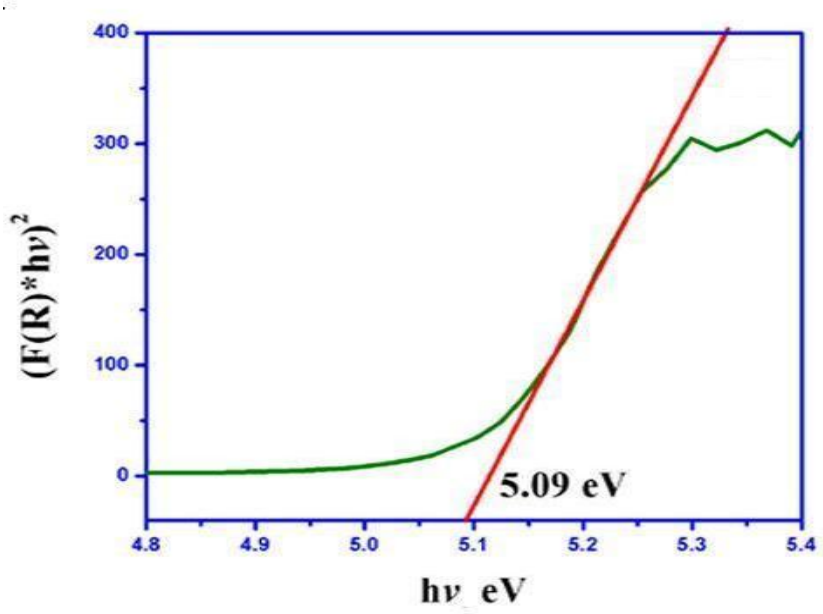

Fig. 6: Band gap energy curve of KMMS

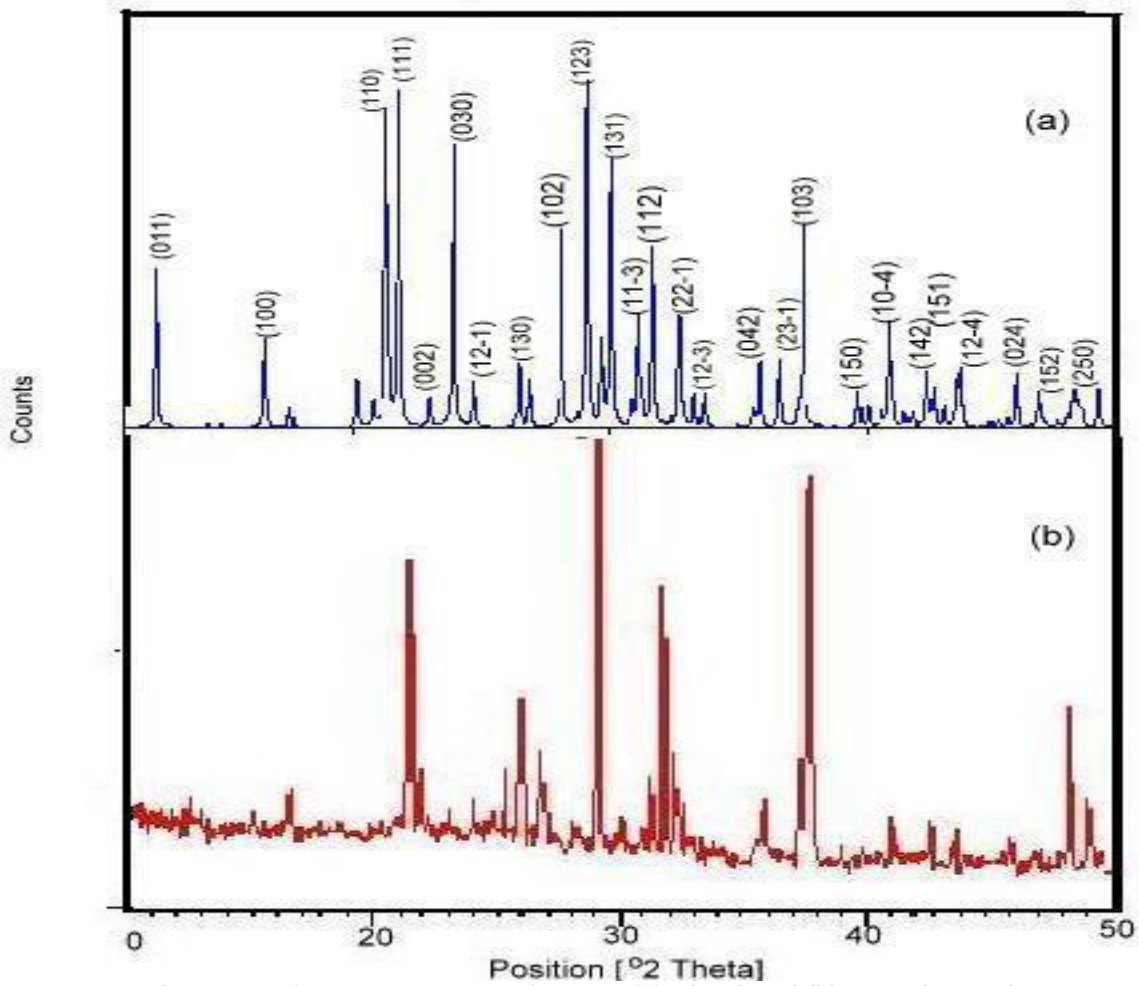

Fig. 7: Powder XRD patterns of KMMS (a) Simulated (b) Experimental

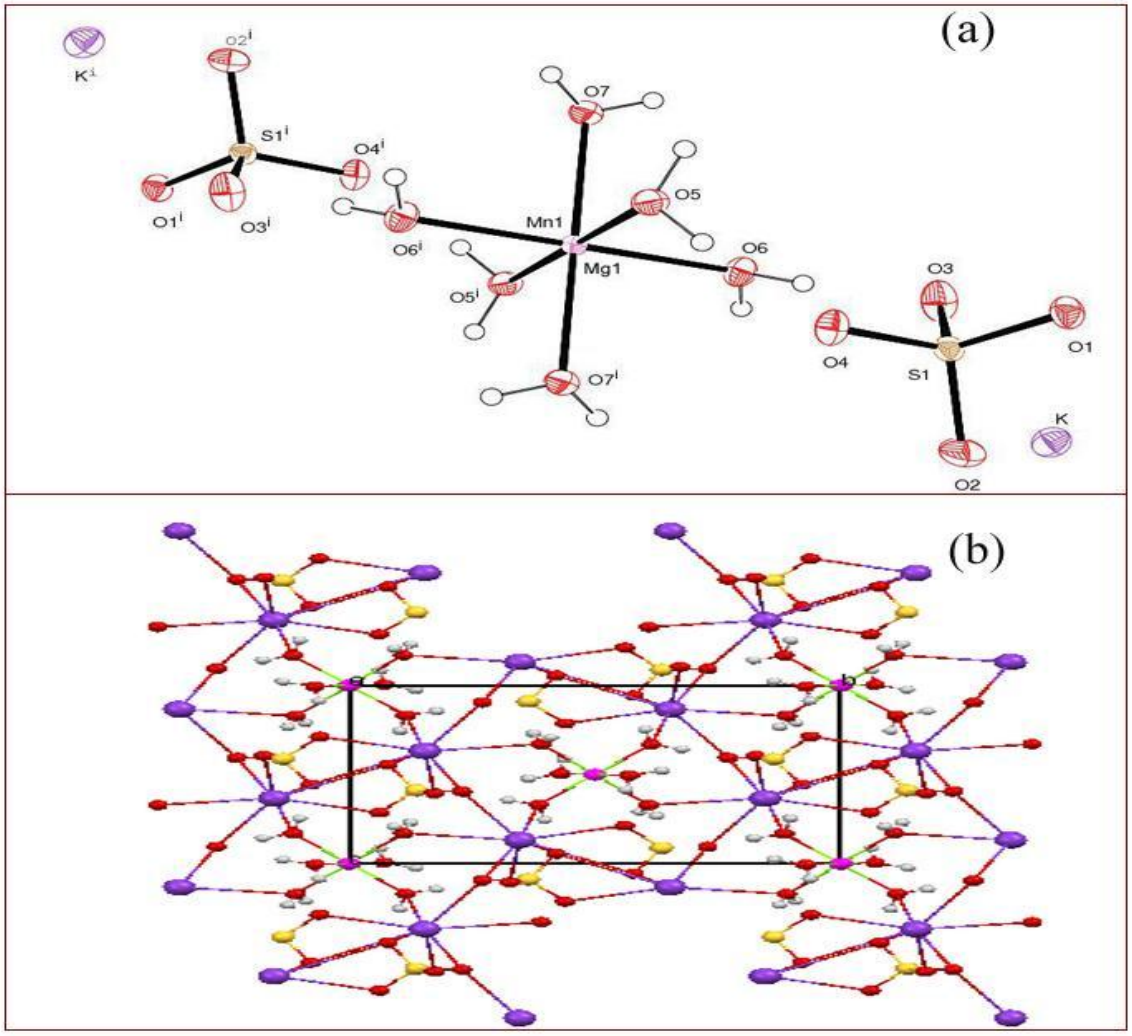

Fig. 8: ORTEP and packing diagram of KMMS mixed crystal

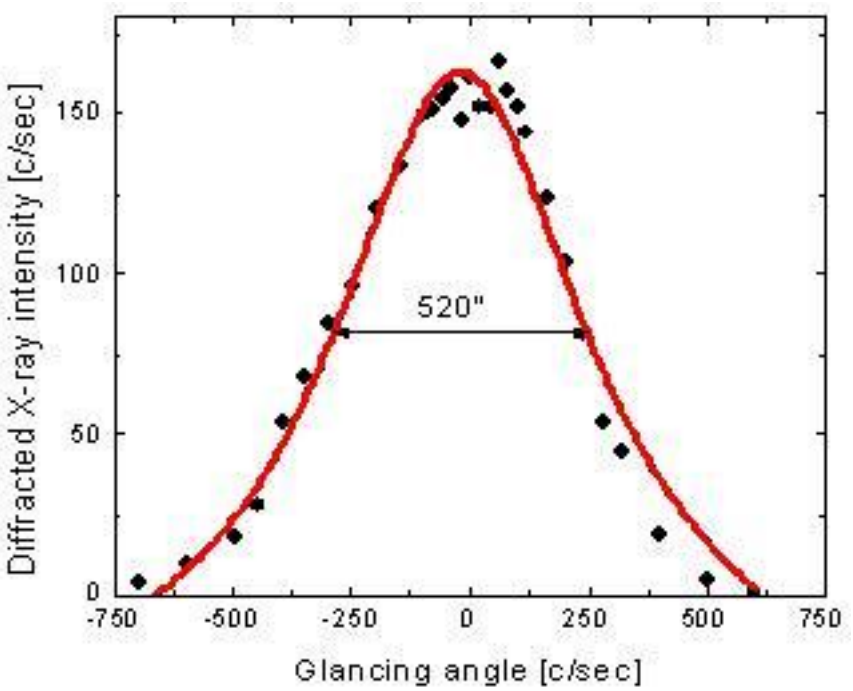

Fig. 9: HRXRD diffraction curve of KMMS mixed crystal

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