

CRYSTAL DEVELOPMENT, THERMAL AND CRYSTALLINE PERFECTION OF POTASSIUM MAGNESIUM COBALT SULFATE HEXAHYDRATE MIXED CRYSTALS

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ABSTRACT

Potassium magnesium cobalt sulfate hexahydrate (KMCS) was synthesized and single crystals were obtained with a slow evaporation solution growth technique (SESGT). KMCS empirical formula is $K_2Mg_{0.26}Co_{0.74}(SO_4)_2 \cdot 6H_2O$ with the weight of equation 428.34. KMCS crystal exposed monoclinic space group P21/c, $a = 6.1457$, $b = 12.2208$, $c = 9.0677$, $\alpha = \beta = 90^\circ$, $\gamma = 105^\circ$, $V = 657.87$, $Z = 2$, 2.162 Mg m^{-3} , in pink colour. The rate of frequency reduction found in powder indicates the crystal stress resulting from the processing of grown crystals. Single crystals are performed with FT-IR and UV-vis spectral studies. High-resolution X-ray diffraction (HRXRD) indicates prevalent site occupation substitution Co (II). For powder X-ray diffraction (XRD) results in the development of crystal stress due to the formation of single crystals. Electron microscopy scanning (SEM) tests the morphological changes in the exterior. The introduction of dopant into the crystalline medium has been verified by energy-dispersive X-ray spectroscopy (EDS). TG-DTA research has been conducted for single crystal thermal studies.

Keywords: Tutton Salt, Thermal Analysis, HRXRD, X-ray Diffraction.

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INTRODUCTION

The salts of Tutton are pure and act as solid reagents and principles of spectroscopy.¹ Tutton's salt are individual of the most recognized isomorphous compound. These are binary sulfates with the common formula $M_2'M''(SO_4)_2 \cdot 6H_2O$, where M' is a monovalent helpful ion such as K, NH_4 , Rb, Cs or Tl and M'' is a divalent ion such as Mg, Ca, Zn, V, Cd, Co, Fe or Ni. Selenates can easily replace the sulfate groups in these compounds. A study of the X-ray structure of these salts $[(NH_4)_2Mg(SO_4)_2 \cdot 6H_2O]$ was initially reported by Hofmann.² Studies on NH_4^+ and SO_4^{2-} ion vibration patterns in Tutton's salt are performed.³⁻⁷ Co^{2+} ions doped optical absorption in potassium Tutton salts are identified as single crystals.⁸ Several researchers have been reported to focus on the doping effects of paramagnetic ions in the salt of Tutton⁹⁻¹¹ and the salt of other Tutton's.¹²⁻¹⁹ In the search for new crystalline resources with enhanced transmission properties and superior thermal strength of KMCS, the slow evaporation process has developed effectively. FT-IR, UV-vis, HRXRD, powder XRD, SEM-EDS and TG-DTA studies have described the grown crystals as extremely useful techniques for material characterization. Therefore, for a variety of product characterization, several researchers have used this technique.²⁰⁻³² Mixed crystals among high-quality visual excellence were obtained by the sluggish evaporation growth method. In the decomposition development, these crystals suffer a mass defeat of around 24%, equivalent to water molecules from octahedral coordination ions of Ni and Co.³³

EXPERIMENTAL

Synthesis and Crystal Growth

All the starting materials used as part of KMCS development process are purchased as AR grade (purity > 98.0 percent). The KMCS were synthesized in the triply distilled water medium by reacting equimolar proportion of $K_2Mg(SO_4) \cdot 6H_2O$ (MPSH) and $CoCl_2$. Whatman filter paper separated the homogenized solution and evaporated it with a constant temperature tub at $40^\circ C$ temperatures. KMCS single crystals of optically good quality were produced within 20 days. KMCS crystals photograph appeared in Fig.-1.



Fig.-1: Photograph of KMCS Crystal

Analysis Techniques

The KBr pellet system records FT-IR spectra using AVATAR 330 FT-IR. The UV-visible absorption spectrometer was identified using the Hitachi UV-Vis spectrometer as part of the otherworldly range 200-600 nm. HR-XRD used the established crystal growth center to assess the sample crystal perfection. The highly collimated and monochromated light from the three dispersive (+,-,-) configuration monochromator Si crystals were used as an investigation into the X-ray beam. The crystal specimen is adjusted in the configuration (+,-, +). The rocking or diffraction curves (DC) are reported by adjusting the angle of view around the Bragg diffraction peak position θ_B . The specimen was initially lapped before recording the DC and chemically scratched in a 1:2 volume proportion non-preferential water and acetone mixture etchant. For single valuable X-ray diffraction (XRD) crystal studies, an X-beam diffractometer Bruker AXS (Kappa Apex II) was used. A Philips XPert Pro Triple-hub X-ray diffractometer was used to conduct the XRD powder at room temperature using 0.008 phase size and 1.540 Å wavelengths. A JEOL JSM 5610 LV SEM was used for surface morphology analysis. EDS is a compound microanalysis method that is carried out in combination with an SEM. An all-inclusive SDT Q600 thermal analyzer of TA instruments at a heating speed of 20 °C min⁻¹ in nitrogen was conducted with TG-DTA analysis.

RESULTS AND DISCUSSION

FT-IR Spectral Analysis

The infrared spectral study was agreed out to explain the substance bonding and provide helpful in sequence on the molecular arrangement of the moiety. FT-IR spectrum from the powdered sample of pure and mixed crystals in the 4000-400 cm⁻¹ wavelength range is shown in Fig.-2(a and b). The FT-IR spectrum of the grown-up crystal shows a wide band at 3380 cm⁻¹, which is assigned to the ν_{OH} of lattices and coordinated water molecules. O-H stretching vibration of crystallization water is allocated to the absorption at 2475 cm⁻¹. Due to SO₄²⁻ asymmetric stretching vibrations, the absorption at 1145 and 983 cm⁻¹, while the frequency at 864 cm⁻¹ represents SO₄²⁻ symmetric stretching vibrations. Mg-O longitudinal optic mode frequency is 754 cm⁻¹ and SO₄²⁻ bending mode is 628 cm⁻¹. A similar interpretation of the parent Tutton's salt (MPSH) FT-IR spectrum and mixed crystal KMCS a slight change in some vibrational frequencies Table-1. It might be due to Co(II) being integrated into the crystalline matrix.

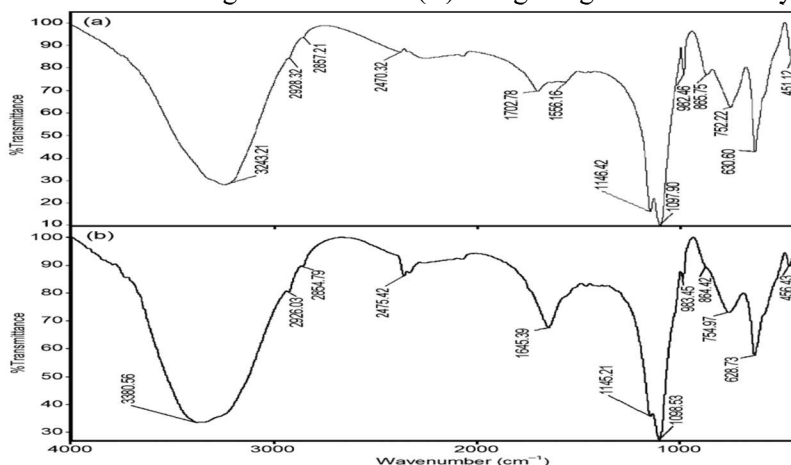


Fig.-2: FT-IR Spectra of (a) MPSH and (b) KMCS Crystals

Table-1: FT-IR Vibrational Frequencies (cm^{-1}) of MPSH and KMCS mixed Crystals.

Assignment	MPSH	KMCS
O-H _s stretching, H ₂ O trace	3243	3380
O-H-O strong hydrogen bonded system	2928, 2857, 2470	2926, 2854, 2475
$\nu_{\text{asym.}}(\text{SO}_4)$	1146, 982	1145, 983
$\nu_{\text{sym.}}(\text{SO}_4)$	865	864
$\delta_{\text{asym.}}(\text{SO}_4)$	630	628
$\delta_{\text{sym.}}(\text{SO}_4)$	451	456

UV-Vis Spectral Analysis

The UV-visible spectrum provides limited data on the structure of the molecule due to the absorption of Ultraviolet and observable light includes the transfer of the electron from the surface to superior power state in σ and π orbital. For the wavelengths between 200 and 600 nm, the absorption range of the newly formed mixed crystals was reported. The absorption spectrum reported is shown in Fig.-3. The absorbance is inversely proportional to the transmission from the UV spectrum of mixed crystals. It is evident that the absorbance around λ_{max} 1.42 is meager and, therefore, maximum transmission. Measuring the absorption coefficient as a purpose of the event beam's frequency ν provides a way for determining a material's bandgap Eg. Calculate the optical band gap in most materials with the Tauc relationship, which is articulated as $(\alpha h\nu) = (A(h\nu - E_g))^r$

A is stable and where r is an index depends on the electronic conversion path accountable for the visual absorption. Tauc's plot of the spectrum of visual absorption calculated at KMCS space temperature is given in Fig.-4. The direct band hole energy with the energy axis at $(\alpha h\nu)^2 = 0$ can be obtained from the cutoff of the subsequent in a straight line line and the specimen's bandgap energy is 4.8 eV.

SEM and EDS Analysis

SEM study provides data on the scenery of the surface and its aptness to manufacture devices. It is also used to detect the existence of imperfection. It has been shown that the viability of various impurities is distinctive in modifying the exterior morphology. The incorporation of Co(II) in MPSH on KMCS crystal faces surface morphology shows the formation of centers of structural defects. The flower-like structure³⁴ was obtained due to the doped sample at 5000 magnification Fig.-5. EDS confirms the presence of magnesium potassium cobalt in the crystal lattice Fig.-6. It indicates that the host crystal's accommodating potential is partial and only a tiny amount is included into the crystalline medium of MPSH. However, the analysis of the exterior at different sites reveals that the absorption over the surface is non-uniform, consistent with the adsorption mechanism at the phase strain ledges.

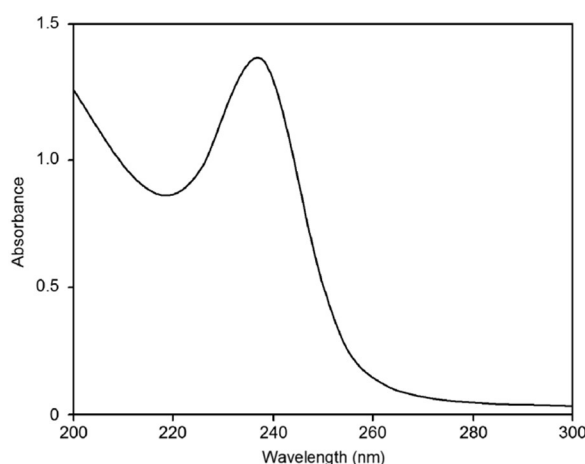


Fig.-3: UV Spectrum of KMCS Crystal

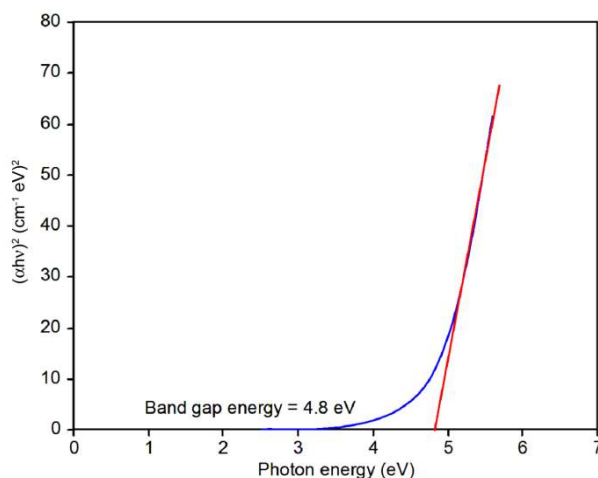


Fig.-4: Band Gap Energy of KMCS Crystal

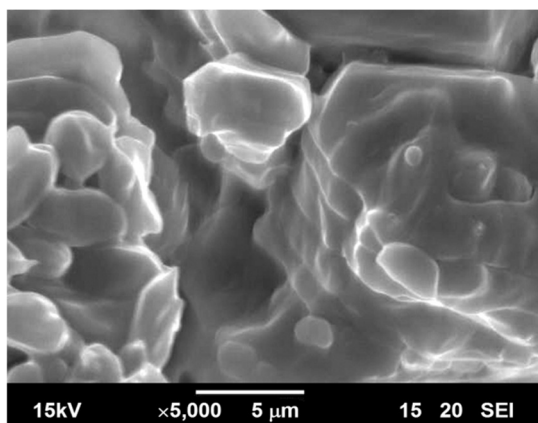


Fig.-5: SEM Image of KMCS Crystal

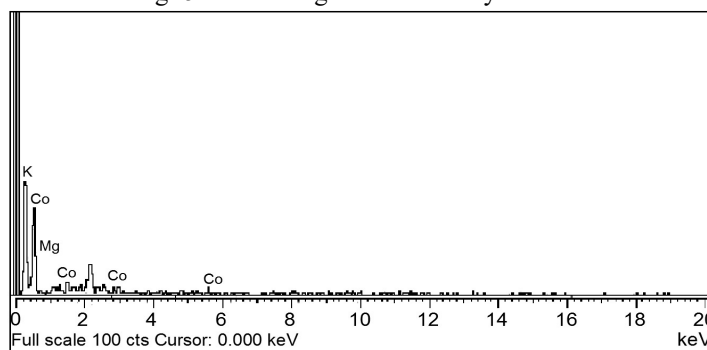


Fig.-6: EDS Spectrum of KMCS Crystal

Thermal (TG-DTA) studies

KMCS TG-DTA curves in the 20-600 °C temperature range are shown in Fig.-7. This indicates the crystal remains constant up to ≈ 90 °C and the breakdown starts at around ≈ 90 °C. This process continues up to 600 °C, after which the residual mass is reduced. It could be accredited to the elimination of water molecules chemically removed. The primary stage of decomposition at a temperature of 90-175 °C results in the removal of four water molecules. The reported 18 percent mass loss agrees with the observed 18.2 percent mass loss. The second decomposition begins at ≈ 175 °C and is accompanied by ≈ 205 °C, which could be due to the failure of two remaining water molecules. The measured and observed mass loss values were 8% and 8.3% of the total mass taken, respectively, in this process. For DTA, two endothermic peaks are observed at approximately 90 and 175 °C. The DTA has seen a somewhat

expanded endothermic peak showing the loss of six water molecules, resulting in the initial mass loss. This is also consistent with studies of TGA. The residual mass is 74 percent, which is consistent with the estimate of 73.5 percent.

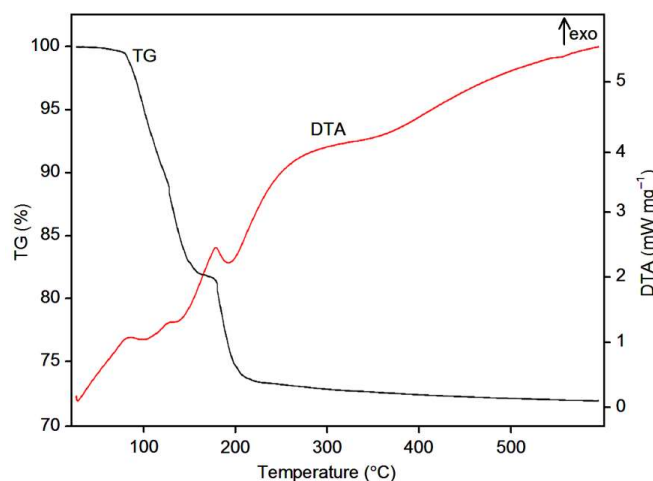


Fig.-7: TG-DTA Curves of KMCS Crystal

XRD Analysis for Crystal Structure

XRD patterns of mixed crystals are compared with unpolluted material patterns and it reveals a single stage with a small decrease in peak intensities coupled with a tiny shift in peak position Fig.-8. This result could be due to the addition of Co(II) in the crystalline matrix of MPSH, as well as the good mixed crystal crystallinity. KMCS was done with a single crystal XRD crystal structure analysis and the ORTEP is shown in Fig.-9. It crystallizes as the parent Tutton's salt (MPSH) in a monoclinic model with centrosymmetric freedom group P21/c and is superior to a small 'R' value of 0.0223 (final R indices). Minor variations in restriction values of mixed crystal cells are observed and compared with parent crystal data Table-2 and structural refinement are shown in Table-3. The $\text{K}_2\text{Mg}_{0.26}\text{Co}_{0.74}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ empirical formula supports the inclusion of a small but important amount of Co(II). Through direct method and succeeding Fourier Differential Synthesis (SHELXS-97)³⁵, the F2 full-matrix minim-square approach optimized the crystal structure with anisotropic thermal parameters for all non-hydrogen atoms (SHELXL-97). ORTEP^{36,37} rendered molecular graphics and SHELXL-97³⁸ and PLATON³⁹ use molecular packing with mercury software³⁷ as preparation material. The compound's three-dimensional structure, KMCS, is formed as counter-ions from $\text{Mg}_{0.26}\text{Co}_{0.74}(\text{H}_2\text{O})_6$ octahedra, SO_4^{2-} and K^+ . Table-4 lists the details for bond lengths, bond angles and geometry of the hydrogen bond. $\text{K}_2\text{Mg}_{0.26}\text{Co}_{0.74}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ crystal structure, isomorphous with $\text{MgK}_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$. The newly formed crystal (KMCS) interatomic distances are verging on like that of pure MPSH. The magnesium / cobalt atom has a six-water oxygen octahedral coordination. Mg-O / Co-O bond distances were observed to change from 2.0343 to 2.1204 Å, and the bond angle varies from 89°38' to 90°62' where each is hydrogen bonded to two sulfate oxygen atoms (≈ 2.75 Å).

Table -2: Lattice Factor Values for MPSH and KMCS Crystals

Crystal	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	<i>V</i> (Å ³)	System
MPSH*	6.13	12.23	9.09	656.25	Monoclinical
KMCS	6.1457	12.2208	9.0677	657.87	Monoclinical

*Ref. ¹¹

Table-3: Crystal Data and Structure Enhancement Parameters for KMCS

Empirical Formula	$\text{Co}_{0.74}\text{H}_{12}\text{K}_2\text{Mg}_{0.26}\text{O}_{14}\text{S}_2$
Formula Weight	428.34
Temperature/K	293(2)
Wavelength/Å	0.71073
Crystal System	Monoclinic

Space Group	$P2_1/c$
Unit Cell Dimensions/Å, °	$a = 6.1457(4)$
	$b = 12.2208(7)$
	$c = 9.0677(5)$
	$\alpha = 90$
	$\beta = 104.9850(10)$
	$\gamma = 90$
Volume/Å ³	657.87(7)
Z	2
Calculated Density/Mg m ⁻³	2.162
Absorption Coefficient/mm ⁻¹	2.018
$F(000)$	434.3
Crystal Size/mm	$0.35 \times 0.30 \times 0.25$
θ Range for Data Collection/°	2.86–27.00
Limiting Indices	$-7 \leq h \leq 7; -15 \leq k \leq 15;$ $-11 \leq l \leq 11$
Reflections collected/unique	6213/1432 [$R(\text{int}) =$ 0.0154]
Completeness to $\theta =$ 27.00	99.9%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.6393 and 0.5342
Refinement method	Full-matrix least- squares on F^2
Data/restraints/parameters	1432/10/121
Goodness-of-fit on F^2	1.115
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0223, wR_2 =$ 0.0640
R indices (all data)	$R_1 = 0.0228, wR_2 =$ 0.0643
Extinction coefficient	0.0076(15)
Largest diff. peak and hole/e Å ⁻³	0.374 and -0.419

CCDC No.1020377.

Table-4: Selected Bond Lengths and Bond Angles of KMCS Crystal

Mg–O/Co–O Octahedron	Hydrogen Bonds	SO ₄ ²⁻ Tetrahedron	K ⁺ Coordination
O(6)–Co/Mg(1)– 2.0343(13)	O(7)–H(7A)···O(2)– 0.879(16)	O(3)–S(1)– 1.4723(15)	K(1)–O(4)– 2.7285(14)
O(7)–Co/Mg(1)– 2.1204(13)	O(5)–H(5A)···S(1)– 0.855(16)	O(1)–S(1)– 1.4790(14)	K(1)–O(2)– 3.2637(19)
O(7)–Co/Mg– 2.1204(13)	O(5)–H(5B)···O(1)– 0.859(16)	O(2)–S(1)–O(3)– 109.66(11)	K(1)–S(1)– 3.5703(7)
O(6)–Co/Mg–O(5)– 89.38(6)	O(7)–H(7B)···S(1)– 0.862(16)	O(4)–S(1)–O(1)– 110.09(8)	O(1)–K(1)– 2.8171(15)
O(6)–Co/Mg–O(5)– 90.62(6)	O(6)–H(6A)···S(1)– 0.896(17)		O(5)–K(1)– 3.1160(15)
	O(6)–H(6B)···S(1)– 0.874(17)		S(1)–O(1)–K(1)– 121.27(8)

			O(1)–S(1)–K(1)– 112.48(6)
			O(1)–K(1)–O(3)– 139.10(4)

There are twelve second closest neighbors to the magnesium / cobalt molecule along these lines and they have the corners of a smooth icosahedron. The sulfate oxygen molecules form the second Mg-O / Co-ion (Mg-O / Co-O $\approx$ 4.5 Å) coordination sphere and are connected by hydrogen bonds to the first neighbors. The bond length and bond angles of the sulfate group vary for each tetrahedral from 1.4723(15) to 1.4790(14) Å and 109.66(11) ° to 110.09(8) ° Table-4.

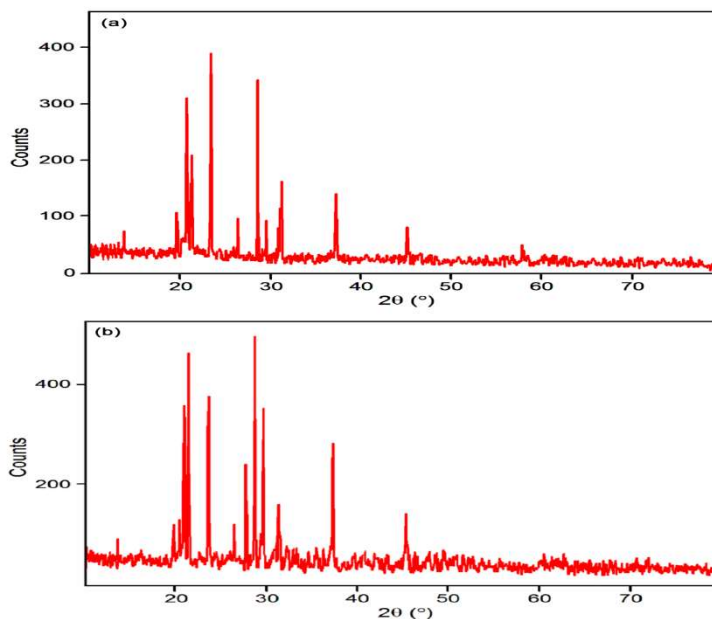


Fig. -8: XRD Patterns of (a) MPSH and (b) KMCS Crystals

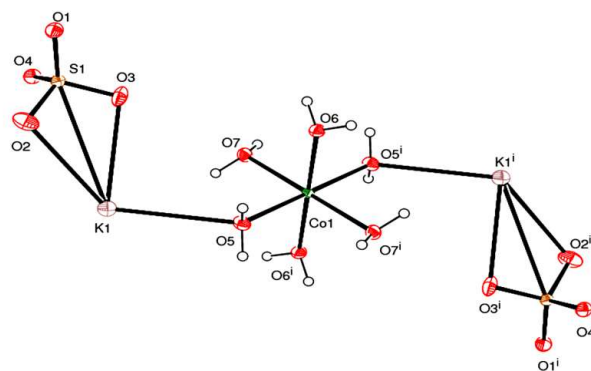


Fig.-9: ORTEP Diagram of KMCS Crystal

High-resolution X-ray Diffraction Analysis (HRXRD)

As the figure shows, the DC's contain a peak and determine that the sample is open of structural grain borders. The intensity increases dramatically for a perfect crystal when the glance angle exceeds the maximum position as predicted. But behind the exact peak position of Bragg, the frequency slowly decreases. The rises in the FWHM demonstrate the statistical distribution of Co dopant on MPSH without any extra peaks (Fig.-10). The FWHM of these curves is 40 arc sec, which is much more than normal from the active X-ray diffraction hypothesis for an preferably perfect crystal.⁴⁰ A short duration with a high frequency spread along the DC wings indicates that both vacancies and interstitial defects are present

in the crystal. Such defects are incredibly general to see in any real crystal, even natural gifted crystals and are usually inescapable due to thermo-dynamic environment. In the present study, a reasonably good crystalline perfection is suggested by the low FWHM diffraction rate.

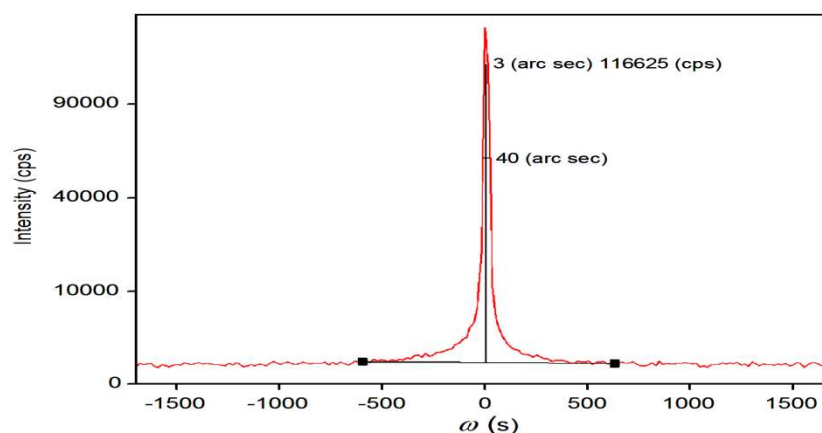


Fig.-10: HRXRD Curve of KMCS Crystal

SHG Efficiency

An important feature of the NLO is the second harmonic generation. The participation radiation was 2.5 mJ/pulse and microcrystalline KDP be used as a medium for perspective. The performance SHG intensities of parent salt (MPSH) and mixed crystal (KMCS) assessed samples). The absence of frequency replication (green light at 532 nm) indicates mixed crystal inactivity in the NLO. In the present investigations, it is clear that the MPSH is of a centrosymmetric type and the inclusion of Co(II) in MPSH did not obliterate the centrosymmetry so as not to promote non-linearity.⁴¹

CONCLUSION

$\text{K}_2\text{Mg}_{0.26}\text{Co}_{0.74}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ (KMCS) transparent pink crystals are grown at space temperature by SESGT. FT-IR and single-crystal XRD analysis characterized material. The vibration patterns suggest that the minor changes in some of the signature frequencies may be due to the introduction of Co(II) into the crystalline matrix. KMCS crystallizes the centrosymmetric space group P21/c in a monoclinic model and is refined to a small 'R' value of 0.0223 (final R indices). In the entire visible field, the characteristic absorption was observed. Such samples can be quite useful for optical system applications due to high visibility. There are several minor structural differences in the study of pure and mixed crystal XRD profiles. Studies indicate that as a effect of the addition of Co(II) ions, the crystal undergoes significant lattice pressure. In HRXRD, the single DC with no additional peaks shows that, respectively, the crystal is free of structural grain boundaries and statistical distribution of Co dopant on MPSH. Thermal analysis shows that the crystals remain thermally stable up to 70 ° C and also supports six water molecules in the crystallization. SEM image shows the flower morphology and study of EDS indicates the existence of ions of Co(II). The salts of Tutton are centrosymmetric in nature and no non-linear optical behavior can be predicted. Dopant's impact has not changed the centrosymmetric structure of MPSH and therefore, Co(II) doping has no effect on non-linear optical behavior.

ACKNOWLEDGEMENT

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Supplementary Material

CCDC 1020377 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data-request/cif.

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