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Effect of Mg^{2+} ion on the growth and properties of Copper sulphate and potassium dichromate crystals

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ABSTRACT

Pure and divalent metal ion Mg^{2+} doped Copper sulphate and Potassium Dichromate crystals have been grown from aqueous solution by slow evaporation technique. The pure copper sulphate and pure potassium dichromate crystals were noted as CUS and KDC. Powder X-ray diffraction studies confirmed the phase formation and magnesium ions doping into KAP crystals. The presence of functional groups in the crystal has been observed by FTIR analysis. Optical transmission studies were carried out by allowing the UV-Vis ray of wavelength between 200 and 1100 nm was pass through the (010) face of the grown crystals. The optical transmission studies reveal that the pure and magnesium ion doped copper sulphate crystals were better transmission in the wave length region of 350 nm to 550 nm. In the case of pure and doped potassium dichromate crystals transmission was better in the wavelength region of 550 nm to 1100 nm. Optical transmission is found to be decreases in pure and magnesium ion doped copper sulphate crystals from 550 nm to 800 nm and above 800 nm it was increases up to 1100 nm.SHG efficiency of all these crystals were not active. The grown crystals were also subjected to FTIR and microhardness studies.

Introduction

Copper Sulphate also called as copper sulphate pentahydrate [$CUS=CuSO_4.5H_2O$], and Potassium Dichromate salt [$KDC=K_2Cr_2O_7$], both belongs to Triclinic crystal system [1] with space group $P\bar{1}$. CUS crystals are used as broad band UV optical filters [2]. Refractive index of these crystals were 1.436 and 1.738 respectively. The metallic ion dopants (Fe^{3+},Cr^{3+}, Zn^{2+}, Cu^{2+}, Mg^{2+} etc.) in some crystals reported to induce significant changes in optical, ferroelectric and non linear optical behaviours [3–6].Pure Copper Sulphate crystals were used as broad band UV optical filters [1]. The powder X-ray diffraction studies reveal that crystal system of the pure and doped crystals were triclinic. The cell parameters of pure Copper sulphate crystal were measured as a = 5.963Å; b = 6.124Å; c=10.740Å and volume v =392.197$Å^3$ [3]. J.K.Brandan,and I.D.Brown[7] measured the cell parameters of pure potassium dichromate crystal as a=5.445 Å, b=7.376 Å and c=13.367 Å and volume v=536.84 Å. These values were compared in table:1. The cell parameters of doped crystals showing that the incorporation of the dopant, has not altered the structure of the crystal. The effects of dopant on growth and properties have been discussed in many articles [8-14]. From this view the author select the divalent metal ion dopant Mg^{2+} as dopant from $MgCl_2$. The addition of metal ions in the organic material like CUS and KDC may perform modification or changes in the lattices or crystal behaviours. Hence the effect of Divalent metal ions (Mg^{2+}) as dopant on the growth, structural, optical and mechanical properties of CUS and KDC crystals have been investigated in the present work.

Experimental

Pure copper sulphate(CUS) and Mg^{2+} doped copper sulphate crystals were grown by slow evaporation solution growth technique at room temperature. Similarly pure potassium dichromate (KDC) and Mg^{2+} doped potassium dichromate crystals were grown by slow evaporation solution growth technique at room temperature with double distilled water as solvent. Recrystallised salt of copper sulphate and potassium dichromate(Merck) was used as source material in separate way. Initially saturated CUS, and KDC solutions was prepared at room temperature and filtered using microfilterpaper of 0.1µm porosity. The 40 ml of saturated CUS solution was taken in two 100 ml beaker.Within these two beakers which contains CUS solution, one was selected and the dopant Mg^{2+} was added (0.5 mol%) and stirred well and filtered by filter paper and placed in dust free atmosphere. Another beaker contains the pure CUS solution also placed in the dust free atmosphere and allowed for evaporation of solution at room temperature. In the similar way Pure and doped potassium dichromate solutions were prepared in another two 100 ml beakers and placed in dust free atmosphere and allowed for evaporation of solution at room temperature. The seed crystals were formed by evaporation of solvent within two days in all the four beakers. The grown seed crystals were harvested. Each one single crystal were again placed in the respective mother solutions and allowed for growth of these crystals until to reach the considerable size. Then these crystals were harvested and allowed for various characterisations. CUS and KDC crystals grown with and without metal ion (Mg^{2+}) addition are shown in Fig.1.There has been no significant change in the colour and crystal morphology due to magnesium ion doping.

Results and discussions

Powder X-ray diffraction studies

The as grown crystals of pure and doped were crushed into fine powder and subjected to powder X-ray diffraction studies using Shimadzu Model XRD 6000 diffractometer. Powder XRD patterns of the grown crystals are shown in Fig.2 and Fig.3.

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Table 1. Lattice parameters of pure and doped CUS and KDC crystals

Grown crystal	a(Å)	b(Å)	c(Å)	V(Å^3)
Pure CUS	10.738	5.952	6.110	390.505
Doped CUS	10.654	5.862	6.213	388.025
Pure KDC	13.367	7.376	7.445	734.039
Doped KDC	13.211	7.271	7.322	703.33

Table 2. Vibrational assignments of pure and doped CUS crystals

Pure CUS	Mg $^{2+}$ doped CUS(cm^{-1})	Tentative assign-ments(cm^{-1})
455	455	C=C out of plane ring bending
520	520	C=C-C out of plane ring deformation
594	598	C=C-C out of plane ring deformation
658	657	C=C out of plane bending
800	883	C=H out of plane bending
993	993	=C-H out of plane bending
1157	1156	C-C stretching
1498	1404	C=C ring stretching ,C=C ring stretching
------	1562	-C=O Carboxylate ion Asymmetric stretching
1619	1646	C=C stretching
1954	------	C=C asymmetric stretching
2097	2095	Absorption of divalent metal
2328	2322	Absorption of divalent metal

Table 3. Vibrational assignments of pure and doped KDC crystals

Pure KDC(cm^{-1})	Mg $^{2+}$ doped KDC(cm^{-1})	Tentative assign-ments(cm^{-1})
555	557	C=C-C out of plane ring deformation
757	760	C-C stretching
889	886	C=H out of plane bending
948	949	=C-H out of plane bending
1307	1305	C=C ring stretching
1380	1389	-C=O Carboxylate ion symmetric stretching
-------	2740	Absorption of divalent metal ion
2886	2832	Absorption of divalent metal ion
--------	3414	O-H stretching hydrogen bond

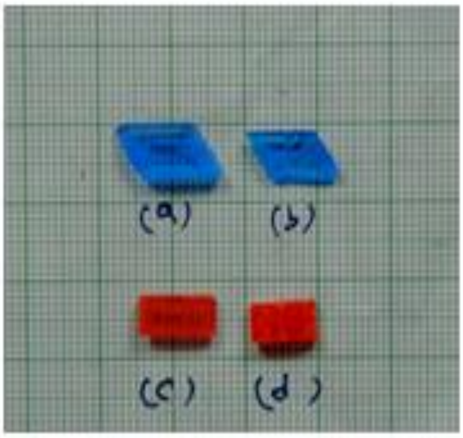

Fig.1. as grown pure and doped crystals. (a) pure copper sulphate crystal,(b) Mg^{2+} doped copper sulphate crystal,(c) pure potassium dichromate crystal and (d) Mg^{2+} doped potassium dichromate crystal

The results confirmed that the CUS crystals formed in triclinic crystal structure with space group $P_{\bar{1}}$ and KDC crystals are in triclinic structure with space group P1or $P_{\bar{1}}$. The XRD pattern shows the peak shifts slightly towards the higher angle side in the case of doped crystal when compared to the undoped CUS and KDC crystals. These shifts in peak positions caused a slight change in lattice parameters when compared to the pure CUS and KDC. There is a noticeable shift in the peak intensity for the Mg^{2+}doped crystals when compared to pure crystals.

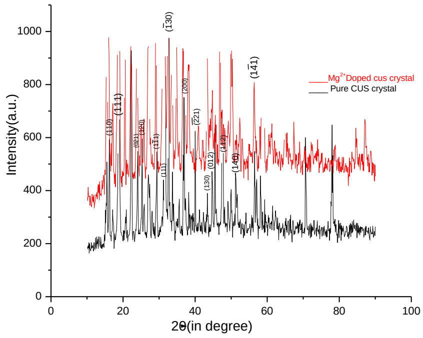

Fig 2. Powder X-Ray spectrum of pure and doped CUS crystals

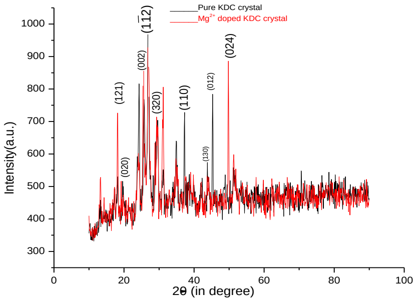

Fig 3. Powder X-Ray spectrum of pure and doped KDC crystals

UV–Vis analysis

UV-Vis spectrum was recorded on a Perkin Elmer Lambda25 spectrometer in transmission mode. FTIR transmittance spectra of pristine and doped CUS and KDC crystals were recorded in the range of 400–4000cm^{-1}using Lamda 35 make Perkin Elmer (SpectrumRX1) spectrometer. UV-Vis spectrum reveals that the pure and magnesium ion doped copper sulphate crystals were better transmission in the wave length region of 350 nm to 550 nm. In the case of pure and doped potassium dichromate crystals transmission was better in the wavelength region of 550 nm to 1100 nm. Optical transmission is found to be decreases from 550 nm to 800 nm and again increases from 800 nm up to 1100nm in pure and magnesium ion doped copper sulphate crystals.

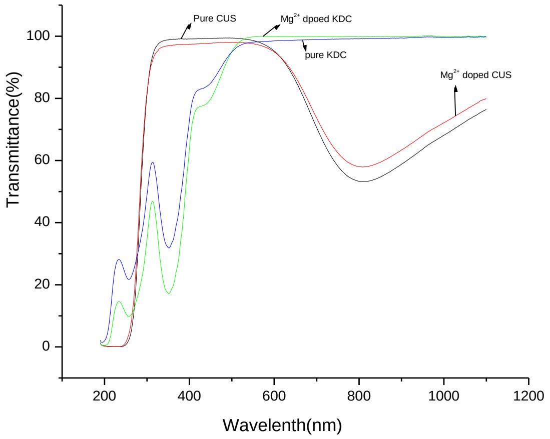

Fig 4. UV-Vis spectrums of pure and doped CUS and KDC crystals

FTIR spectral analysis

FTIR transmittance spectra of pristine and doped CUS and KDC crystals were recorded in the range of 400–4000cm^{-1}using Lambda 35 make Perkin Elmer (SpectrumRX1) spectrometer. FTIR studies of pure and doped CUS and KDC crystals were measured and shown in fig.5 and fig.6. Its vibrational assignments were tabulated in table 2 and table 3. It could be concluded that the doping of divalent metal ion into the crystal site be from 2250 cm^{-1} to 3000 cm^{-1}[1].

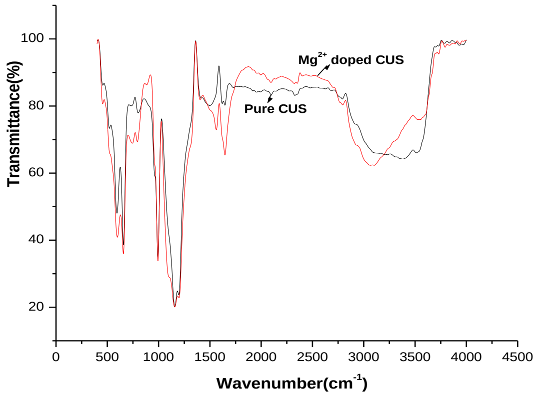

Fig 5. FTIR curves for pure CUS and Mg $^{2+}$ doped CUS crystals

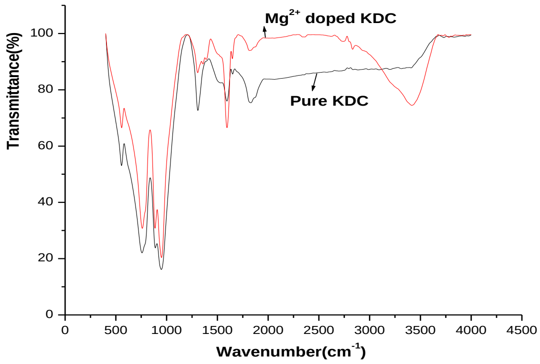

Fig 6. FTIR Curves of pure KDC and Mg $^{2+}$ doped KDC crystals

Microhardnes measurements

The as grown pure and doped CUS and KDC crystals were subjected to Vickers micro hardness test using Shimadzu model HMV-2T micro hardness tester. The indentations were made on the surface of the grown crystals by varying the load from 25 g to 100 g at room temperature with a constant indentation time of 5s.The graph plotted with load and Hardness number is shown in Fig.7. The hardness number is more in the case of Mg $^{2+}$ doped CUS than all other crystal. Hardness number increases for all crystals when load increases.

SHG measurements

The second harmonic generation conversion efficiency of the samples was measured using Kurtz powder technique. A Q switched ND:YAG laser beam of wave length 1064 nm was used within an input energy of 5.02 mJ/pulse and the pulse width of 8 ns the depletion rate being 10 Hz. The SHG radiations of 532 nm (green light) emitted were collected by a photo multiplier tube (PMT-Philips Photonics model 8563) and the optical signal incident on the PMT was converted into voltage output at the CRO (Tektronix-TDS 3052). The SHG values were found to be not active for all these grown crystals.

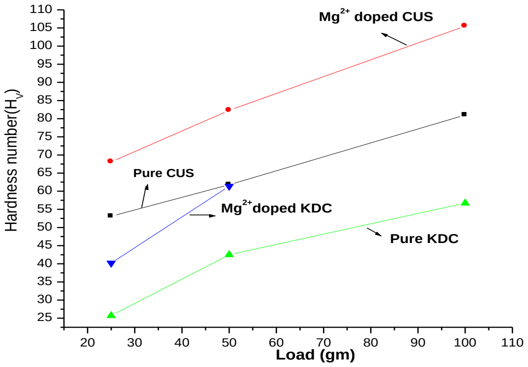

Fig 7. micro hardness values of as) grown crystals

Conclusion

Pure and doped copper sulphate and potassium dichromate crystals were grown from slow evaporation solution growth technique. The divalent metal ion doping was not affecting the crystal structure. The FTIR studies give the various vibrations of all the grown crystals. UV-Vis spectrum reveals that the pure and magnesium ion doped copper sulphate crystals were better transmission in the wave length region of 350 nm to 550 nm. In the case of pure and doped potassium dichromate crystals transmission was better in the wavelength region of 550 nm to 1100 nm. Optical transmission is found to be reduces in pure and magnesium ion doped copper sulphate crystals from 550nm up to 800 nm and again increases above 800 nm and reach maximum at 110nm. Micro hardness is more to divalent metal ion doped copper sulphate crystal than all other crystals. Hence it is good candidate for mechanical stability. The optic nature was better in high wavelength (infrared) region to pure and doped potassium dichromate crystal whereas better in low wavelength (ultraviolet) region to pure and doped CUS crystals.

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