Influence of Doping on K_2SO_4 Crystal Properties

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Abstract

Single crystals of pure and Cu^{+2},Fe^{+2} doped potassium sulfate were grown from aqueous solutions by the slow evaporation technique at room temperature. with dimension of (11x9 x4)mm^3 and (10x 8x 5)mm^3 for crystal doping with Cu &Fe respectively. The influence of doping on crystal growth and its structure revealed a change in their lattice parameters(a=7.479 Å ,b=10.079 Å ,c=5.772 Å)for pure and doping (a=9.687 Å, b=14.926 Å ,c= 9.125 Å) & (a=9.638 Å , b= 8.045 Å ,c=3.271 Å) for Cu & Fe respectively. Structure analysis of the grown crystals were obtained by X-Ray powder diffraction measurements. The diffraction patterns were analyzed by the Rietveld refinement method. Rietveld refinement plots for showing the experimental (red circles)calculated (black line) and difference profiles (blue line); green tick marks indicate reflection positions XRD measurements show the crystal system of orthorhombic.

Key words: crystal growth, K_2SO_4 , doping , Cu^{+2} ,Fe^{+2} X-ray diffraction, Differential scanning calorimetric (DSC).

Introduction

The basis of various technology advancement is the crystal growth. The control of the grown crystal during crystallization is very important to the industry. Grown under different conditions and also by different methods like, melt growth , vapor phase growth ,solution growth and gel growth ,are described by [1] and references there in . solution growth aqueous is one of the most efficient and simplest processes which can be employed for crystal growth .In addition The ease in handling and the readiness in its miscibility with the solvents make it an attractive technique for crystal growth. A number of factors such as degree of saturation ,type of solvent ,presence of impurities and the change in growth conditions presumably affect significantly the morphology and properties of the crystal [2] . Potassium sulfate crystals are used in the field of analytical chemistry as reagent medicine, manufacture of glass and feed additive .Potassium sulfate (PS) K_2SO_4belongs at room temperature to the orthorhombic space group D_{2h}^{16}=(Pnma) and has four formula units per unit cell, with lattice parameters ,a= 7.476 Å, b= 10.071 Å and c= 5.763 Å [3]. The substance transforms upon heating at $T_t \approx 587$ °C into a hexagonal structure D_{6h}^{4} =$P6_3$/mmc with a=5.92 Å and c=8.182 Å where the oxygen positions of the $SO4^{-2}$tetrahedra are only partially occupied [4]. The hexagonal high temperature phase of the crystal is known asα-$K_2SO_4$and the orthorhombic phase as β-K_2SO_4. Analogous phase transformations (PT')from α- to β-type phase are shown for the other K_2SO_4-family crystals (e.g. Na_2SO_4, like K_2CrO_4, and K_2SeO_4) [5, 6]. Another PT of second order at the temperature of 56 K was detected in K_2SO_4crystal. The crystal symmetry of this low temperature phase (γ-K2SO4) is assumed to be of monoclinic [7]. Recently ,the addition of Cd^{+2} to the nutrient solution during K_2SO_4Crystal [8].Due to useful application of doping it is worthy to work on doping of K_2SO_4. Doping is possible if a suitable host can be found. The cupric ion and ferrate ion can be doped in the K_2SO_4 crystal, but the degree of application of the data to the pure (Cu ;Fe)$_2$SO$_4$ system depends very highly on the nature of the host.

Experimental details

Crystal growth

Pure crystal of K_2SO_4 was grown using aqueous solution by slow evaporation technique (at room temperature) .Saturated solution was prepared from synthesized K_2SO_4 salt ,with 2 Molar using a double distilled water as solvent . This solution was continuously stirred for about (6)hour with magnetic stirrer with rate of 250 rpm at room temperature. Finally thus solution is heated at 70 C° in order to obtain a complete dissolved of the materials.

The growth process was performed in a multi-jar crystallizer to ensure identical growth conditions. In a period of 60 days, we were able to grow colorless, transparent K_2SO_4 single crystals which is shown in Figure(1a).

Dopant crystal of K_2SO_4:Cu and K_2SO_4:Fe crystals were grown by slow evaporation technique, from 2M solutions containing 5 wt% of $CuSO_4.5H_2O$ and $FeSO_4.7H_2O$ respectively. The growth rate crystals was much higher than of pure K_2SO_4 (i.e)the growth period is about ~20 days , we get the grown crystal for K_2SO_4:Cu and K_2SO_4:Fe are shown in Figs. 1b, 1c respectively.

Re- crystallization is carried in order to improve the grown crystal and step-up refinement its .Some crystals are picked from the growth apparatus and dissolve in double distilled water. This solution is treated in the same procedure as that mentioned above. We get crystal for K_2SO_4:Cuandfor K_2SO_4:Fe .

Instrument

X-ray Diffract meter

The X-ray diffraction was recorded using SHIMADZU model Japan (6000) diffractmeter with $Cu\text{-}K_\alpha$ radiation of wavelength (λ= 1.54056 Å).The filament current and operating voltage were kept at 30mA and 40KV respectively.

Thermal Analysis

Differential scanning calorimetric technique (DSC) were carried out using LINSEIS model Germen(STA PT-1000).Sample of (25 mg) is used with reference of AL_2O_3 crucibles .Heating and cooling runs with rate of 5ºC /min during recorded of the chart.

Results and Discussion

The grown crystal

We were able to grow colorless, transparent K_2SO_4 single crystals with dimensions of(10x4x2)mm^3 is shown in Figure(2a) , and the grown crystal of dimensions (11x9x4)mm^3 for K_2SO_4:Cu & (10x 8x5)mm^3 for K_2SO_4:Fe are shown in Figs. 2b, 2c respectively.

XRD Diffraction studies

The structure of the grown crystal was studied by powder X-ray diffraction method .The recorded diffraction pattern of pure K_2SO_4 and doping crystals by Cu &Fe respectively, are shown in the figure(3a ,3b and 3c).From the XRD pattern, the lattice parameter value of potassium sulfate crystal was found to be (a=7.4796 Å, b=10.0793 Å, c=5.7721 Å, α=90,β=90°, γ=90°) .This indicates that potassium sulfate crystallizes in orthorhombic system. The diffraction planes are indexed with the help of the computer program, with the Rietveldt refinement using FULLPROF as shown in Fig. 3a. The lattice parameters from powder XRD of the grown crystal and also unit cell dimension of pure K_2SO_4.The results are in agreement with reported values [3] .comparison of lattice parameters is shown in table -1-

Differential scanning calorimetric (DSC) analyzes

A heating rate of 5ºC /min was recorded for the grown pure samples(K_2SO_4) in the same chart as shown in Fig. 4.The weight of the sample taken for investigation was 22.2 mg .Which shows an endothermic peak around 300C°(onset point 298 C° with reaction point -8.070μV at 298.4C°and offset 301.2 C° with peak maximum -16.497μV at 300.5 C° and area -12.14μV S/mg) which gives a strong support to the newly detected phase transition. As the heating is continuous ,another an endothermic peak around582 C°(onset 578.6 C° with reaction point -1.759μV at 580.9 C° and offset 584.3 C° with peak maximum -3.452μV at 582.6 C° and area -9.73μV S/mg) and when were cooling there is an exothermic peak around at≈581 C° (onset point 580.9 C° with reaction point 2.531 μV at 580.3 C° and offset 572.6 C° with peak maximum 5.088μV at 577.7 C° and area 10.73μV S/mg. This refers to crystallization at this region and detected a phase transition. This phase transition of the crystal have hexagonal structure at high temperature≈583C°is known as α-$K_2SO_4$and the orthorhombic phase as of the crystal is known as β-K_2SO_4 at room temperature [4].

B-Doping with Cu ions

A heating rate of 5ºC /min was recorded for the grown samples(5wt.%Cu.K_2SO_4) in the same chart as shown in Fig. 4b.The weight of the sample taken for investigation was18.94 mg .Which shows an endothermic peak around 300C°(onset point 298 C° with reaction point -10.183μV at 298.4C°and offset 301.6 C° with peak maximum -18.563μV at 300.8 C° and area -16.06 μV S/mg) which gives a strong support to the newly detected phase transition. As the heating is continuous, another endothermic peak around 585 C°(onset 577.8 C° with reaction point -4.170μV at 580.5 C° and offset 584.3 C° with peak maximum -5.122

μV at 582.3 C° and area -9.98 μV S/mg) and when were cooling there is an exothermic peak around at≈581 C° (onset point 581.2 C° with reaction point -1.775 μV at 580. C° and offset 570.4 C° with peak maximum -0.5711 μV at 577.8 C° and area 11.91 μV S/mg. This refers to crystallization at this region.

C- Doping with Fe ions

A heating rate of 5ºC /min was recorded for the grown samples(5wt.% Fe.K_2SO_4) in the same chart as shown in Fig. 4c.The weight of the sample taken for investigation was 20.63mg .which shows an endothermic peak around 300C°(onset point 298 C° with reaction point -12.347μV at 298.4C°and offset 301.5 C° with peak maximum -20.796μV at 300.7C° and area -13.93μV S/mg) which gives a strong support to the newly detected phase transition. As the heating is continuous, another an endothermic peak around582 C°(onset 577.9 C° with reaction point -6.887 μV at 580.8 C° and offset 583.7 C° with peak maximum -7.666μV at 581.9 C° and area -10.26μV S/mg) and when were cooling there is an exothermic peak around at≈581 C° (onset point 581.2 C° with reaction point -3.621 μV at 580.2 C° and offset 571.0 C° with peak maximum -2.099 μV at 577.9 C° and area 12.04 μV S/mg. This refers to crystallization at this region.

Conclusion

Colorless and transparent crystals of pure potassium sulfate were grown using water as the solvent at ambient temperature. The slow evaporation at room temperature of the solvent yielded good quality crystals. Single crystal of $K_2SO_4$was transparent colorless. Orthorhombic structure and unit cell parameter values match very well with the reported XRD standard data values. at room temperature K_2SO_4 pure and doping crystals having Orthorhombic structure and transition into hexagonal structure at high temperature ≈583C°. It is supported by DSC study.

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Table No.(1)Reported the lattice parameter of pure and dopant

parameters	**PDF 01-070-1488** **Reported data [3]**	**Present work**		
		K_2SO_4	**K_2SO_4:Cu**	**K_2SO_4:Fe**
a (Å)	7.476	7.479	9. 687	9.638
b(Å)	10.071	10.079	14. 926	8.045
c (Å)	5.763	5.772	9.125	3.271
α (°)	90	90	90	90
β (°)	90	90	90	90
ɣ (°)	90	90	90	90
V(mm^3)	433	435	1319.3	253.6

Figure No. (1a): pure crystal of K_2SO_4

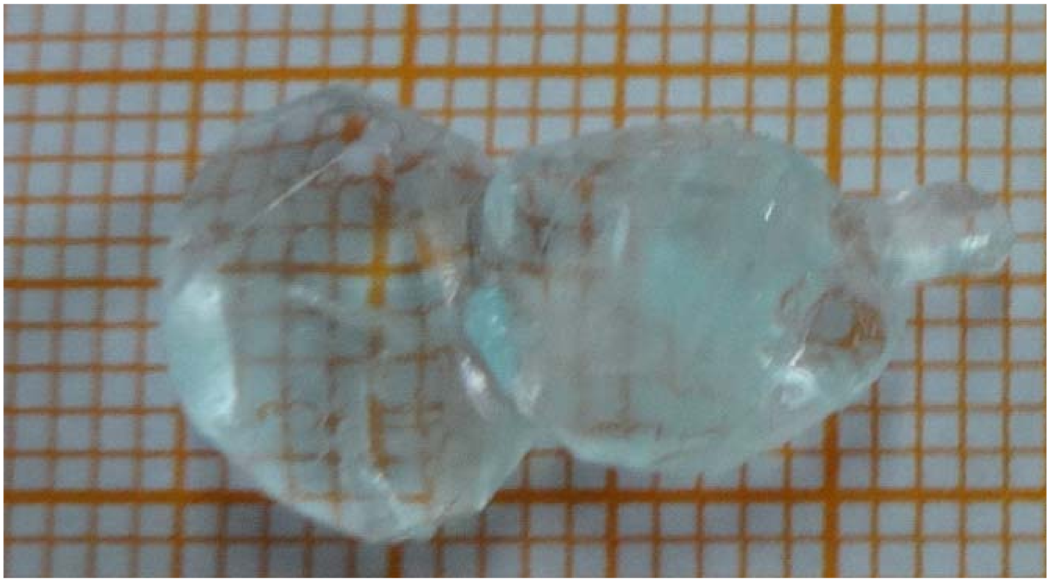


Figure No. (1b): Photograph of K_2SO_4:Cu

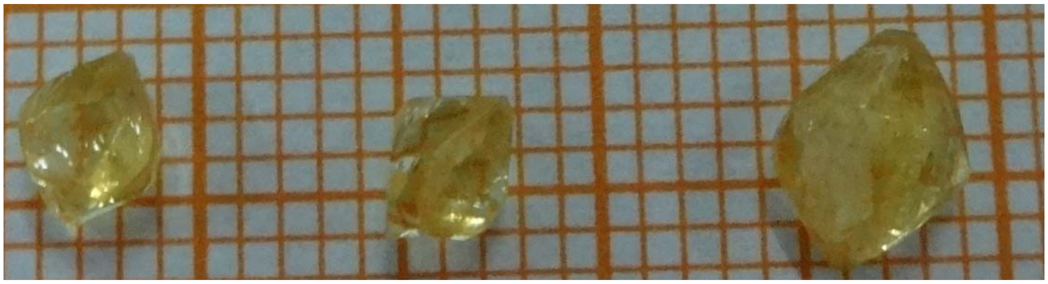


Figure No. (1c): Photograph of K_2SO_4:Fe

Figure No. (2a): Re-crystallization of crystal pure K_2SO_4

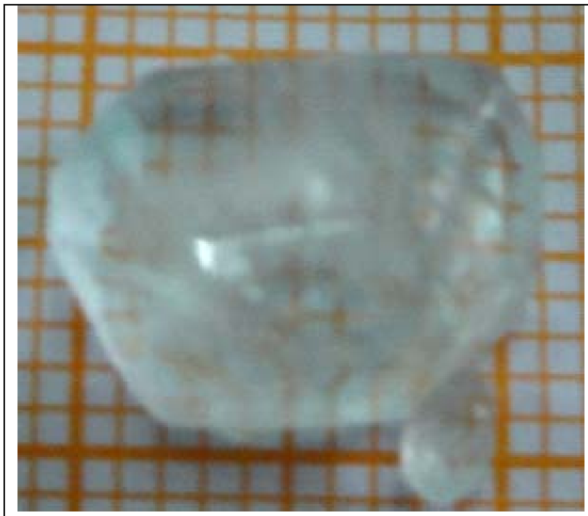
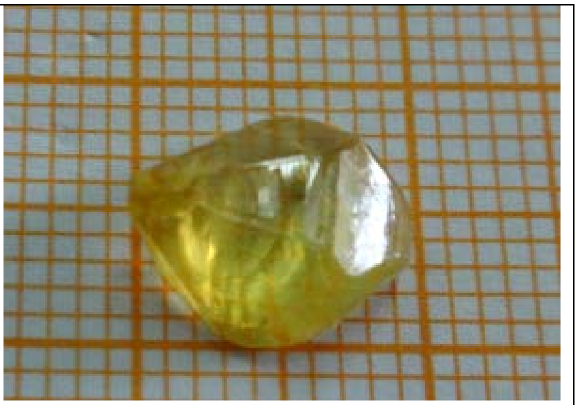
	

Figure No.(2b): Re-crystallization of crystal K_2SO_4:Cu

(2c): Re-crystallization of crystal K_2SO_4:Fe

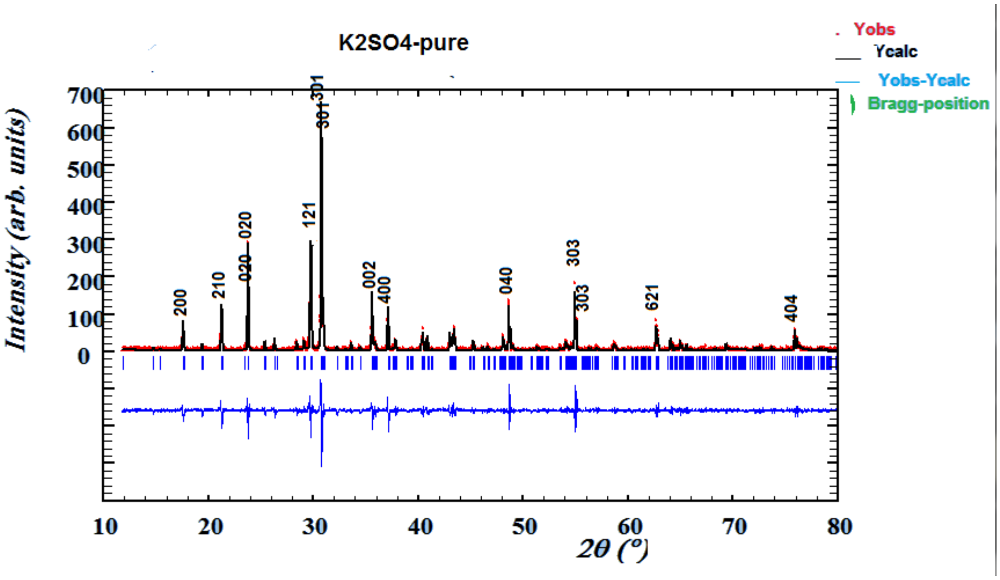


Figure No.(3a): Refinement the X-ray diffraction pattern from crushed single crystal of K_2SO_4

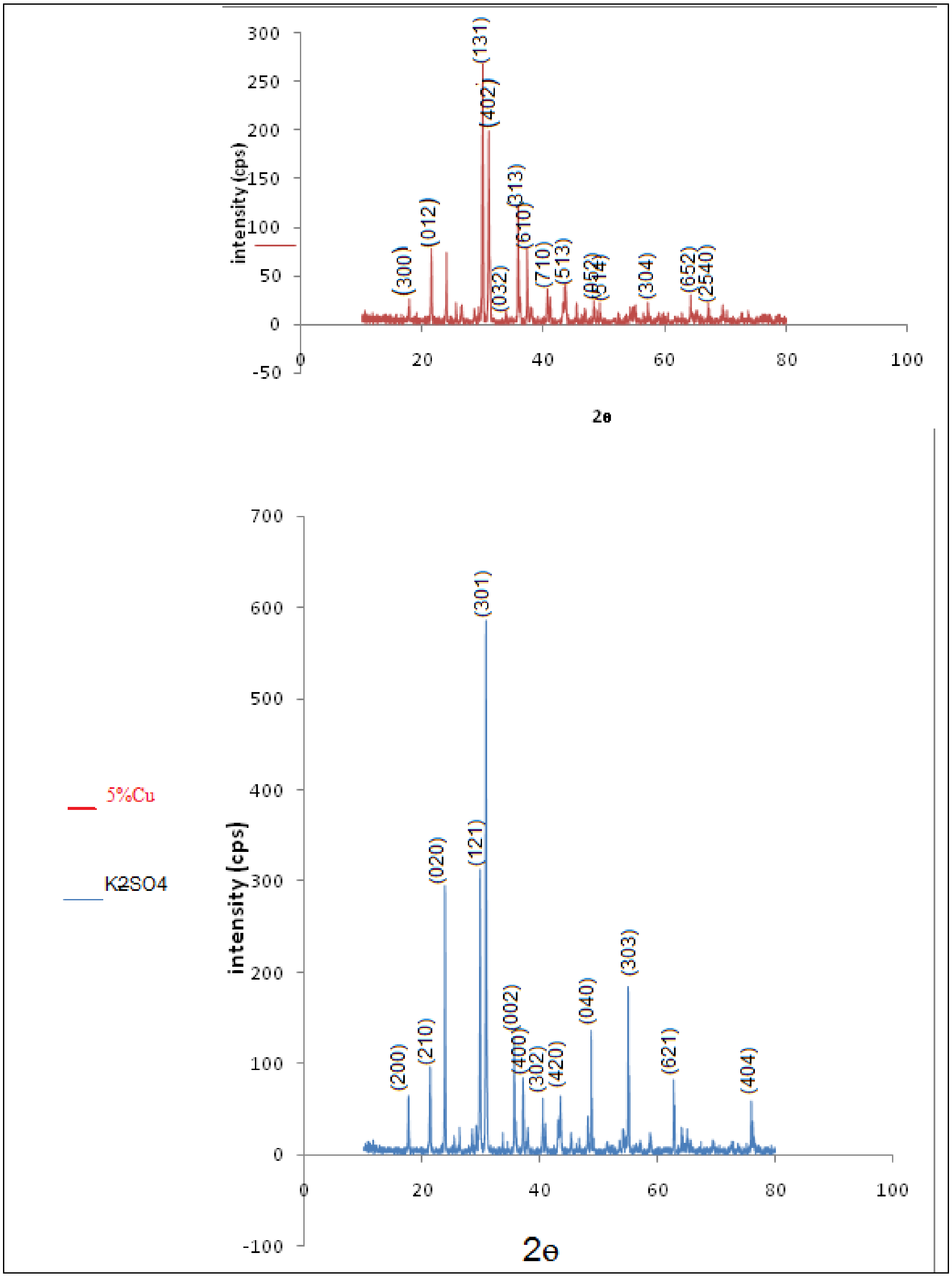


Figure No. (3b): powder XRD pattern of pureK_2SO_4
5wt.%Cu.K_2SO_4 crystal

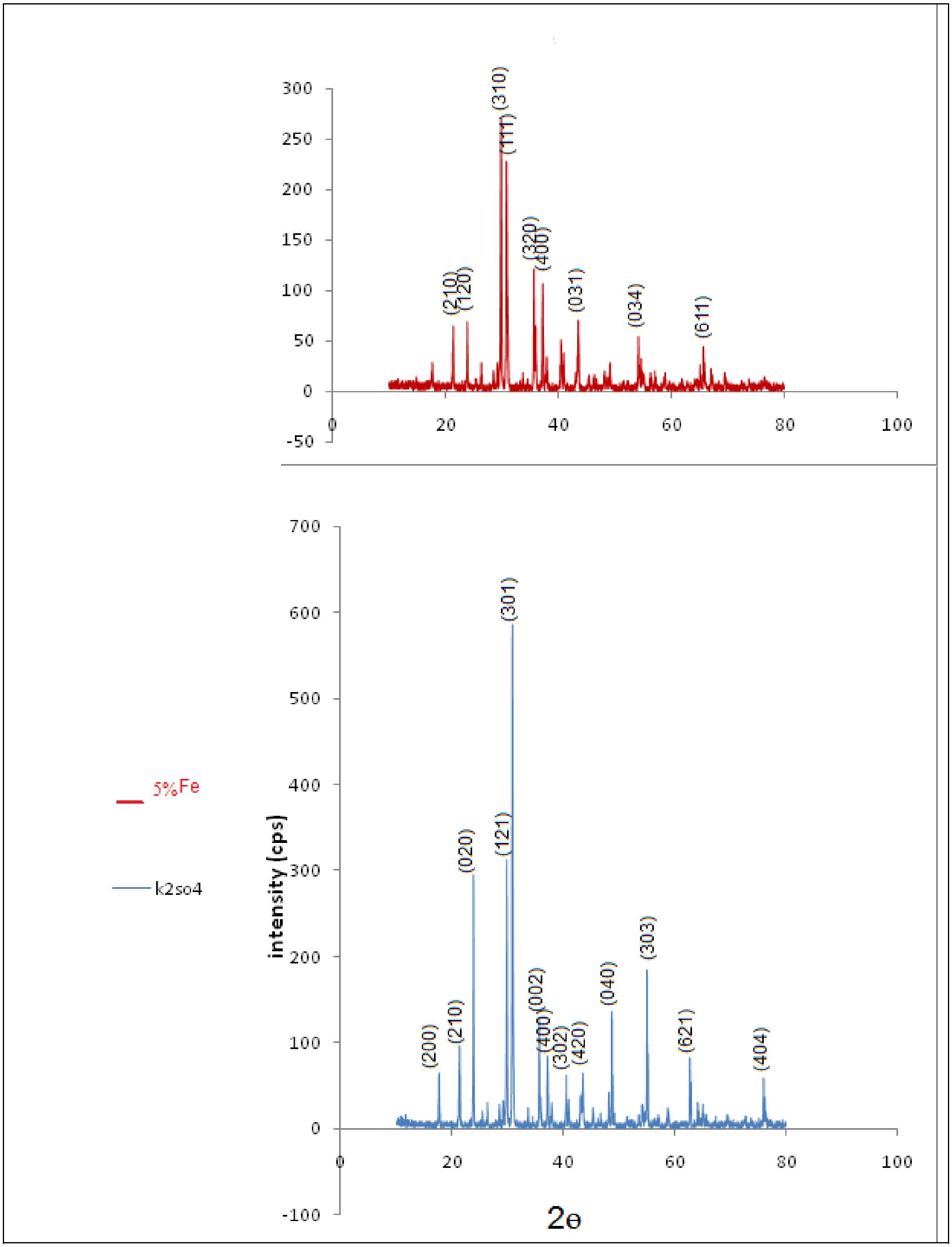
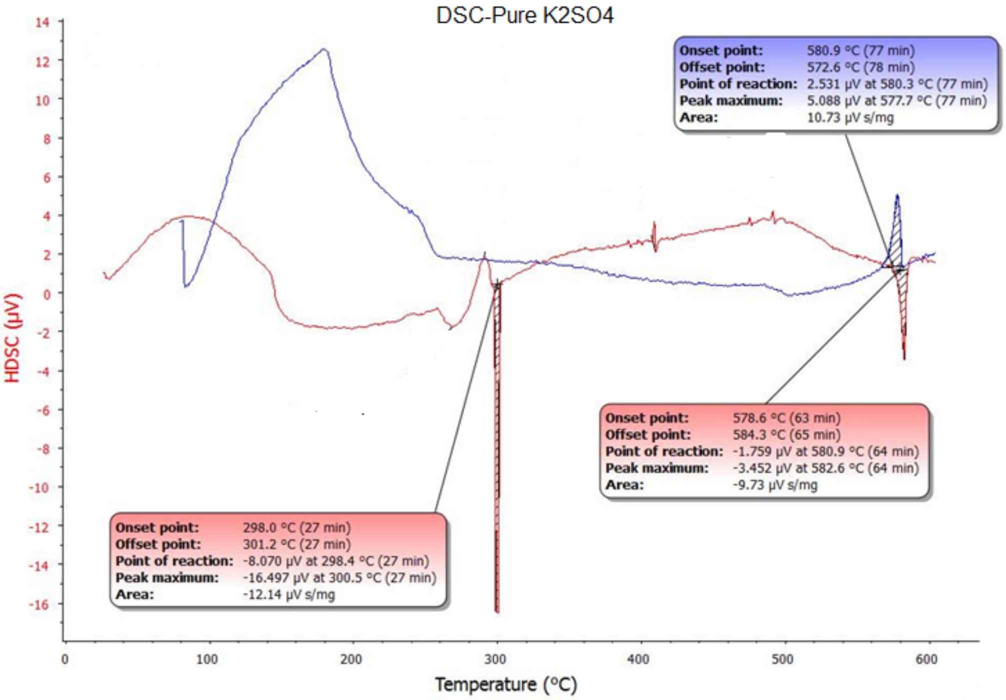


Figure No. (3c): XRD pattern of pure K_2SO_4
5wt.% .Fe.K_2SO_4 crystal

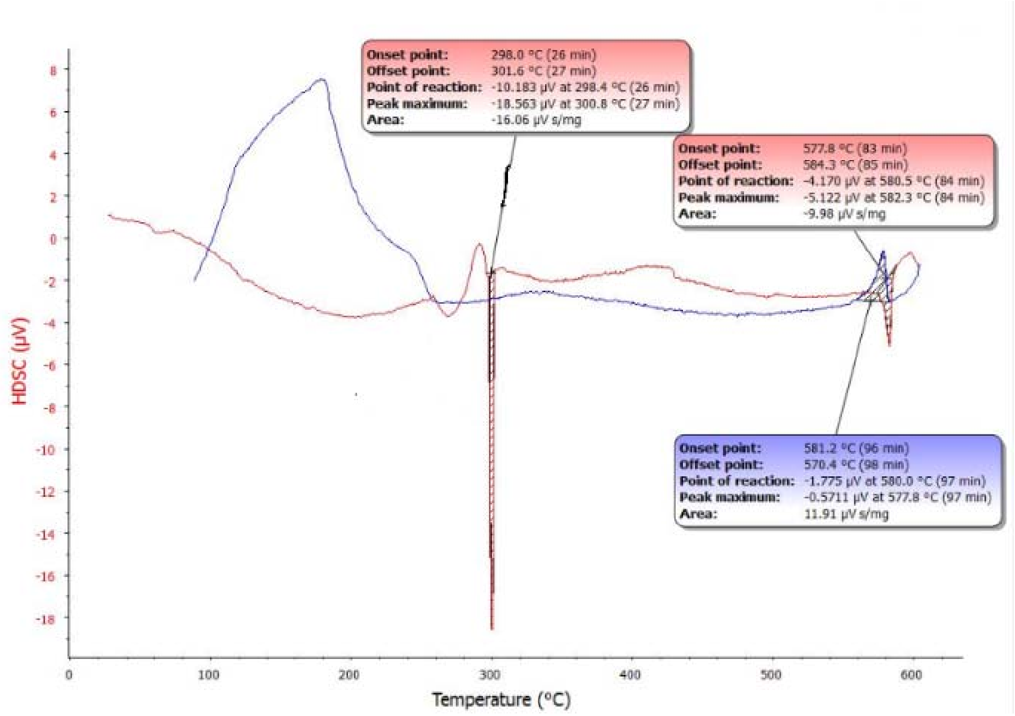

DSC-Pure K2SO4

Onset point: 580.9 °C (77 min)
Offset point: 572.6 °C (78 min)
Point of reaction: 2.531 µV at 580.3 °C (77 min)
Peak maximum: 5.088 µV at 577.7 °C (77 min)
Area: 10.73 µV s/mg

Onset point: 578.6 °C (63 min)
Offset point: 584.3 °C (65 min)
Point of reaction: -1.759 µV at 580.9 °C (64 min)
Peak maximum: -3.452 µV at 582.6 °C (64 min)
Area: -9.73 µV s/mg

Onset point: 298.0 °C (27 min)
Offset point: 301.2 °C (27 min)
Point of reaction: -8.070 µV at 298.4 °C (27 min)
Peak maximum: -16.497 µV at 300.5 °C (27 min)
Area: -12.14 µV s/mg

Figure No. (4a) DSC curve for pure crystal of K_2SO_4


Onset point: 298.0 °C (26 min)
Offset point: 301.6 °C (27 min)
Point of reaction: -10.183 µV at 298.4 °C (26 min)
Peak maximum: -18.563 µV at 300.8 °C (27 min)
Area: -16.06 µV s/mg

Onset point: 577.8 °C (83 min)
Offset point: 584.3 °C (85 min)
Point of reaction: -4.170 µV at 580.5 °C (84 min)
Peak maximum: -5.122 µV at 582.3 °C (84 min)
Area: -9.98 µV s/mg

Onset point: 581.2 °C (96 min)
Offset point: 570.4 °C (98 min)
Point of reaction: -1.775 µV at 580.0 °C (97 min)
Peak maximum: -0.5711 µV at 577.8 °C (97 min)
Area: 11.91 µV s/mg

Figure No. (4b): DSC curve for crystal doping 5wt.%Cu. K_2SO_4

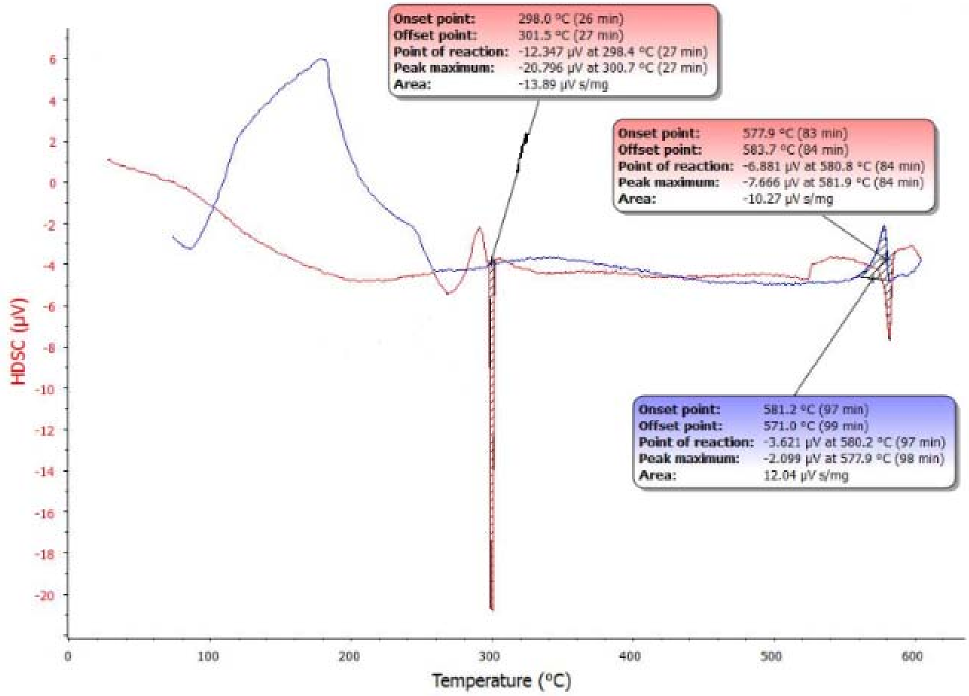


Figure No. (4c): DSC curve for crystal doping 5wt.%Fe. K_2SO_4

اثر التطعيم في خصائص بلورة كبريتات البوتاسيوم K_2SO_4

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الخلاصة

نماء بلورات أحادية لكبريتات البوتاسيوم النقية والمشوبة ب Cu^{+2} وFe^{+2} من المحلول المائي بوساطة تقنية التبخر البطيء في درجة حرارة الغرفة. وبأبعاد (11x9x 4) mm^3 (10x 8x 5) mm^3 للبلورات المشوبة ب Cu& Fe على التوالي.ودراسة اثر التطعيم في النماء البلوري والخصائص التركيبية , إذ تغيرت أبعاد خلية الوحدة لكبريتات البوتاسيوم المطعمة بالنحاس والحديد. (a=7.479 Å ,b=10.079 Å ,c=5.772 Å) للنقية والمشوبة , (a=9.687 Å, b=14.926 Å ,c= 9.125 . (a=9.638 Å , b= 8.045 Å ,c=3.271 Å) تم الحصول على تحليل بنية البلورات بوساطة مقياس حيود الأشعة السينية للمسحوق و استخدام تصفية ريتفيلد. أظهرت قياسات XRD إن التركيب البلوري لهذه البلورات هو معيني متعامد المحاور(orthorhombic) .

الكلمات المفتاحية : نماء بلورات ,كبريتات البوتاسيوم ,التطعيم , Fe^{+2}, Cu^{+2} , حيود الأشعة السينية, تصفية ريتفيلد .