Synthesis and Growing up a New Coloured Crystal from An Isomorphous Substances by Using The Overgrothes Phenomenon and Studied Its Pysical , Mecanical and Crystallographic Properties

Jassem Mohamad Abd Al Hassien
Dep. of Chem. , Col. of Sci. , Univ. of Babylon
Jasem_hilla @yahoo.com

(NJC)

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Abstract

Three crystals of sulfate salt were prepared under lab environments , these are : $KAl(SO_4)_2.12H_2O$, $Cr_2(SO_4)_3$ and $KAlCr(SO_4)_2.12H_2O$. The physical and mechanical properties for the $KAl(SO_4)_2.12H_2O$ and $KAlCr(SO_4)_2.12H_2O$ crystals were studied . We deal with the latter crystal which called overgrowths and prepared from the isomorphous substances (aluminum sulfate and chromium sulfate) .We prepared this crystal by insertion few Cr atoms in the same places of Al atoms in the $KAl(SO_4)_2.12H_2O$ cubic lattic crystal . The crystallographic properties of an overgrothes crystal were studied. The new crystal crystallizes in the cubic system , space grope pa-3 . The cell dimentions are : a = b = c = 12.135 A^O, $\alpha = \beta = \gamma = 90^o$, volume of Al cell = 1786.98 $*10^6$ pm^3 , volume of Al – Cr cell = 1800.26 $*10^6$ pm^3 and Z=4 . The volume of cell indicates that the chemical composition of the two layers of crystal are different as it shown in formula data obtained from X – Ray analysis . the retsults obtained from FT-IR and UV. Visib. Spectrum are also support this conclusion .

Keywords : Al sulphate – crystal , Cr sulphate – crystal , overgrowthes crystal , X – Ray analysis , isomorphose substances .

الخلاصة

حضرت ثلاثة بلورات لملح الكبريتات في الظروف المختبريه هي : $KAl(SO_4)_2.12H_2O$ and $KAlCr(SO_4)_2.12H_2O$, $Cr_2(SO_4)_3$. تم دراسة الخواص الفيزياويه والميكانيكيه للبلورتين $KAl(SO_4)_2.12H_2O$ and $KAlCr(SO_4)_2.12H_2O$, والبلورة التي يعنيها بحثنا هذاهي ($KAlCr(SO_4)_2.12H_2O$) والتي حضرت بظاهرة النماء المفرط من مواد isomorphous) كبريتات الالمنيوم وكبريتات الكروم) , وكان الشكل البلوري لها هو المكعبي والتي لايختلف عن الشكل البلوري للبلوره الاصليه ($KAl(SO_4)_2.12H_2O$)

وتم تحضير هذه البلوره بحشر قليل من ذرات الكروم في نفس المواقع التي تحتلها ذرات الالمنيوم في الشبكه البلوريه امكعبيه لها . تعود كلا البلورتين الى نظام Pa–3 من انظمة المجموعه الفراغيه و ان ابعاد

الخليه لهما هي $\alpha = \beta = \gamma = 90^{o}$, a = b = c = 12.135 A^{O} , volume of Al cell = 1786.98 , $*10^{6}$ pm^{3}

ان الخواص الفيزياويه والميكانيكيه للبلورتين , Z=4 , volume of Al – Cr cell = 1800.26 $*10^{6}$ pm^{3} متشابهه تقريبا وان اختلاف حجم الخليه بينهما يدل على التركيب الكيمياوي المختلف قليلا لهما . ان معطيات فحص FT–IR و UV.Visb. تدعم هذه النتائج .

كلمات الدلاله : بلورة كبريتات الالمنيوم ، بلورة كبريتات الكروم ، بلورة النماء المفرط ، تحليل اشعة اكس ، المواد الآزومورفوزيه

Introduction

Isomorphose substances are analogous in their chemical and electrical properties , which form crystals belong to the same crystalline system and the same class of symmetry and it can develop the same forms , so these substances able to form overgrowths crystals and solid solutions in which one of these crystals can be generated from the other if the atoms of an element are substituted by the atoms of another element without changing the crystal system [1,2] . The technique of isomorphous substitution , some times , referred to as isomorphous replacement has served to improve the understanding of metalloprotein active sites by replacing spectroscopically silent metals with ions that possess electronic or magnatic properties [3,4] . Jacobsen et al [5] applied this phenomenon by using sevsral isomorphous ligands to prepare cobalt(II) complexes , he found thate the crystalline system for all these complexes were monoclinic . Crystalline salts of the structur M^{I} $M^{III}(SO_4)_2.12H_2O$ refe rred to as alums ($M^{I}=Na^{+}$, K^{+} , …. $M^{III} = Al^{3+}$, Fe^{3+} , Cr^{3+} , ……) , all of thes structures have cubic crystalline system [6] . there are many methods to draw the crystal theoretical structure such as cluster method [7 , 8] , electronic density function method [9 , 10 ,11] , but the main practically methods are X-Ray powder diffraction technique and X-Ray diffraction by single crystal [12] . The ionic radii of Al^{3+} in six coordination bonding is 0.54 A^{O} and it for Cr^{3+} in similar bonding is 0.62 A^{O} [13 , 14] . In many minerals the replacing between Al^{3+} and Cr^{3+} ions caused couloring these minerals such as beryl crystal ($Be_3Al_2Si_6O_8$) when few Cr^{3+} ions replace of Al^{3+} ions becomes green , coroundom (Al_2O_3) also coulored to red by replacing few Cr^{3+} ions of Al^{3+} ions [15] . The formation and growth of crystals begin of the formation of crystal nucleii is called embryo crystals which are the centers on which and the crystal will growth around it [16] . The overgrowths may be occurs in nature , Brian Jones showed and studied a complex syntaxial overgrowths which are common on many dolomite crystals in the bluff formation exposed along the coastline of Grand Cayman , British West Indies [17] .

Experimental

Chemicals :

All chemicals used were of analytical reagent grade . The preparation of crystals was carried out in inorganic chemistry labs in Babylon university . All the spectra analysis were carried out by the instruments in the scince college labs in Babylon university .

Preparation of Al – alum crystal : It was prepared by mixing equimolecular portions of potassium and aluminium sulphate allowed the mixture to crystallize at 10 ^{o} C , 1 atm , 60 minute

, colourless crystal was obtained and isolated by filtaration .

Preparation of Cr - crystal : It was obtained by reducing potassium dichromate solution by sulpher dioxide in sulphuric acid under lab conditions and allowed to crystallize a dark purple crystals , leave it for 24 hours , the crysal was isolated by filtaration .

$$k_2Cr_2O_7 + 3SO_2 + H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + H_2O$$

Preparation the overgrowths – crystal : Purple crystal of chromium sulphate was suspended in slightly super – saturated solution of aluminum alum by time a colourless – fin purple layer was fomed and deposited on the purple center crystal . This action was continue with time to grow while preserving its orginal geometrical form until a colourless layer was obtaind in the course of time .Figure 5 shows the photograph of this overgrowth .

Physical and Mechanical Properties:

Property	**Al – crystal**	**Al –Cr – crystal**
Luster	vitreous nonmetallic	also
Colour	clear	voliet
Streak	white	also
Mohs Hardness	2.5	3.5
Tenacity	brittle	also
Density	5.0 g/cm^3	5.5 g/cm^3
Cleavage	good	also
M. P.	91^{O}C	96^{O}C
Solubility in H_2O	insoluble	also
Conductivity in aqueos solu.(0.02M)	4.31 ms/cm	4.57 ms/cm
Transparency	translucent	also

Optical Studies :

FT – IR Spectra :

FT – IR spectrum were recorded by FTIR – 84005 Shimadzu instrument for the two layers of the overgrowths crystal with the range (400 – 4000) cm^{-1} with KBr disk . Figures 1 and 2 show the spectrum of these samples .

X – Ray Structure Determinations :

X – Ray measurements was made on a PANalytical X – Ray diffractometer with monochromated Cu – Kα radiation and a 12 KW rotating a node getenerator was used for determination of the cell unit and data collection . Crystallographic data and the refinement procedure are given in table 1and 2. The X – Ray spectrum were shown in figure 3 and 4 . The structure was solved by direct methods using SHELXS 97 program and expanded using fourier techniques [19] .

UV.Visb. Spectra :

The electronic spectra of the two layers of the crystal in aqeous solutions (10^{-3}M) were recorded by using UV – 1650PC SHIMADZU instrument with quartiz cells . figures 6 and 7 show the spectra of this techniqu .

Table 1 : Crystal data and structure refinement for Al – crystal :

Name and formula

Reference code:	01-070-4921
PDF index name:	Potassium Aluminum Sulfate Hydrate
Empirical formula:	$AlH_{24}KO_{20}S_2$
Chemical formula:	$KAl(SO_4)_2(H_2O)_{12}$

Crystallographic parameters

Crystal system:	Cubic
Space group:	Pa-3
Space group number:	205
a (Å):	12.1350
b (Å):	12.1350
c (Å):	12.1350
Alpha (°):	90.0000
Beta (°):	90.0000
Gamma (°):	90.0000
Calculated density (g/cm^3):	1.76
Volume of cell (10^6 pm^3):	1786.98
Z:	4.00
RIR:	1.44

Status, subfiles and quality

Status:	Diffraction data collected at non ambient temperature Alternate Pattern
Subfiles:	Inorganic Common Phase Forensic Pharmaceutical ICSD Pattern
Quality:	Blank (B)

Comments

ANX:	ABC2X20.
Wyckoff Sequence:	d4 c3 b a (PA3-).
CAS Number:	7784-24-9.
Temperature:	173 K.
ICSD collection code:	280547.
Test from ICSD:	REF

References

Primary reference:	*Calculated from ICSD using POWD-12++*
Structure:	Nyburg, S., Steed, J., Aleksovska, S., Petrusevski, V., *Acta Crystallogr., Sec. B: Struct. Sci.*, **56**, 204, (2000)

Peak list

No.	h	k	l	d [A]	2Theta[deg]	I [%]
1	1	1	1	7.00620	12.624	8.7
2	2	0	0	6.06750	14.587	0.1
3	2	1	0	5.42690	16.320	30.3
4	2	1	1	4.95410	17.890	13.2
5	2	2	0	4.29040	20.686	100.0
6	2	2	1	4.04500	21.956	43.2
7	3	1	1	3.65880	24.307	5.8
8	2	2	2	3.50310	25.405	0.3
9	0	2	3	3.36560	26.462	2.5
10	1	2	3	3.24320	27.480	52.3
11	4	0	0	3.03380	29.418	24.4
12	4	1	0	2.94320	30.345	14.9
13	4	1	1	2.86020	31.247	10.5
14	3	3	1	2.78400	32.125	29.8
15	4	2	0	2.71350	32.983	12.4
16	4	2	1	2.64810	33.822	7.2
17	3	3	2	2.58720	34.643	7.4
18	4	2	2	2.47700	36.237	6.4
19	4	3	0	2.42700	37.010	0.1
20	4	3	1	2.37990	37.770	4.6
21	5	1	1	2.33540	38.518	7.7
22	4	3	2	2.25340	39.978	4.2
23	1	2	5	2.21550	40.692	4.4
24	4	4	0	2.14520	42.088	2.1
25	4	4	1	2.11240	42.773	5.2
26	4	3	3	2.08110	43.449	1.6
27	1	3	5	2.05120	44.115	2.1
28	6	0	0	2.02250	44.775	6.5
29	6	1	0	1.99500	45.426	5.5
30	5	3	2	1.96860	46.070	7.6
31	0	2	6	1.91870	47.340	17.1
32	1	2	6	1.89520	47.964	1.6
33	1	4	5	1.87250	48.583	2.1
34	5	3	3	1.85060	49.195	5.9
35	6	2	2	1.82940	49.804	2.9
36	5	4	2	1.80900	50.405	2.9
37	6	3	1	1.78920	51.002	3.0
38	4	4	4	1.75150	52.182	0.1
39	2	3	6	1.73360	52.762	0.1
40	5	4	3	1.71620	53.339	1.2
41	7	1	1	1.69920	53.915	1.6
42	6	4	0	1.68280	54.484	4.0
43	6	4	1	1.66690	55.047	1.0
44	5	5	2	1.65140	55.609	1.0
45	2	4	6	1.62160	56.722	6.9
46	7	2	2	1.60730	57.273	4.7
47	1	3	7	1.57980	58.365	1.4
48	6	5	0	1.55370	59.443	0.6
49	6	5	1	1.54120	59.974	1.9
50	8	0	0	1.51690	61.036	0.1
51	8	1	0	1.50520	61.562	0.5
52	1	4	7	1.49370	62.088	1.7
53	7	3	3	1.48250	62.610	0.2
54	0	2	8	1.47160	63.127	5.5
55	1	2	8	1.46090	63.643	1.2
56	6	5	3	1.45040	64.159	0.1

57	6	6	0	1.43010	65.181	3.2
58	6	6	1	1.42030	65.688	0.2
59	7	4	3	1.41070	66.192	1.7
60	1	5	7	1.40120	66.699	0.8
61	6	6	2	1.39200	67.198	1.0
62	6	5	4	1.38290	67.700	1.4
63	7	5	2	1.37400	68.198	0.3
64	0	4	8	1.35670	69.190	1.6
65	8	4	1	1.34830	69.684	2.8
66	7	5	3	1.33200	70.663	1.3
67	8	4	2	1.32400	71.154	1.2
68	0	2	9	1.31620	71.641	1.9
69	9	2	1	1.30860	72.122	1.9
70	6	6	4	1.29360	73.092	1.9
71	9	2	2	1.28630	73.575	1.8
72	1	5	8	1.27910	74.058	1.3
73	1	3	9	1.27210	74.535	0.4
74	8	5	2	1.25830	75.494	0.7
75	9	3	2	1.25160	75.970	0.4
76	8	4	4	1.23850	76.919	1.3
77	0	4	9	1.23210	77.393	0.2
78	9	4	1	1.22580	77.865	0.5
79	9	3	3	1.21960	78.337	0.3
80	10	0	0	1.21350	78.807	1.0
81	9	4	2	1.20750	79.275	1.2
82	10	1	1	1.20150	79.750	0.1
83	8	6	2	1.18990	80.687	4.3
84	10	2	1	1.18420	81.156	0.7
85	9	4	3	1.17870	81.615	0.1
86	7	7	3	1.17310	82.088	0.4
87	10	2	2	1.16770	82.550	1.1
88	10	3	0	1.16230	83.018	1.0
89	10	3	1	1.15700	83.483	1.4
90	2	3	10	1.14160	84.870	0.5
91	8	5	5	1.13660	85.332	1.1
92	3	5	9	1.13160	85.799	0.5
93	10	4	0	1.12670	86.263	1.2
94	10	4	1	1.12190	86.724	1.3
95	10	3	3	1.11710	87.190	0.4
96	10	4	2	1.10780	88.109	0.2
97	2	6	9	1.10320	88.572	1.1
98	4	5	9	1.09860	89.041	1.4

Table 2 : Crystal data and structure refinement for Al -Cr crystal :

Name and formula

Reference code:	01-070-8492
Common name:	Potassium Aluminum Chromium Sulfate Hydrate
PDF index name:	Potassium Aluminum Chromium Sulfate Hydrate
Empirical formula:	$Al_{0.95}Cr_{0.05}H_{24}KO_{20}S_2$
Chemical formula:	$K (Al_{0.95}Cr_{0.05}) (SO_4)_2 (H_2O)_{12}$

Crystallographic parameters

Crystal system:	Cubic
Space group:	Pa-3
Space group number:	205
a (Å):	12.1650
b (Å):	12.1650
c (Å):	12.1650
Alpha (°):	90.0000
Beta (°):	90.0000
Gamma (°):	90.0000
Volume of cell (10^6 pm^3):	1800.26
Z:	4.00
RIR:	1.39

Subfiles and Quality

Subfiles:	Inorganic ICSD Pattern
Quality:	Blank (B)

Comments

ANX:	ABC2X20.
Wyckoff Sequence:	d4 c3 b a (PA3-).
ICSD collection code:	094546. Significant Warning: ICSD Warning: The coordinates are those given in the paper but the atomic distances do not agree with those calculated during testing.The coordinates are probably correct.

References

Primary reference:	*Calculated from ICSD using POWD-12++*
Structure:	Rozhdenstvenskaya, I.V., Frank-Kamenetskaya, O.V., Shtukenberg, A.G., Bannova, I.I., *J. Struct. Chem. (USSR)*, **42**, 628, (2001)

Peak list

No.	h	k	l	d [A]	2Theta[deg]	I [%]
1	1	1	1	7.02350	12.593	10.9
2	2	0	0	6.08250	14.551	0.3
3	2	1	0	5.44040	16.280	32.1
4	2	1	1	4.96630	17.846	15.8
5	2	2	0	4.30100	20.634	100.0
6	2	2	1	4.05500	21.901	42.9
7	3	1	1	3.66790	24.246	5.7
8	2	2	2	3.51170	25.342	0.9
9	0	2	3	3.37400	26.395	2.2
10	1	2	3	3.25120	27.411	49.1
11	4	0	0	3.04120	29.344	20.8
12	4	1	0	2.95040	30.269	15.1
13	4	1	1	2.86730	31.168	9.5
14	3	3	1	2.79080	32.045	25.1
15	4	2	0	2.72020	32.900	12.8
16	1	2	4	2.65460	33.737	9.2
17	3	3	2	2.59360	34.555	7.2
18	4	2	2	2.48320	36.143	5.4
19	4	3	0	2.43300	36.915	0.2
20	4	3	1	2.38580	37.673	3.7
21	3	3	3	2.34120	38.419	5.8
22	0	2	5	2.25900	39.875	2.5
23	1	2	5	2.22100	40.587	4.2
24	4	4	0	2.15050	41.979	1.6
25	4	4	1	2.11760	42.663	3.6
26	4	3	3	2.08630	43.335	0.9
27	1	3	5	2.05630	44.000	1.8
28	6	0	0	2.02750	44.658	7.3
29	6	1	0	1.99990	45.308	4.3
30	5	3	2	1.97340	45.952	6.0
31	0	2	6	1.92350	47.215	12.4
32	1	2	6	1.89980	47.840	0.9
33	1	4	5	1.87710	48.456	1.9
34	5	3	3	1.85510	49.068	4.8
35	6	2	2	1.83390	49.673	3.4
36	5	4	2	1.81340	50.274	2.0
37	6	3	1	1.79360	50.868	2.3
38	4	4	4	1.75590	52.041	0.1
39	6	3	2	1.73790	52.621	0.1
40	5	4	3	1.72040	53.198	1.4
41	7	1	1	1.70340	53.772	2.0
42	6	4	0	1.68700	54.337	3.9
43	6	4	1	1.67100	54.901	1.0
44	5	5	2	1.65540	55.463	0.9
45	2	4	6	1.62560	56.570	5.0
46	7	2	2	1.61130	57.118	3.4
47	1	3	7	1.58380	58.203	1.2
48	6	5	0	1.55760	59.279	0.4
49	6	5	1	1.54500	59.812	1.4
50	8	0	0	1.52060	60.872	0.1
51	8	1	0	1.50890	61.395	0.4
52	1	4	7	1.49740	61.918	1.4
53	7	3	3	1.48620	62.437	0.3
54	0	2	8	1.47520	62.955	5.0
55	2	4	7	1.46450	63.469	1.2
56	6	5	3	1.45400	63.981	0.1

57	6	6	0	1.43370	64.997	2.6
58	6	6	1	1.42380	65.506	0.3
59	7	4	3	1.41420	66.007	1.4
60	1	5	7	1.40470	66.511	0.9
61	6	6	2	1.39540	67.013	0.9
62	6	5	4	1.38630	67.511	0.8
63	7	5	2	1.37740	68.007	0.1
64	0	4	8	1.36010	68.993	1.2
65	8	4	1	1.35170	69.483	1.9
66	3	5	7	1.33530	70.462	0.5
67	2	4	8	1.32730	70.950	0.8
68	0	2	9	1.31950	71.434	1.4
69	9	2	1	1.31180	71.918	1.2
70	6	6	4	1.29680	72.883	1.3
71	9	2	2	1.28950	73.363	1.1
72	1	5	8	1.28230	73.843	0.9
73	9	3	1	1.27520	74.323	0.2
74	8	5	2	1.26140	75.276	0.4
75	2	3	9	1.25470	75.749	0.4
76	8	4	4	1.24160	76.692	0.7
77	0	4	9	1.23520	77.162	0.3
78	9	4	1	1.22880	77.639	0.4
79	7	5	5	1.22260	78.108	0.6
80	10	0	0	1.21650	78.575	0.7
81	8	6	1	1.21050	79.040	0.7
82	10	1	1	1.20450	79.512	0.1
83	8	6	2	1.19290	80.442	2.8
84	10	2	1	1.18720	80.908	0.6
85	9	4	3	1.18160	81.372	0.1
86	1	5	9	1.17600	81.842	0.4
87	6	6	6	1.17060	82.301	0.9
88	8	6	3	1.16520	82.766	0.5
89	10	3	1	1.15990	83.228	1.2
90	2	3	10	1.14440	84.614	0.3
91	7	7	4	1.13940	85.073	0.6
92	3	5	9	1.13440	85.537	0.2
93	10	4	0	1.12950	85.998	0.7
94	10	4	1	1.12460	86.464	0.7
95	9	6	1	1.11990	86.917	0.2
96	2	4	10	1.11050	87.840	0.1
97	2	6	9	1.10590	88.300	0.7
98	4	5	9	1.10140	88.755	1.0
99	10	4	3	1.08810	90.134	0.1
100	9	6	3	1.08370	90.601	0.8
101	8	8	0	1.07520	91.520	0.5
102	11	2	2	1.07110	91.972	0.6
103	1	3	11	1.06290	92.890	0.1
104	10	4	4	1.05880	93.358	0.1
105	9	6	4	1.05480	93.820	0.3
106	2	3	11	1.05090	94.275	0.3
107	10	6	0	1.04310	95.203	0.5
108	1	6	10	1.03930	95.663	0.1
109	1	4	11	1.03560	96.116	0.3
110	11	3	3	1.03180	96.586	0.2
111	2	6	10	1.02810	97.050	0.1
112	2	4	11	1.02450	97.507	0.2
113	9	6	5	1.02090	97.969	0.1

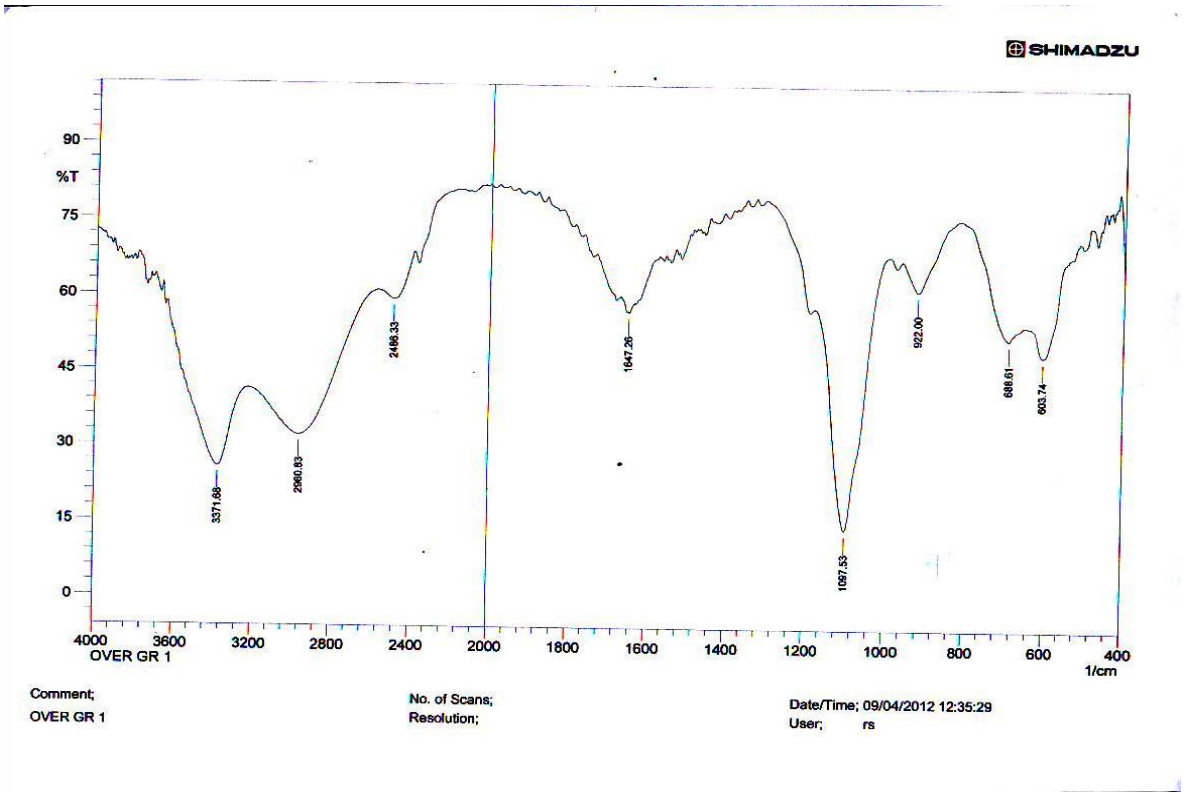

Figure 1 : FT – IR spectrum for Al - crystal

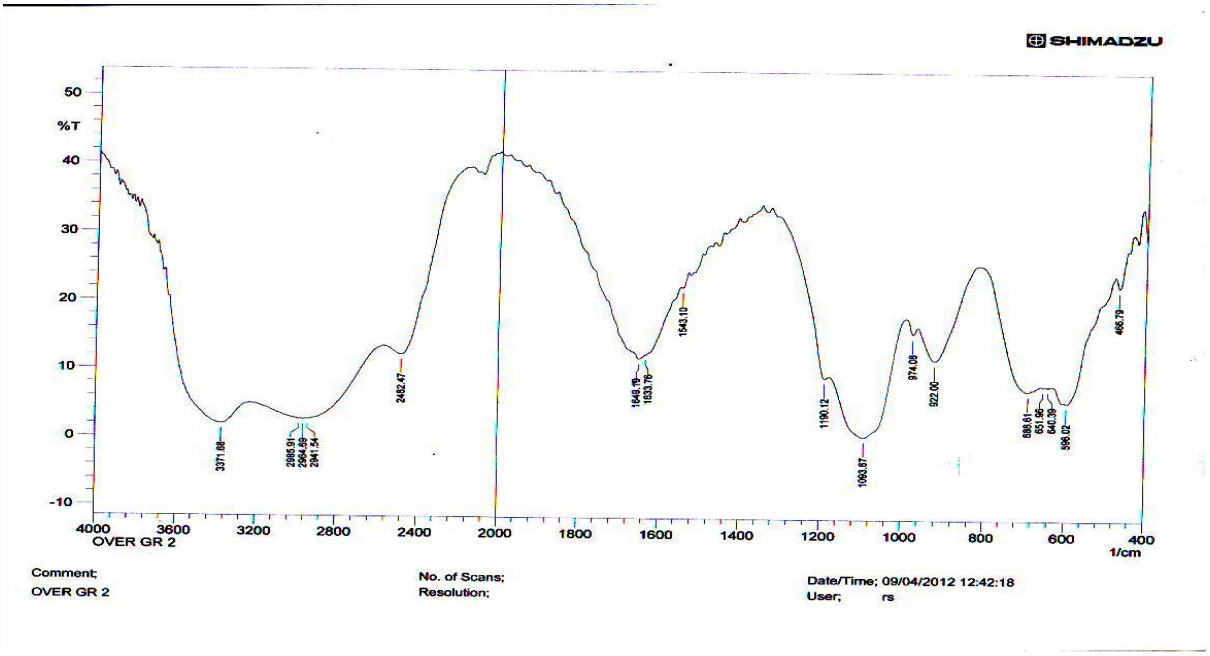

Figure 2 : FT – IR spectrum for Al - Cr - crystal

Stick Pattern

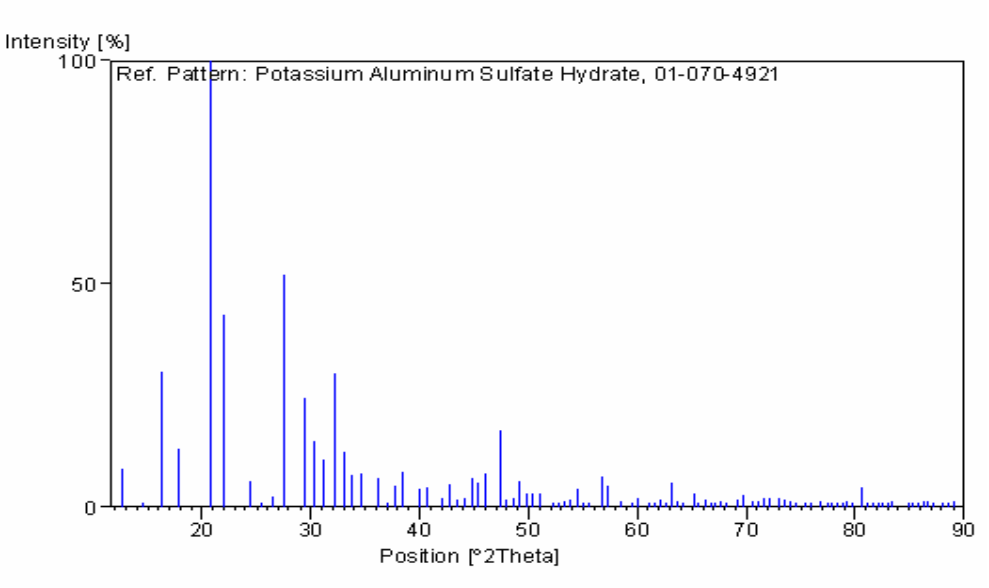

Figure 3 : X – Ray spectrum of the Al - crystal

Stick Pattern

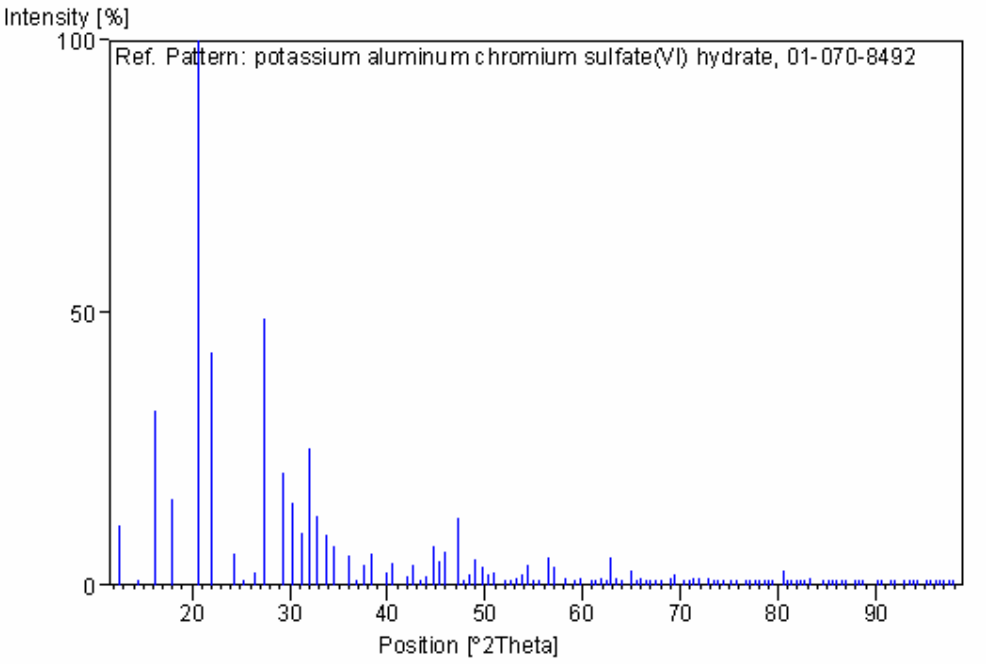

Figure 4 : X – Ray spectrum of the Al - Cr crystal

Figure 5 : The photograph of the overgrothes under our investigation

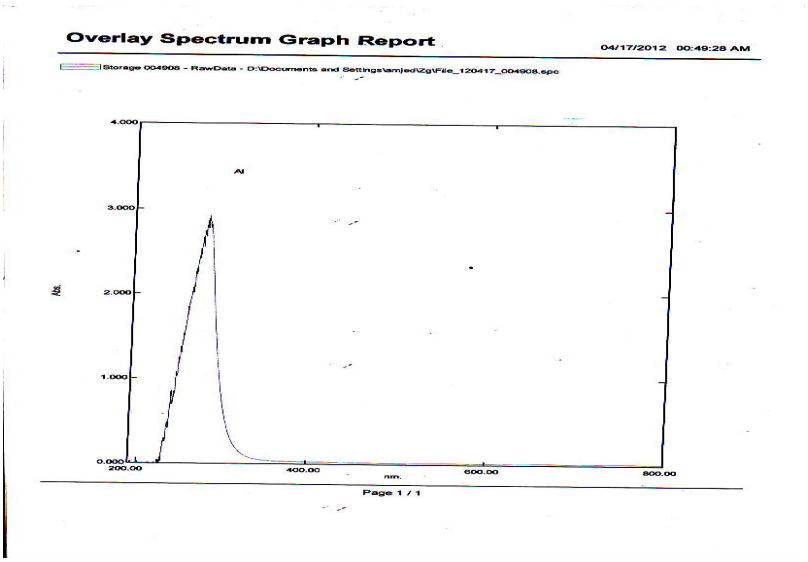

Figure 6 : UV.Visb. spectrum of the Al - crystal

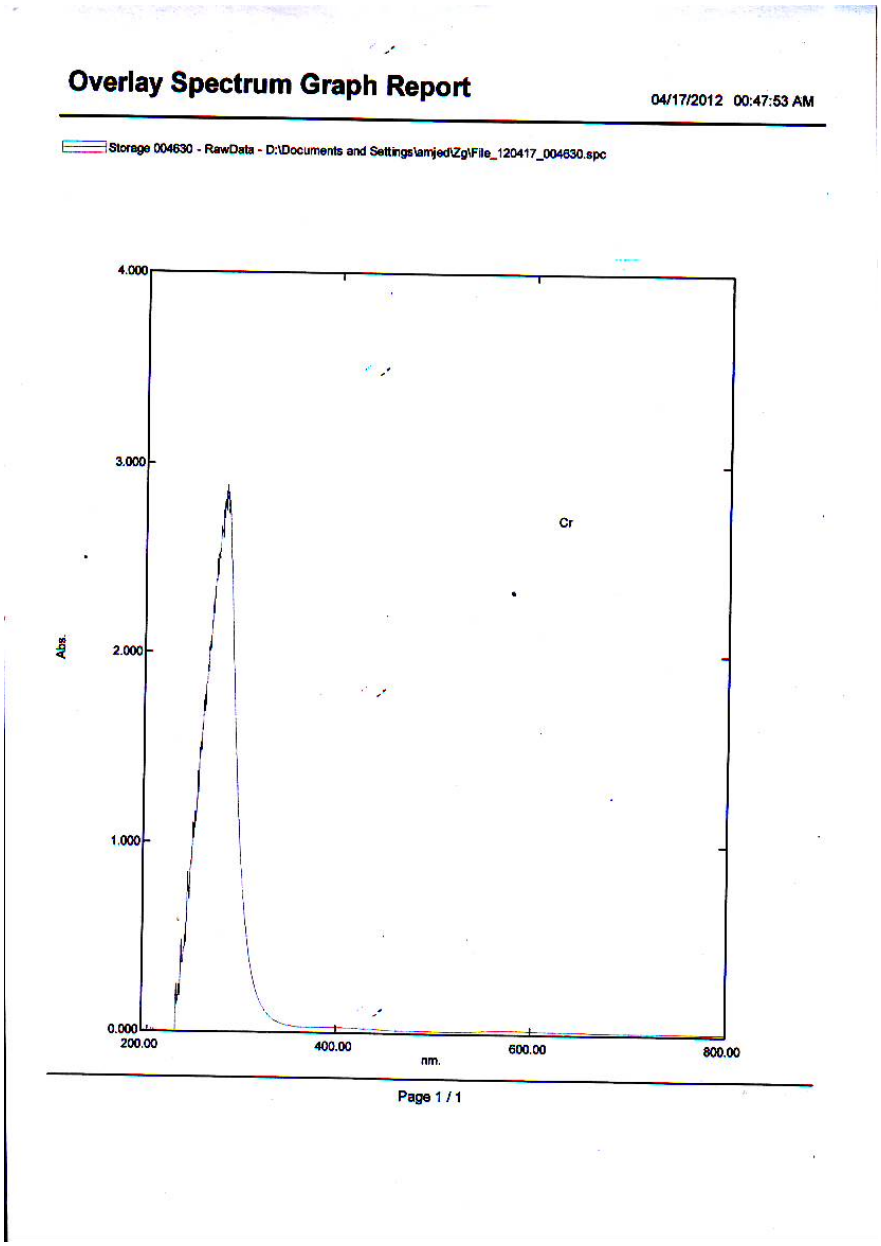

Figure 7 : UV.Visb. spectrum of the Al - Cr crystal

Results and Discutions

Figures 1 shows the FT – IR spectra of the outer layer of overgrowth crystal (Al – crystal) and figures 2 shows the FT – IR spectra of the middle layer of the overgrowth crystal which contain few Cr atoms in crystal space lattice of Al – crystal . Comparing the main IR frequenvies of the two layers , the following data were found : there were five strong absorpition peaks in both samples , 3371 cm^{-1} is due to stretching of OH group , 2960 cm^{-1} is due to stretching of H in H_2O molecules , 1647 cm^{-1} is due to the bending of hydrogen water molecules , 1097 cm^{-1} is due to the S=O stretching and 603 cm^{-1} is due to S – O stretching . There are week peaks below 600 cm^{-1} may be is due to Al – O stretching . The crystal data and refinement parameters of the two samples are summarized in table 1 and table 2 , the X –Ray spectrum are shown in figure 3

and figure 4 . the crystal lographic parameters for the two samples are similar . The Cr atoms are inserted inside the space lattice of the colourless Al – crystal to introduce the voliet isomorphouse crystal .The two layer inhibite the cubic system crystal due to the similarity of there electrical and chemical properties of Al and Cr atoms . figure 5 and figure 6 show the UV. Visib. Spectrum of the two layers , both including aband at 280 nm , hence there is no shift confirming a same crystal system in both samples . From the datd of physical and mechanical properties we see that all the measured parameters are nearly equal for the two samples , that indicate for the similarity of the two layers of the overgrothes crystal .

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