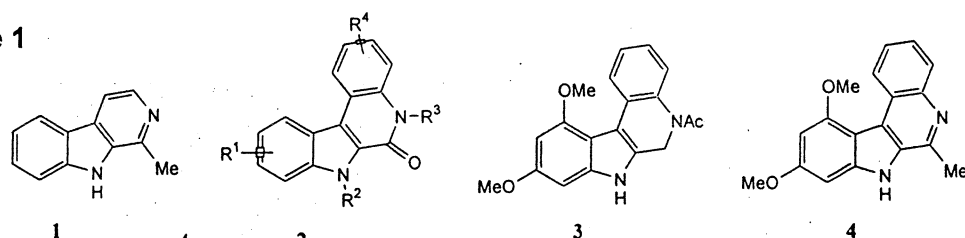


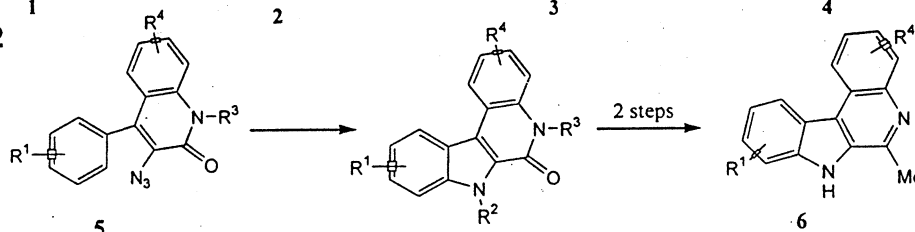
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Scheme 1



Scheme 2



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Aims and Scope

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CRYSTALLIZATION AND CHARACTERIZATION OF CHROMIUM-CONTAINING SILICALITE-1

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ABSTRACT

Chromium-containing silicalite-1, designed CrS-1, was synthesized by the hydrothermal method and characterized by XRD and FTIR techniques. The objectives of the research are to study the synthesis of CrS-1 and investigate the effect of crystallization temperatures and times toward its character. All samples of CrS-1 crystallized in orthorhombic structure and *Pnma* space group. The phase observed in the XRD patterns of CrS-1 synthesized from 150 to 190 °C for 11 days showed only MFI-type phase. The CrS-1 prepared under static condition for 1 day at 150 °C indicated α -SiO₂ phase, on the contrary, the samples conditioned for 2 to 8 days at 150 °C are only MFI phase.

Keywords: Crystallization, synthesis, chromium silicate CrS-1, incorporation.

INTRODUCTION

Silicalite, synthesized first by Union Carbide group [1], is an aluminium-free zeolites, belonging to the structure type MFI (Mobile Five) in the IUPAC nomenclature. It shows a three dimensional pore system consisting of two intersecting sets of tubular channels: a linear one parallel to the [010] direction having openings of 5.4 x 5.6 Å, and sinusoidal one parallel to the [100] direction with openings of 5.1 x 5.5 Å. Ten-membered rings of SiO₄ tetrahedra defined both channels [2-3]. From the crystallographic point of view all synthetic MFI zeolites show a polymorphic orthorhombic to monoclinic phase transition. The transition temperature and mechanism are closely related to the composition and defect density of the tetrahedral framework, besides of course the nature and amount of the molecules absorbed in the zeolitic channels. At room temperature the as-synthesized samples of hydrogen free ZSM-5 and TS-1 (MFI-type titanosilicate) are orthorhombic and *Pnma* space group, whereas hydrogen-containing ZSM-5 and TS-1 with very low titanium are monoclinic and *P2₁/n* space group [4-7].

The isomorphous substitution of Al(III) and/or Si(IV) by other di-, tri-, tetra-, penta-, and hexavalent metal ions is generally considered as a tool for modifying the acidic and catalytic properties of zeolites. Some authors have claimed the possibility of incorporating a large number of elements in framework positions, but only a few (V, Cu, Cr, Fe, B, and Ti) have been proved, leading to the

information of microporous materials with catalytic properties different from those of the parent aluminosilicates. Among the large number of synthetic zeolite structures, MFI proves to be the most versatile towards isomorphous substitution: literally some papers have been published on the synthesis, physico-chemical characterization and catalytic properties of V- [8-9], Cu- [10-11], Cr- [12], Fe- [13], B- [14-15], and Ti-MFI [6,9,14,16]. In these cases, the incorporation of the heteroatom has been unambiguously assessed by structural and spectroscopic evidence. The unit cell parameters and volume have a linear dependence on the degree of substitution.

The objectives of the present work are to study the synthesis of Cr-containing MFI-type structure (CrS-1), investigate the effect of crystallization temperatures and times toward character of CrS-1 obtained. CrS-1 has shown a remarkably high efficiency and molecular selectivity in oxidation reactions under mild conditions, such as the oxidative of olefinic double bonds, for example methyl acrylate and methyl methacrylate afforded methyl glyoxylate and methyl pyruvate respectively, the oxidation of aromatic side chains with tertbutylhydroperoxide (TBHP) or O₂ as oxidant to give the corresponding ketones in high selectivities [2].

EXPERIMENTAL SECTION

Material

The chromium-containing molecular sieves with MFI structure, designed CrS-1, were

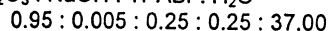
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synthesized hydrothermally using tetraethyl-orthosilicate (TEOS, Merck, 98%) as the Si source, while potassium dichromate ($K_2Cr_2O_7$, Merck) was the main chromium source. Tetrapropylammonium bromide (TPABr, Aldrich), NaOH (Merck) and H_2O were used as a template, the mineralizer (mobilizing) and a solvent respectively.

Procedure

Preparation of CrS-1

In a typical preparation, 0.612 g of TPABr was mixed in Teflon jar with 0.090 g of NaOH and 3 mL of H_2O thoroughly. This mixture was stirred for 1 hour before adding to it a solution of 0.013 g of $K_2Cr_2O_7$ in 3 mL of distilled water under stirring. The mixture obtained was stirred for 1 hour. Finally the remaining 1.936 mL of TEOS was slowly added and stirred for 4 hours to obtain a clearly transparent colloid. Then the clear gel, whose composition was:



then transferred into a Teflon-lined autoclave and was heated at 150 °C under autogenous pressure for 11 days. After the crystallization was over, the autoclave was quenched in cold water. The solid was taken out from the Teflon, filtered and washed thoroughly with distilled water, and dried at 60°C in an oven for 12 hours. Occluded TPA^+ cations were removed from the zeolite channels by heating as-synthesized samples in an air atmosphere with a heating rate of 5°C min⁻¹ to a final temperature of 600°C and then maintained at this temperature for about 4 hours. The same procedure was repeated for various temperatures i.e. 160, 170, 180 and 190 °C respectively. All of the obtained crystals were symbolized as (a), (b), (c), (d) and (e). Based on the crystallization temperature (150°C) that obtained the samples posses highly crystalline, the same procedure was repeated for various times: 1, 2, 5, and 8 days to obtain the symbolized crystal (f), (g), (h) and (i).

Characterization

All products have been characterized using conventional techniques. X-ray diffraction patterns were obtained using a powder diffractometer (Shimadzu XRD-6000) operating in the reflection mode with Cu-K α radiation. The diagrams were recorded from $2\theta = 5^\circ$ to 35° in 0.03 steps. The X-ray diffraction patterns were analyzed to determine the hkl plans by using Samson [17] and U-fit programs [18]. The unit cell dimensions were refined by a least-squares method. FTIR spectra were obtained using a Shimadzu 8201PC spectrometer with KBr wafers. Spectra were recorded from 400 to 4000 cm⁻¹.

RESULT AND DISCUSSION

Synthesis

Table 1 summarizes the molar compositions of the starting mixtures and the synthesis conditions of CrS-1 by hydrothermal method. The gel transparent obtained was transferred to Teflon-lined autoclaves and crystallized under autogenous pressure and static conditions at 150 °C for 11 days. After cooling of autoclaves the white solid product was recovered, filtered washed and dried at 60 °C in an oven for 12 hours. The (a) white solid sample was obtained by calcination in an air atmosphere at 600 °C for 4 hours. The same procedure was repeated at various temperatures (160, 170, 180 and 190 °C) to obtain the (b) to (e) samples. The (f) to (i) samples were crystallized under autogenous pressure and static conditions at 150 °C for various times: 1, 2, 5 and 8 days respectively.

Powder XRD Patterns

The X-ray powder diffraction patterns of pure CrS-1 phases obtained at different temperature are depicted in Fig 1. The high intensity of the peaks and the absence of any baseline drift indicated that the samples were highly crystalline without any impurities phase, i.e. CrO_3 or Cr_2O_3 .

Table 1 Molar starting composition and synthesis conditions of CrS-1

Sample	Crystallization temperature (°C)	Crystallization time (days)	$x = [Cr]/[Cr]+[Si]$	TPA^+/OH^-
(a)	150	11	0.0104	1
(b)	160	11	0.0104	1
(c)	170	11	0.0104	1
(d)	180	11	0.0104	1
(e)	190	11	0.0104	1
(f)	150	2	0.0104	1
(g)	150	4	0.0104	1
(h)	150	6	0.0104	1
(i)	150	8	0.0104	1

Table 2 Crystallographic data of the calcined samples recovered at different crystallization temperature

Temperature (°C)	a (Å)	b (Å)	c (Å)	V (Å ³)
150	19.90	19.31	13.42	5156.19
160	20.25	19.89	13.31	5357.82
170	20.01	19.29	13.55	5227.60
180	19.98	19.83	13.42	5313.59
190	19.88	19.36	13.41	5162.24

Table 3 2 θ , the relative intensity and *hkl* of CrS-1 calcined samples recovered at different crystallization temperature

2 θ and relative intensity of CrS-1										<i>hkl</i>
150°C		160°C		170°C		180°C		190°C		
2 θ	<i>I</i> / <i>I</i> ₁	2 θ	<i>I</i> / <i>I</i> ₁	2 θ	<i>I</i> / <i>I</i> ₁	2 θ	<i>I</i> / <i>I</i> ₁	2 θ	<i>I</i> / <i>I</i> ₁	
8,006	100	7,945	100	7,922	97	7,932	95	7,951	100	101/011
8,878	55	8,885	54	8,823	52	8,845	52	8,917	61	200
9,144	18	9,160	17	9,090	18	9,100	17	9,130	17	111/020
13,293	11	13,298	10	13,228	10	13,250	10	13,275	10	300
14,006	15	13,994	14	13,932	15	13,948	15	13,974	15	012
14,842	20	14,841	20	14,809	20	14,825	20	14,830	19	301
15,586	10	15,599	10	15,532	10	15,550	10	15,577	10	311
15,956	14	15,961	14	15,894	14	15,920	14	15,941	14	202/131
								17,861	10	400
20,877	30	20,881	29	20,818	31	20,848	32	20,860	31	113
23,121	94	23,126	92	23,060	100	23,090	100	23,099	94	142
23,340	49	23,360	48	23,270	50	23,290	52	23,320	47	501
23,730	25	23,740	26	23,670	27	23,700	29	23,700	23	341
23,990	51	23,990	50	23,920	52	23,950	55	23,888	51	051
24,380	17	24,370	17	24,320	18	24,350	20	24,349	17	151/242
25,903	8	25,893	8	25,846	8	25,873	9			233
								26,614	13	052
				26,929	15	26,940	21			014
26,994	14	26,997	15			26,953	16	26,974	16	152
29,940	21	29,939	21	29,873	23	29,905	22	29,917	21	034
30,260	9	30,326	10	30,183	11	30,218	11	30,243	11	433

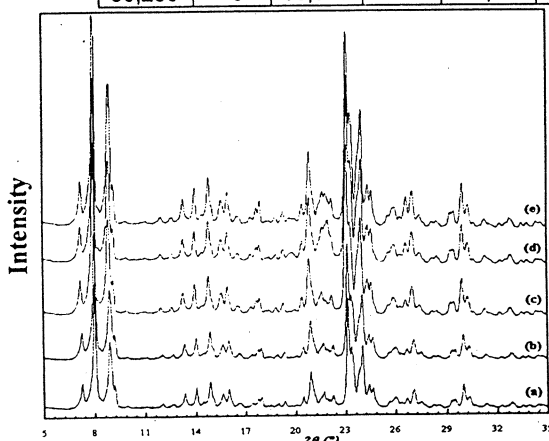


Figure 1 X-ray powder patterns taken from the CrS-1 calcined samples experiencing crystallization in different temperature: (a). 150, (b). 160, (c). 170, (d). 180 and (e). 190 °C

We studied the crystallization of the CrS-1 phase from 150 to 190 °C at 11 days, and during this temperature only MFI phase was observed. The intensity of XRD peaks increase progressively with increasing crystallization temperature. The cell parameters of CrS-1 recovered at different crystallization temperatures are mentioned in Table 2, while the annex 1 shows an example refines lattice parameters and determine *hkl* plans. The cell dimensions on Table 2 were obtained from crystallographic analysis by using Samson and U-fit programs. Table 2 shows that the XRD patterns of all CrS-1 recovered at crystallization temperatures from 150 to 190 °C reveal in orthorhombic crystal system with *P* Bravais lattice, which the indexing is performed in Table 3. Generally, crystal system of MFI-type zeolite can be met in orthorhombic with *Pnma* space group or monoclinic with *P2₁/n* space group [5], therefore, all CrS-1 at crystallization

temperatures from 150 to 190 °C crystallized in the *Pnma*-orthorhombic structure.

The X-ray powder diffraction patterns of the Cr-containing molecular sieves with MFI structure crystallized at different times are shown in Fig 2. For the (f) white solid sample, the XRD pattern exhibits an extra-peak around $2\theta = 21.67^\circ$, characteristic of crystalline α -SiO₂ [19]. The (g) to (i) white solid samples have a high crystallinity and purity. The intensity of XRD peaks of the samples increase with increasing crystallization times. All CrS-1 recovered at different crystallization times, have an orthorhombic structure and *Pnma* space group (Table 4), while the indexing of *hkl* plans is performed properly complete in Table 5. The cell parameters on Table 4 were calculated by Samson program and refined by U-fit program.

Table 4 Crystallographic data of the calcined samples recovered at different crystallization time

time (days)	a (Å)	b (Å)	c (Å)	V (Å ³)
1	20.15	19.39	13.38	5228.06
2	20.14	19.55	13.47	5302.79
5	20.10	19.43	13.43	5245.53
8	20.18	19.98	13.46	5428.73

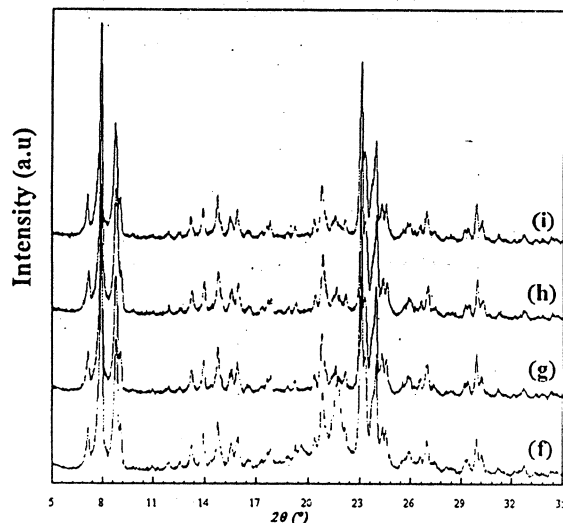


Figure 2 X-ray powder patterns taken from the CrS-1 calcined samples experiencing crystallization in different times: (f).1, (g). 2, (h). 5, and (i). 8

Table 5 2θ , the relative intensity and *hkl* of CrS-1 calcined samples recovered at different crystallization time

2θ and relative intensity of CrS-1								<i>hkl</i>
1 day		2 days		5 days		8 days		
2θ	<i>I/I</i> ₁	2θ	<i>I/I</i> ₁	2θ	<i>I/I</i> ₁	2θ	<i>I/I</i> ₁	
7,895	100	7,880	100	7,908	100	7,859	100	101/011
8,793	57	8,776	55	8,804	58	8,757	52	200
9,100	16	9,040	18	9,070	18	9,020	17	111/020
13,213	10	13,203	10	13,215	10	13,164	9	300
13,912	14	13,893	14	13,918	14	13,871	13	012
14,753	19	14,721	20	14,755	19	14,699	19	301
15,511	10	15,489	9	15,521	10	15,468	8	311
15,874	14	15,852	13	15,885	13	15,830	13	131/202
17,780	7	17,770	8	17,820	7	17,741	8	400
20,817	28	20,785	28	20,821	26	20,766	25	113
21,665	34							α -SiO ₂
22,100	12	22,108	8	22,137	7	22,084	7	023
23,062	83	23,024	92	23,061	84	22,999	86	142
23,280	46	23,260	45	23,270	42	23,220	39	501
23,680	26	23,640	24	23,680	23	23,670	24	341
23,920	46	23,822	51	23,930	46	23,950	55	051
24,320	16	24,258	18	24,320	15	24,231	15	151/242
24,520	15	24,506	15	24,550	14	24,489	15	133
25,820	8	25,780	8	25,820	7	25,720	6	233
26,919	13	26,908	14	26,944	12	26,882	13	104
29,871	17	29,847	21	29,883	18	29,825	20	261
30,180	8	30,161	9	30,197	8	30,141	9	314

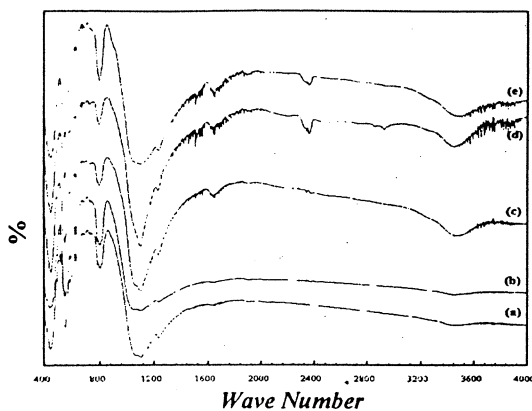


Figure 3 FTIR spectra of the CrS-1 calcined samples at different crystallization temperatures : (a). 150, (b). 160, (c). 170, (d). 180 and (e). 190 °C

The results of the analysis show that all CrS-1 recovered at different crystallization times from 1 to 8 days crystallized in the orthorhombic structure and *P* Bravais lattice, therefore all CrS-1 have an orthorhombic structure and *Pnma* space group.

FTIR Spectra

FTIR spectra of the Cr-containing molecular sieves with MFI structure obtained at different temperature and time of crystallization are depicted in Fig 3 and 4 respectively. Pure silicalite-1 has FTIR bands at 1230, 1100, 800, 550 and 450 cm^{-1} , which assigned to different vibrations of tetrahedral and framework atoms of MFI zeolite [20]. The band at 550 cm^{-1} confirms the presence of double five rings and is generally regarded as a characteristic probe for the existence of the MFI structure, while at 450, 800, 1100 and 1230 cm^{-1} are mainly assigned to the asymmetric bend stretch, the symmetric stretch, the symmetric stretch and the symmetric bend stretch respectively [21]. On the contrary, two peaks are present at 585 and 630 cm^{-1} which are assigned to vibration of the Cr=O and Cr-O bonds [22]. Fig 3 and 4 show that the broadening ratios of the band at 800 cm^{-1} to that at 450 cm^{-1} (I_{800}/I_{450}) decrease with increasing crystallization temperatures or crystallization times. These cases prove that the crystallinity of CrS-1 increase with increasing crystallization temperatures or crystallization times.

Model of the Chromium Incorporation on the Framework Silicalites-1

From Pauling's theory of the chemical bond [23], framework substitution, in which the metals are coordinated tetrahedrally by four oxygen ions, should be possible if the ratio of the radii of the cation and the oxygen atom is between 0.225 and 0.414. In contrary, Arends *et al.* [2] reported that

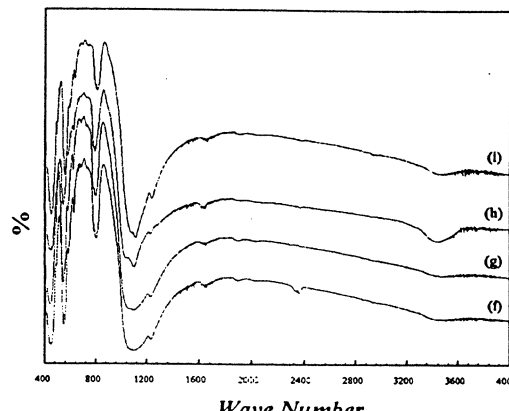


Figure 4 FTIR spectra of the CrS-1 calcined samples at different crystallization times: (f). 1, (g). 2, (h). 5, and (i). 8 days

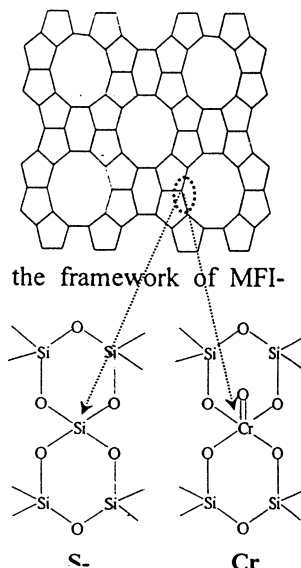


Figure 5 Model of the Cr incorporation on the framework of silicalites-1 MFI-type structure

framework incorporation is also possible for metal cations for which $r(M^{n+})/r(O^{2-})$ is slightly higher than 0.414. The oxidation state of the metal ion and hence, the structure may be substantially different in the calcined material from that in the as-synthesized redox molecular sieves. The valence state of the metal cations is that of original material incorporated in the synthetic gel, e.g. V(IV), Cr(III), Mn(II) and Co(II), when calcined, the valence state in the final material can change to: V(V), Cr(VI), Mn(III) and Co(III). Chromium-substituted molecular sieves generally contain chromium(III) in the as-synthesized material, but this is converted to chromium(VI) upon calcination. Since chromium(VI) always contains two extra framework Cr=O bonds it can only be

anchored to the surface and cannot be isomorphously substituted. Model of the Cr incorporation on the framework of MFI-type structure silicalites-1 can be predicted as in Fig 5.

CONCLUSION

In this paper, we have shown that it is possible to synthesis chromium-containing silicates MFI-type structure using $K_2Cr_2O_7$ as the chromium source, TEOS as the silicon source, TPABr as template, NaOH as the mineralizer and H_2O as solvent. The phase observed in the XRD patterns of the CrS-1 calcined samples synthesized from the crystallization 150 to 190 °C for 11 days is only MFI-type phase. The crystallinity of CrS-1 calcined samples increase progressively with increasing crystallization temperature. The CrS-1 sample prepared under static condition for 1 day at 150°C indicated α - SiO_2 phase. On the contrary, the samples conditioned for 2, 5, and 8 days at 150°C were only MFI phase. All of the CrS-1 calcined samples recovered at different crystallization temperatures and times, crystallized in the orthorhombic structure and *Pnma* space group.

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Annex 1: an example for parameters calculation of CrS-1

The unit cell dimensions were refined by a least-squares method

Title: CrS-1 calcined sample recovered at crystallization temperature 150°C

Parameters:

a = 19.902895 (0.047470) (*)

b = 19.309593 (0.031154) (*)

c = 13.416503 (0.025153) (*)

Volume = 5156.1875 (30.2835)

Special parameters:

z = 0.010492 (0.033027) (*) Zero shift

Largest correlation coefficients:

(a) - (b) : 0.60464579

(a) - (c) : 0.58850000

(b) - (c) : 0.43950637

(a) - (z) : 0.00734595

(c) - (z) : 0.00691493

Crystal system: orthorhombic

Bravais lattice: Primitive

Wave length: 1.54059810

Weighting scheme: unit weight

of cycles: 1 (max:10)

of hkl : 18

Cycle 1 "Chi**2" = 1.934E-0006

h	k	l	2θobs	2θcor	2θcalc	d(2θ)	int
1	0	1	8.006	7.996	7.941	-0.055	100
2	0	0	8.878	8.868	8.879	0.011	55
1	1	1	9.144	9.134	9.167	0.033	18
3	0	0	13.293	13.283	13.335	0.053	11
0	1	2	14.006	13.996	13.964	-0.031	15
3	0	1	14.842	14.832	14.885	0.053	20
3	1	1	15.586	15.576	15.579	0.003	10
2	0	2	15.956	15.946	15.920	-0.025	14
1	1	3	20.877	20.867	20.855	-0.012	30
1	4	2	23.121	23.111	23.116	0.006	94
5	0	1	23.340	23.330	23.291	-0.039	49
3	4	1	23.730	23.720	23.720	0.001	25
0	5	1	23.990	23.980	23.959	-0.021	51
1	5	1	24.380	24.370	24.378	0.008	17
2	3	3	25.903	25.893	25.837	-0.055	8
1	5	2	26.994	26.984	26.993	0.009	14
0	3	4	29.940	29.930	30.018	0.088	21
4	3	3	30.260	30.250	30.221	-0.028	9

$$D = (\sum(\Delta(2\theta)))/n_{hkl} = 0.029600$$

$$R = (\sum(2\theta_{obs} - 2\theta_{calc})^2)/(n_{hkl} - n_{var}) = 0.042589$$