Journal of Thermal Analysis and Calorimetry, Vol. 81 (2005) 477–487

THERMAL ANALYTICAL STUDY OF DIFFERENT PHASES OF POTASSIUM HEXACYANOFERRATE(II) CRYSTAL

Effects of growth conditions, heat treatment and γ-irradiation on the unit cell parameters

M. A. Gaffar[*] *and M. H. Omar*

Physics Department, School of Science and Engineering, The American University in Cairo, Cairo 11511, Egypt

The unit cell parameters of virgin and thermally treated potassium hexacyanoferrate(II)trihydrate (KFCT) crystals are measured at room temperature. Considerable changes in the lattice constants are observed for as-grown or pre-cooled to the liquid nitrogen temperature samples after heating up to selected higher temperatures for different times. The detected variations may be due to partial or total removal of the three water molecules of crystallization and the transformation of Fe^{2+} to Fe^{3+}. DSC, DTA and TG are used to study physical and chemical changes associated with the observed crystallographic variations. The effect of γ-irradiation with a dose of $5\cdot10^5$ Gy on the crystal structure of KFCT is also examined. Two computer software programs are used to analyze the data of the X-ray diffraction patterns and the results are compared.

Keywords: *crystal structure, γ-irradiation, potassium hexacyanoferrate, thermal effects*

Introduction

Potassium hexacyanoferrate(II)trihydrate $K_4[Fe(CN)_6]\cdot3H_2O$, hereinafter KFCT, is a member of a family of crystals having the general formula $A_4[B(CN)_6]\cdot3H_2O$ where *A* is K or NH_4 while *B* is Fe, Mn, Ru or Os. In crystalline KFCT the three water molecules are located in layers perpendicular to the [010] axis and between each layer there are two layers of the $Fe(CN)_6^{4-}$ groups interspersed by K^+ ions while the Fe^{2+} ion is located at the center of the regular octahedra formed by six cyanide ions [1]. KFCT undergoes an interesting second-order ferroelectric phase transition at about 249 K. This transition is an order–disorder type in which the spontaneous polarization arises along the $[10\bar{1}]$ direction from a collective ordering of the water molecules [2–4]. At the phase transition point the crystal symmetry changes upon cooling from monoclinic paraelectric, space group $C_{2h}(C2/c)$, to monoclinic ferroelectric, space group $C_s(C_c)$ [5]. Under practical conditions of crystal growth, KFCT often appears with a polytropic structure in which alternating monoclinic and tetragonal layers are formed [6, 7].

Below 218 K, KFCT structure is ferroelectric monoclinic with factor group C_s^4 [8, 9]. Upon heating, the anomaly at 218 K disappears and KFCT shows ferroelectricity up to about 249 K. By further heating, an axis of the second order appears which is perpendicular to the symmetry plane. This results in the high temperature monoclinic phase with symmetry C_{2h}^6 (Z=4) factor group [8, 9]. The twin habit of KFCT and the metastable nonferroelectric tetragonal phase may result in clamping of substantial portions of the sample giving rise to multiple transitions as well as large thermal hysteresis [10].

One can find many publications on the study of physical properties of KFCT using different techniques like Raman, infrared, NMR and Mössbauer spectroscopes and X-ray absorption near the edge structure [11–22]. Ferroelectricity [23], dielectric permittivity [24, 25], specific heat [26], conduction [27], optical [28] and phase transition [29–32] in KFCT have been also extensively studied. Publications on technological applications of KFCT have been reported recently [33–36].

In the present study the lattice constants of virgin (as grown) KFCT crystals are calculated from the X-rays diffraction pattern scanned at room temperature. The effect of cooling virgin KFCT samples down to the liquid nitrogen temperature is studied. In addition, the effect of heating KFCT samples up to 50°C for 20 min, then to 120°C for 4 h, then to 360°C for 4 h, then to 510°C for 2 h and finally up to 850°C for 2 h on the lattice parameters is discussed. Differential scanning calorimetry (DSC), differential thermal analysis (DTA) and thermogravimetric analysis (TG) were used to study possible chemical changes associated with the detected crystallographic variations. The effect of γ-irradiation on the unit cell parameters of KFCT is also included in this work. Two computer software programs were used to analyze the X-ray dif-

---

[*] Author for correspondence: mgaafar@aucegypt.edu

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

fraction patterns and the results were compared. This work may be interested since, to the best of our knowledge, this effect has not been reported before.

Experimental

Single crystals of KFCT were grown using the slow evaporation technique at constant temperature from KFCT aqueous solution. The layered nature of the grown crystals is observed in addition to inclusions in some cases. Details about crystallization process can be found elsewhere [29]. We were able to grow, over a period of about seven weeks, large (4×3.5×2 cm), transparent in most parts, well-defined planes and light yellow colored KFCT single crystals.

The X-ray diffraction patterns were obtained using a Philips 1700 series diffractometer that is equipped with a curved graphite crystal monochromator, an automatic divergence slit, a vertical goniometer and an automatic sample changer with Xenon proportional detector. The target used is Cu (λK_α=1.5418 Å) operating at 40 kV and 30 mA. The system is usually calibrated using a standard silicon disk and/or powder (d_{111}=3.1355 Å) as an external standard.

KFCT in powder and single crystal forms, was irradiated with $5\cdot10^5$ Gy γ-dose at room temperature using ^{60}Co source (Alcyon II CGR, France) at constant dose rate of 20 kGy h^{-1}.

Results and discussion

Choice of the computer programs

The two computer software programs, namely ‘Treor’ and ‘Dicvol-91’, were checked for the suitability of the present study by recalculating the lattice parameters of potassium hexacyanoferrate(II)trihydrate using the *d*-spacing as extracted from the files of the International Center for Diffraction Data (ICDD). The data used belongs to card no. 72-0450 due to Kiriyama *et al*. [1]. Excellent agreement between the lattice parameters of KFCT calculated in the present study using the ‘Dicvol-91’ software and those given in the card. The figure of merit of our calculations, according to the definition of [37, 38], is M=37.8 and F=75.1(.0011,610), respectively which reflects the good performance of this computer program. If the ‘Treor’ software is loaded by the same reflections given to the ‘Dicvol-91’ program (49 reflections) the most accepted solution is a monoclinic structure with a=9.6615 Å, b=9.4189 Å, c=9.6401 Å and β=121.76° with F_{49}=9(.01817,301) and 2 lines are unindexed. The volume of the unit cell in this case is 745.86 Å^3. However, among the given solutions there are an orthorhombic structure with a=9.4295 Å, b=16.8753 Å, c=9.3904 Å and V=1494.25 Å^3 with F_{49}=8(.01876,370) and one unindexed line and a tetragonal solution with a=9.4150 Å, c=16.8814 Å and V=1496.4 Å^3 with F_{49}=11(.0233,208) and 10 unindexed lines. The program choice of the accepted solution in this case seems to be based upon the smallest unit cell volume and less number of unindexing lines rather than the highest F-factor. Table 1 gives a comparison between the lattice parameters in the three cases considering the orthorhombic solution of the ‘Treor’ software as an acceptable solution (just for comparison).

During the recalculations some differences were detected between the (*hkl*) of planes given in the card and the corresponding planes in our calculation using the *d*’s of the card and the ‘Dicvol-91’ software. We believe that the difference is due to misprints in the card. The misprints and the corrected (*hkl*) are listed in Table 2.

Effect of heat treatment

The aim of this study can be divided into two parts. The first, is a study of the effect of cooling on the crystal structure of KFCT. The second is an investigation of the effect of heating up to 850°C in steps (different temperatures for different times) on the lattice constants of KFCT. We believe that this study may be helpful to clarify the confusion resulting from contradictory information regarding not only the crystal structure of KFCT but also physical properties of this crystal.

Figure 1 depicts the X-rays diffractograms of two virgin samples showing the two modifications of

Table 1 A comparison between the lattice constants of KFCT recalculated in the present study and those given in the ICDD card no. 72-0450

Reference	a/Å	b/Å	c/Å	β/degree	V/Å^3	a/b	c/b	System	Figure of merit
as-given	9.396	16.860	9.413	90.30	1491.2	0.557	0.558	monoclinic	R-factor=0.143
treated by ‘Dicvol’	9.3964	16.8598	9.4122	90.30	1491.1	0.557	0.558	monoclinic	F_{49}=75.1(.0011,208)
treated by ‘Treor’	9.3962	16.8537	9.4281	90.00	1493.1	0.558	0.559	orthorhombic	F_{99}=15(.01783,392)
present study ‘Dicvol’	9.2686	17.0443	9.7424	92.08	1538.1	0.544	0.572	monoclinic	F_{50}=15.5(.0049,657)

KFCT namely the monoclinic and the tetragonal ones. The diffractograms of three KFCT samples thermally treated under different conditions and one sample irradiated by γ-rays are given in Fig. 2 so that the difference can be easily detected. The spectra of the samples after heating up to 50, 120, 360 or 510°C show considerable difference from that of the un-treated sample in both the position and profile of some reflections. It is important to know that the crystal structure of the material after heating is independent of the starting structure whether it is monoclinic or tetragonal.

As-grown crystals and effect of cooling

The monoclinic modification

The X-ray diffractogram of a KFCT sample grown at 306 K (with monoclinic structure) is shown in Fig. 1a. The spectrum of the same sample pre-cooled to the liquid nitrogen temperature shows the same pattern indicating that the cooling process has no effect on the crystal structure of KFCT a result which contradict that of Toyoda *et al*. [5], The cooling regime was as follows; the liquid nitrogen was poured in a Dewar flask in which a test tube contained powder of KFCT is kept. After two days the liquid nitrogen was thrown out and the Dewar was left to slowly warm up (during ~24 h) to the room temperature. The process was repeated three times, the X-ray diffraction was scanned and the data was treated using ‘Dicvol-91’ software. The result of the computer program is given in Table 1. We were unable to reach the same lattice parameters of the ICDD card no. 72-0450 however; our values are not far from those of the card. The maximum deviation detected is 3.38% in the case of parameter *c* while the minimum deviation is 1.08% in the case of parameter *b*. This expected difference may be attributed to the difference in growth conditions. It is worthy to know that the plane indexing obey the rule of the space group $C_{2h}(C2/c)$ and most of the plane indices are the same as those in the ICDD card no. 72-0450.

As an example of interesting results found in literature regarding crystallization process of KFCT it was reported that, under practical conditions of crystal growing, KFCT often appears either with alternating monoclinic and tetragonal layers or with totally the tetragonal modification [6, 7]. This simply means that the monoclinic modification never exists unique and the diffractogram in this case would represent a

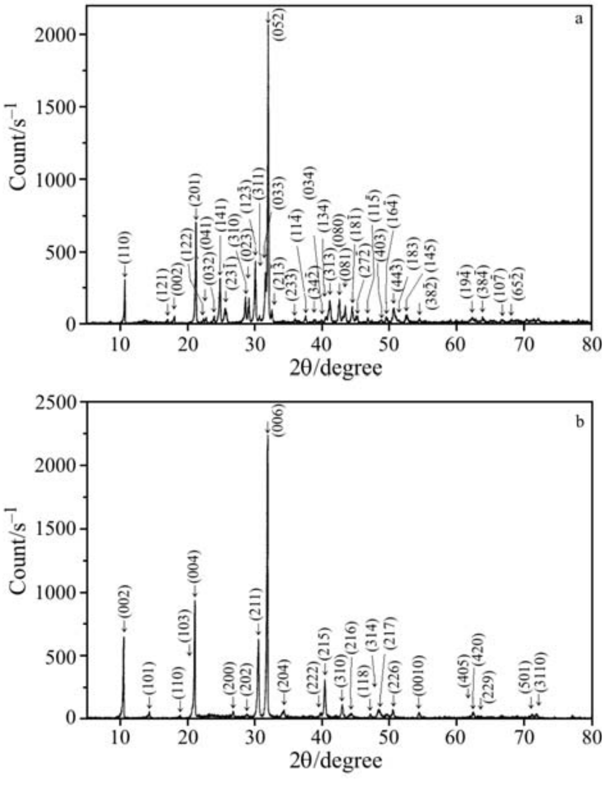

Fig. 1 X-ray diffractograms of a – the monoclinic and b – the tetragonal modifications of a potassium hexacyanoferrate(II)trihydrate single crystal scanned at the room temperature

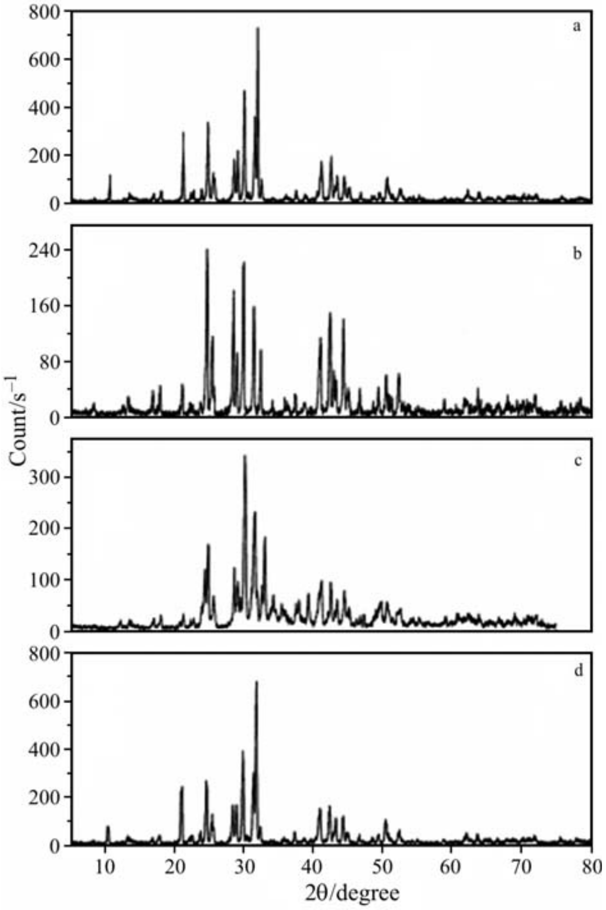

Fig. 2 X-ray diffractograms of potassium hexacyanoferrate(II)trihydrate after heating up to a – 50°C, b – 120°C, c – 360°C and d – after irradiating with 0.5 MGy γ-dose

Table 2 Misprints detected in the indexing of the reflecting planes given in the ICDD card no. 72-0450

Spacing, *d*/Å	Misprint	Correct	Spacing, *d*/Å	Misprint	Correct	Spacing, *d*/Å	Misprint	Correct
	h k l	*h k l*		*h k l*	*h k l*		*h k l*	*h k l*
6.2001	1 1 1	1 1 $\bar{1}$	2.3345	1 7 0	0 7 1	1.8373	$\bar{1}$ 1 5	1 1 $\bar{5}$
4.2970	1 3 1	1 3 $\bar{1}$	2.2332	$\bar{1}$ 5 3	1 5 $\bar{3}$	1.7880	$\bar{3}$ 3 4	3 3 $\bar{4}$
3.7680	$\bar{2}$ 2 1	2 2 $\bar{1}$	2.2224	$\bar{2}$ 4 3	2 4 $\bar{3}$	1.7821	$\bar{2}$ 8 2	2 8 $\bar{2}$
3.3336	$\bar{2}$ 0 2	2 0 $\bar{2}$	2.1061	$\bar{4}$ 0 2	4 0 $\bar{2}$	1.6853	$\bar{4}$ 6 2	4 6 $\bar{2}$
3.1000	$\bar{2}$ 2 2	2 2 $\bar{2}$	2.0518	0 4 4	4 4 0	1.4903	$\bar{2}$ 0 6	2 0 $\bar{6}$
3.0860	3 1 0	0 1 3	2.0433	$\bar{4}$ 2 2	4 2 $\bar{2}$	1.4903	$\bar{2}$ 8 4	2 8 $\bar{4}$
2.9352	$\bar{1}$ 1 3	1 1 $\bar{3}$	1.8840	$\bar{2}$ 8 1	1 8 2	1.4835	$\bar{3}$ 7 4	5 6 $\bar{2}$
2.9352	$\bar{3}$ 1 1	3 2 0	1.8840	$\bar{4}$ 4 2	4 4 $\bar{2}$	1.4011	$\bar{3}$ 1 6	3 1 $\bar{6}$
2.6147	$\bar{2}$ 4 2	2 4 $\bar{2}$	1.8734	$\bar{1}$ 7 3	1 7 $\bar{3}$			

two-phase system. For instant, this result may be helpful in understanding the negative solution given by 'Treor' software in our recalculation using the data of the card 72-0450. However, Toyoda *et al*. [5] reported that cooling KFCT down to the liquid nitrogen temperature removed the tetragonal metastable phase while heating KFCT or just in high vacuum at 40°C may remove the three water molecules [28]. Punin and Zhogoleva [39] revealed that KFCT crystals of polytypic modifications were formed under all experimental conditions regardless of the crystallization temperature and the composition of the solution. However, the percentage content of the two phases varies with crystallization conditions. The four-layer tetragonal phase (4T) was stable above 313 K while the two-layer monoclinic phase (2M) was stable below this temperature. The restrictiveness of temperature control of phase formation depended upon the composition of the solution. Addition of K_2CrO_4 to the solution sharply increased the amount of 2M phase in the region of stability of the 4T phase while addition of KOH stabilized the tetragonal phase both above and below 313 K nevertheless, the addition of stabilizing impurities did not gave completely single phase.

The tetragonal modification

Crystals grown at temperatures higher than 320°C have the structure of the tetragonal modification. Experiments carried out at temperatures lower than 320°C and with slow stirring rate may also lead to the tetragonal modification. On the other hand, crystals grown at 316 K or lower with stirring rate of 80 rpm or higher resulted in crystals with monoclinic structure.

The *d*-values of the X-ray diffraction pattern Fig. 1b of the as-grown sample as well as the cooled one are very close to those of the tetragonal modification given by the ICDD card no. 14-0695. The data of this card was processed using the two computer programs 'Dicvol-91' and 'Treor'. If the 39 reflection lines given in the card were loaded in the 'Treor' software 'no accepted solution' was resulted. After excluding six most-weak reflections (I<1%) from the load there was a solution. An identical solution was also achieved if the same reflections were loaded in the 'Dicvol-91' software. The results of our treatment are included in Table 3 together with the result given by the ICDD card no. 14-0695 for comparison. From the table, a clear difference between the lattice constants of the unit cell given by the card and those given by our recalculation is observed. Parameter c is half its value in the card, the cross-sectional area a^2 is also half that of the card. Hence the volume of the unit cell in the card is four times that of our calculations. It is important to mention the following remarks about the ICDD card no. 14-0695. First, more than 40% of the given reflections are with intensity less than 1%, the maximum Bragg angle is 60° and a Guinier type camera was used in that study. Second, a difference of about 5% between the measured and calculated density is also observed which may indicate that the sam-

Table 3 Lattice constants of virgin and pre-cooled samples of KFCT

Reference	a/Å	c/Å	V/Å^3	System	Figure of merit
as-given, card no. 14-0695	9.394	33.72	2975.70	tetragonal	F_{30}=43(.00071,99 2)
re-calculated by 'Treor'	6.6419	16.8636	743.93	tetragonal	F_{33}=34(.01005,98)
re-calculated by 'Dicvol'	6.6425	16.8565	743.76	tetragonal	F_{32}=31(.0112,92)
present, calculated by 'Treor'	6.6411	16.8525	743.26	tetragonal	F_{31}=20(.01163,136)
present, calculated by 'Dicvol'	6.6430	16.8494	743.55	tetragonal	F_{32}=15.2(.0152,139)

ple used was imperfect. In addition, it was noted that the specimen used probably consists of a mixture of the tetragonal and monoclinic forms. This could be the reason for the answer ‘no accepted solution’ given by the ‘Treor’ if all the reflections are loaded.

The data of the tetragonal modification detected in the present study was treated by the two softwares used and the result is included in Table 3. From the table it is clear that our result and that of the card after our reconsideration is very close to each other.

Interesting results were obtained from a study using thermogravimetric analysis (TG) and differential scanning calorimetry (DSC) of virgin and cooled KFCT samples.

Thermogravimetric analysis (TG)

A loss or gain in mass should be accompanied by chemical and physico-chemical changes in the structure of the material. TG was carried out in the temperature range from ambient up to high temperatures in air or nitrogen flow to clarify the effect of heating upon the mass, and hence the structure of KFCT. Figure 3 shows the mass change and its derivative of KFCT sample heated with a rate of 5°C min^{-1} up to 600°C in nitrogen flow with a rate of 30 mL min^{-1} using DuPont-2000. From the figure it is clear that a dehydration process starts at about 45 and ends at ~110°C in two successive stages during which a percentage reduction in the sample mass by about 13.5% is observed. This value is close to the value 12.8% representing the relative molecular mass of the three water molecules to the molecular mass of the potassium hexacyanoferrate(II) molecule. The first stage starts at 45 and ends at ~65°C a temperature, which was assigned by the shoulder in the derivative curve of the TG (circled in Fig. 3). Up to this temperature a mass loss of ~8.5% is detected which represents the evolution of two out of the three water molecules of crystallization. The second stage of the dehydration process extended between 65 and 110°C through which the third water molecule escaped from the crystal lattice of KFCT. The dehydration process in this manner is of special interest since it was observed during IR investigations [36] that the three water molecules in the crystal lattice of KFCT forming two groups, $(H_2O)_I$ and $(H_2O)_{II}$, and each group has its peculiar character. This difference in character was attributed to a difference in the chemical bonding between certain water molecule and the crystal lattice because of its location in the network. Accordingly, it is not surprising that the two groups left the crystal lattice of KFCT one after the other during the heating process. Our result represents a confirmation to the grooping character of water molecules in KFCT. In addition, it has become of considerable interest to study the effect of heating up to about 50°C for a short time upon the crystal structure of KFCT.

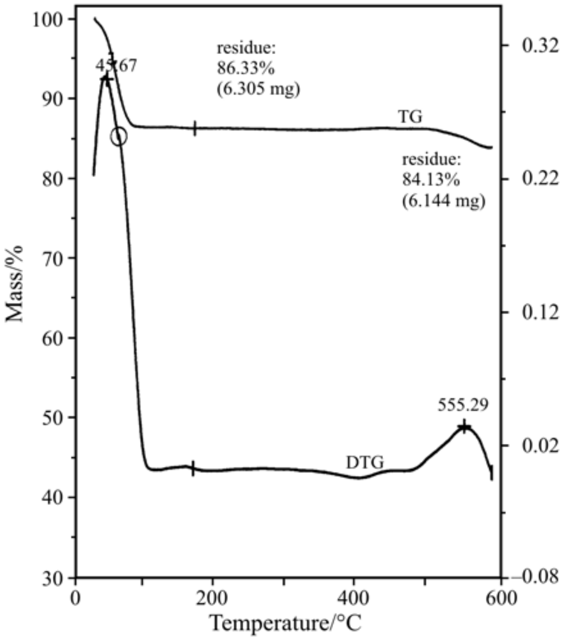

Fig. 3 Thermogravimetric curves showing the mass loss due to the evolution of the three water molecules from the lattice of a potassium hexacyanoferrate(II)trihydrate crystal; heating rate 5°C min^{-1}, nitrogen flow rate 30 mL min^{-1}

The TG was then repeated for a sample previously heated up to 120°C, i.e. sample without the water molecules. The heating rate was 5°C min^{-1} in air flow with a rate of 30 mL min^{-1}. Figure 4 shows the TG trace of this experiment. From the figure it is clear that a sharp increase, by ~4%, took place in the sample mass at 360°C followed by a slight decrease and then another slow continuous increase in mass, by about ~4.5%. The second step extended over ~170°C. After repeating the TG experiment using fresh sample

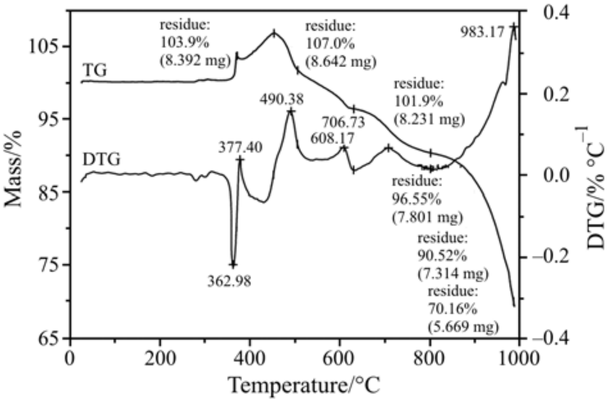

Fig. 4 Thermogravimetric response in air (flow of 30 mL min^{-1}) showing the reaction of anhydrous potassium hexacyanoferrate(II) with oxygen at about 360°C

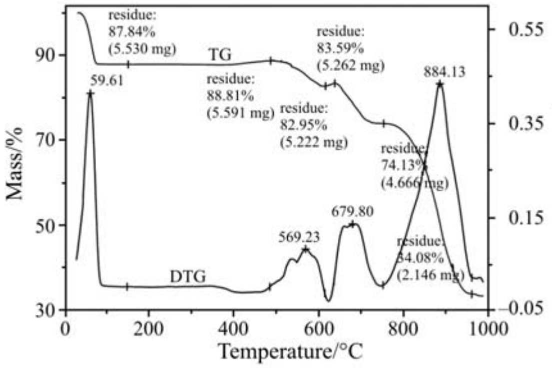

Fig. 5 Thermogravimetric response (heating rate 10°C min^{-1}) in nitrogen (flow of 30 mL min^{-1}) of potassium hexacyanoferrate(II)trihydrate. N.B. Reaction at 360°C is not displayed

in a nitrogen gas flow with a rate of 50 mL min^{-1}, the sharp increase in mass disappeared completely while the slow continuous increase in mass is still observable but with an increase in mass by about ~1.4%, Fig. 5. This may be attributed to small oxygen content in the nitrogen gas used. The two observed processes might be well understood in the light of a change in the iron chemical form from Fe^{2+} to Fe^{3+} in the presence of air (oxygen), which was easily detected, by the observed change to the light brown colour. The proposed equation of reaction is as follows:

$$K_4[Fe(CN)_6]+0.5O_2 \xrightarrow{heat} K_3[Fe(CN)_6]+0.5K_2O_2 \qquad (1)$$

Following this process by continuous heating in air K_2O_2 would change to KO_2 according to the reaction:

$$K_2O_2 \xrightarrow{O_2} 2KO_2 \qquad (2)$$

Calculations of the increase in molar mass of the material due to the absorption of an oxygen atom in each step confirm the above mentioned equations.

From the thermogram it is clear that a change in the structure would take place if KFCT is heated in air up to temperatures higher than 360°C. Three probabilities for the final product may exist according to the maximum heating temperature (MHT) attained. The product is a two-phase system $K_3[Fe(CN)_6]$ and K_2O_2 if the MHT is 360°C. If the MHT is between 360 and 530°C, the product may be a three-component system, $K_3[Fe(CN)_6]$, K_2O_2 and KO_2. For MHT exceeding 530°C the product probably is $K_3[Fe(CN)_6]$ and KO_2. A confirmation to the observed chemical and physical changes observed at ~360°C will be presented later in this paper while discussing the DTA of a KFCT sample.

It is worthy to know that when the experiment was repeated in nitrogen flow with another sample having the tetragonal modification, the TG curve shown in Fig. 4 was resulted. From the figure we could not detect the two-stage evolution process of water molecules and instead a reduction of mass by 12.2% up to ~90°C was observed. This may indicate a difference in the position (hence hydrogen bonding) of the three water molecules in the two modifications of KFCT crystal.

Differential scanning calorimetry (DSC)

Figure 6 shows the DSC of virgin sample scanned up to 600°C using Shimadzu DTA-50 with a rate of 5°C min^{-1} in nitrogen atmosphere with a flow rate of 30 mL min^{-1}. A structural variation indicated by a sharp endothermic peak is observed at ~110°C. This structural variation is due to the evolution of the three water molecules and most likely indicates a change from the tetragonal modification (structure of virgin or even after cooling to the liquid nitrogen as-grown crystal) to the monoclinic structure of the anhydrous form of potassium hexacyanoferrate(II). The same result was also detected for KFCT sample cooled down to the liquid nitrogen temperature over night (more than 12 h). This result was not expected in the light of the obtained information from the literature. It is important to know that all our measurements were done using almost perfect, free from observable defects and transparent crystalline layers of KFCT and that each experiment was repeated twice.

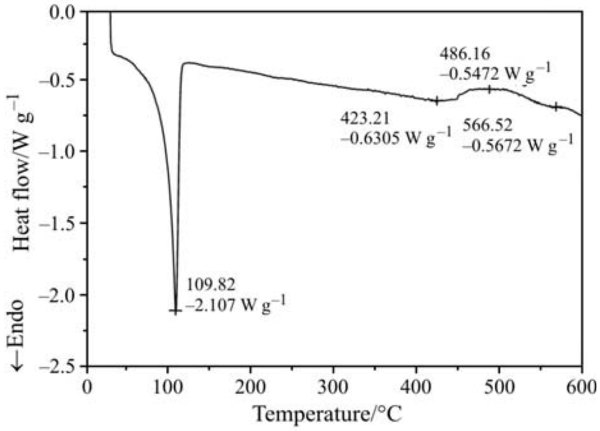

Fig. 6 Differential scanning calorimetry of potassium hexacyanoferrate(II)trihydrate showing the crystallographic phase change at 110°C (heating rate 5°C min^{-1})

Between 423 and 566°C there is a broad extended exothermic reaction. This may be due to a chemical reaction with oxygen, which is a result of insufficient nitrogen flow, or due to the presence of some oxygen in the used nitrogen gas. More clarification of this point will be considered during the discussion of the DTA.

Heating up to 50°C for 20 min

Based upon the result of Fig. 3 we assumed that slightly heating of KFCT for minutes might convert the crystal to the monohydrate modification therefore the following experiment was conducted. The X-ray diffraction pattern of slightly heated (at 50°C for 20 min) KFCT sample is not far from the monoclinic modification of KFCT, nevertheless this pattern is different from the pattern given by the ICDD card no. 25-1354 representing potassium hexacyanoferrate(II)monohydrate. The data of this card was retreated by 'Dicvol-91' and 'Treor' to check the lattice constants given since our result does not match the corresponding values in the card in addition to the small value given for the figure of merit. The system given by the card is a tetragonal one with the constants a=9.394 Å, c=33.72 Å, V=2975.7 Å^3, Z=8 and S.G. I4$_1$/a (88) with F_{23}=1(0.127,171) and one unindexed line. The recalculation by 'Treor' software revealed no solution accepted while the 'Dicvol-91' solution is a=9.234 Å, c=34.002 Å, V=2899.25 Å^3 with F_{23}=0.9(0.0695,369). Our data using the 'Treor' and 'Dicvol' computer programs is given in Table 4. There is no detectable difference between the two solutions, even when the 'Treor' program was loaded by its maximum capacity. The only difference is observed in the case of figure of merit of the two trails carried out by 'Treor'. This may be attributed to the difference in the number of reflections inserted in each case and weak reflections included in the case of processing with full-loaded program. The reason for the non-coincidence between our result and that of the literature may be the very critical temperature and time needed to convert KFCT totally to its monohydrate form. This point, perhaps needs more clarification.

Heating up to 120°C for 4 h

After heating KFCT up to 120°C for 4 h the powder changed to light yellow and the pattern was changed considerably from that of KFCT. This may be due to a change to the anhydrous form of potassium hexacyanoferrate(II) $K_4[Fe(CN)_6]$, here after KFC. The data of the X-ray diffraction pattern was processed using the two software programs and the result was found very close to the data of the ICDD card no. 32-0801. For more clarification, and as another test for the two-computer software programs used here, the d-values given in this card were used to recalculate the lattice constants of KFC. Table 5 gives a comparison between the lattice constants of our sample and those given in the ICDD card no. 32-0801 in addition to the results of the recalculation using the two computer softwares. The maximum deviation between our results and that of the card does not exceed 0.15%.

It is worthy to know that the indexing of all the planes are the same in the three cases up to the maximum d (1.745 Å) given in the card. It is also important to know that the KFC material used in the study leading to the data of the ICDD card no. 32-0801 was achieved after heating potassium hexacyanoferrate(II) monohydrate at 115°C for 3 weeks. The indexing of planes with d-values less than 1.754 Å and down to a value of 'd' equals 1.218 Å that does not exist in the ICDD card no. 32-0801 is given in Table 6.

Differential thermal analysis (DTA)

Figure 7 shows the time and temperature dependence of the DTA response of pre-cooled KFCT sample scanned up to 800°C with a constant rate of 5°C min^{-1} in ambient atmosphere. The trace shows a small endothermic peak at the beginning of the run with a maxi-

Table 4 Lattice constants of KFCT heated up to 50°C for 20 min

Program	a/Å	b/Å	c/Å	V/Å^3	β/degree	Figure of merit
'Treor', full load	13.0238	16.7068	9.04547	1669.94	121.95	F_{99}=10(.0099,1050)*
'Treor', half load	13.0250	16.7056	9.04622	1669.94	121.96	F_{50}=20(.004751,548)
'Dicvol-91'	13.0377	16.699	9.04300	1670.87	121.93	F_{50}=6.5(.0140,544)

*with one unindexed line

Table 5 A comparison between the lattice constants of KFC calculated in the present study and those given in the ICDD card no. 32-0801

Reference	a/Å	b/Å	c/Å	V/Å^3	Figure of merit
as-given in the card	14.010(7)	21.027(6)	4.1751(3)	1229.94	F_{30}=23(.0157,83)
re-treated by 'Treor'	13.9936	21.0240	4.17715	1228.92	F_{32}=14(.0131,184)
re-treated by 'Dicvol-91'	14.0196	21.0000	4.18048	1230.78	F_{32}=8.8(.0197,185)
our sample 'treated by Treor'	13.9965	21.0495	4.17295	1229.43	F_{38}=16(.00518,483)
our sample 'treated by Dicvol-91'	13.9499	21.1204	4.17192	1229.17	F_{38}=2.2(.0354,483)

Table 6 Indexing of KFC planes having '*d*' values less than 1.745 Å

Spacing, *d*/Å	*h k l*	Spacing, *d*/Å	*h k l*	Spacing, *d*/Å	*h k l*
1.5680	8 6 0	1.3985	10 1 0	1.2560	4 4 3
1.5010	0 14 0	1.3985	2 15 0	1.2150	10 7 1
1.4610	9 5 0	1.3730	1 2 3	1.2150	9 4 2
1.4610	5 12 1	1.3220	1 15 1		

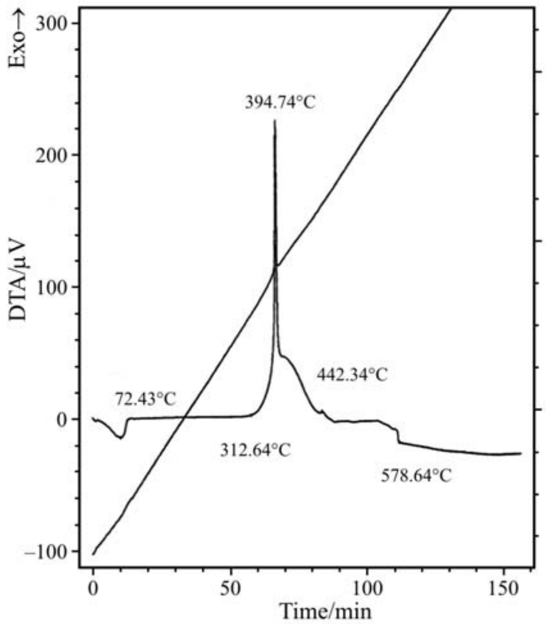

Fig. 7a Time dependence of the DTA response of a potassium hexacyanoferrate(II)trihydrate sample scanned between room temperature and 800°C

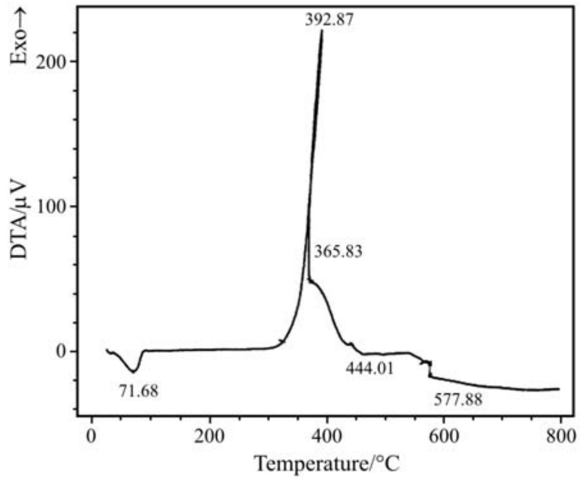

Fig. 7b Temperature dependence of the DTA response of a potassium hexacyanoferrate(II)trihydrate sample scanned between room temperature and 800°C

mum at about 72.5°C referring to the evolution of the three water molecules from the KFCT lattice. A very sharp peak referring to a fast chemical reaction may be associated with a structural change that started at ~310 and ended at 371°C as clearly observed by a steep exothermic peak. A lot of heat was released due to this chemical reaction which resulted in a fast increase (by more than 30°C) in the temperature of the sample (mass of about 20 mg). This process is followed by a less pronounced (but quite detectable) slow chemical reaction process extending up to ~444°C and manifests itself as a less step wise response. These two signals might represent the two chemical reactions proposed by Eqs (1) and (2).

Heating up to 360°C

In the ICDD data bank, the values given for the lattice parameters of $K_3[Fe(CN)_6]$, here after K_3FC, are not without inconsistent. This is, of course, because of a difference in the method of sample preparation and/or a sample impurity content. For more clarification, data collected from the ICDD about crystal structure of K_3FC together with the results of our calculations for a sample heated up to 360°C are presented in Table 7. The results of the calculations using the 'Dicvol-91' and 'Treor' software programs are almost the same. However, a deviation from the data given in the literature is observed. If our results are compared with the results of the card no. 77-2222 a minimum deviation of ~0.5% in the case of parameter *a* and a maximum deviation of ~4.3% in the case of parameter *c* could be observed. This difference may be because of the existence of another phase (K_2O_2) with K_3FC even after excluding the lines that probably are belonging to this phase from the data inserted in the computer software. It is important to know that the indexing of the planes in the two solutions of 'Dicvol-91' and 'Treor' obeys the selection rule of the same space group of the monoclinic system as given in the literature.

Heating up to 510°C

The pre-heated material was then subjected to thermal heating up to 510°C at which KO_2 is supposed to be formed. The resultant powder was scanned by X-ray and the diffraction pattern was treated by the two computer programs 'Dicvol-91' and 'Treor'. The result of the treatment is presented in Table 8. From the table it is clear that the solution given by the two computer programs is the same within the experimental error. The material is still monoclinic as it was after heating up to 360°C. Its colour has changed to dark

Table 7 A comparison between the lattice constants of $K_3[Fe(CN)_6]$ given in the ICDD and data of KFCT heated up to 360°C calculated in the present study

Samples	a/Å	b/Å	c/Å	Z	β/degree	V/Å^3	Figure of merit
card no. 22-0818	13.471	10.417	8.402	4	90.11	1179.03	F_{30}=16(.0105,181)
card no. 75-2114	7.06(3)	10.38(4)	8.4(3)	2	107.00	588.68	RF=0.30
card no. 73-0650	7.03(4)	10.31(5)	8.35(4)	2	107.20	578.14	RF=0.077
card no. 83-2108	13.422(4)	10.399(6)	8.381(4)	4	90.00*	1169.78	RF=0.046
card no. 77-2222	14.021(2)	10.401(1)	8.339(2)	4	107.21	1161.65	RF=0.027
our sample ‘treated by Treor’	14.0857	10.4857	8.6912		110.33	1203.70	F_{58}=5(.023,626)
our sample ‘treated by Dicvol’	14.0903	10.4622	8.6980		110.27	1202.80	F_{50}=2.7(.0303,622)

*orthorhombic structure

Table 8 Lattice constants of $K_3[Fe(CN)_6]$ heated up to 510°C

Computer program	a/Å	b/Å	c/Å	β/degree	V/Å^3	Figure of merit
‘Dicvol-91’	13.9853	12.7921	8.4311	106.64	1445.13	F_{46}=5(.0107,848)
‘Treor’	13.9881	12.7924	8.4263	106.61	1444.87	F_{45}=12(.004689,850)

Table 9 The lattice constants of as-grown and pre-cooled irradiated KFCT crystals

Samples	a/Å	b/Å	c/Å	V/Å^3	Figure of merit
standard, (ICDD card no. 32-0801)	14.010(7)	21.027(6)	4.1751(3)	1229.94	F_{30}=23(.0157,83)
irradiated, treated by ‘Treor’	14.0501	21.0554	4.1640	1231.84	F_{42}=5(.01769,479)
irradiated, treated by ‘Dicvol-91’	14.0464	21.0568	4.1653	1231.98	F_{42}=4.7(.0191,479)

brown and its unit cell parameters are increasing. The increase is thought to be mainly due to irreversible thermal effect and/or the formation of the second phase. It may also be possible to incorporate K_3FC as defect centers with the crystal lattice.

Heating up to 850°C

Further heating of anhydrous potassium hexacyanoferrate(II) in air up to 850°C led to the formation of a dark brown hygroscopic material. The proposed equation of the chemical reaction probably took place up to this temperature is:

$$K_3[Fe(CN)_6]+3O_2 \xrightarrow{\sim 850^\circ C} KFeO_2+2KO_2+(CN)_6 \quad (3)$$

According to the TG (Fig. 4) the residual material is ~88.0% of the starting anhydrous potassium hexacyanoferrate(II). The total molecular mass of $KFeO_2$ plus $2KO_2$ is 269.146 which represents 82.0% relative to the molecular mass of KFC. This confirms our idea about changes took place during heating up to 850°C. After the residual material was washed with distilled water and then filtered to remove KO_2 the material was subjected to X-ray study. The X-ray pattern revealed that $KFeO_2$ converted to an amorphous structure.

Effect of γ-irradiation

To our knowledge the effect of γ-irradiation on the crystal structure of KFCT has not been done before. We investigated the effect of γ-irradiation on the lattice constants of KFCT crystal. It is well known that γ-irradiation strongly affect most of physical and chemical properties of ferroelectrics. Recently, considerable changes in the IR spectrum of the ferrocyanide ion and the three water molecules were detected after irradiating KFCT with different γ-doses [35, 36].

Irradiating samples of KFCT shows considerable changes in their lattice parameters. Two samples were irradiated with the same γ-dose $5\cdot10^5$ Gy. One of them was virgin (as-grown) while the other was pre-cooled to the liquid nitrogen temperature. Difference was not detected between the X-ray diffraction pattern in the two cases. The X-ray patterns were computed and the result is given in Table 9. From the table it is clear that the system, as given by both the ‘Dicvol’ and the ‘Treor’ programs, is orthorhombic with lattice constants very close to those of the KFC sample. This result indicates that the effect of γ-irradiation with a dose as high as $5\cdot10^5$ Gy on KFCT is the same as heating up to 110°C due to which the crystal looses its water of crystallization. We believed that a critical γ-dose may be found below which the structure of the sample will be unaffected and above which the structure may convert to that of KFC. In addition, it is expected that pre-irradiated with a γ-dose of $5\cdot10^5$ Gy KFCT, the crystal would never return back to its ferroelectric state if it is cooled down the phase transition temperature at ~249 K. Starting with small doses, gradual increase in the γ-dose would result in a gradual increase in the disordering of the water molecules of crystallization. Consequently this would lead to a gradual reduction in the value of the spontaneous polarization of KFCT. At high γ-doses the crystal would loose its three water molecules, may be one after the two, and the spontaneous polarization vanishes. In general, it was observed that spontaneous polarization of ferroelectrics decreases under the influence of γ-irradiation in different doses. This is an interesting point and it needs more experimental verification.

Conclusions

- Two computer software programs, 'Dicvol-91' and 'Treor' were used to analyze X-ray diffraction pattern of KFCT crystals. In some cases the accepted solution extracted from the two programs is the same while in other cases either it is different or there is no accepted solution. This difference may be because of a difference in the strategy of each program and/or their maximum capacity. We believe that for a number of reflections less than 5 the 'Dicvol-91' program is recommended while for total number of reflections greater than 50 the 'Treor' program is recommended. Both may be used and the result can be compared in other than these two extreme cases.
- The effect of heat treatment on the crystal structure of KFCT revealed significant variations in the unit cell parameters of the crystal. The as-grown crystal has a tetragonal or monoclinic structure depending upon conditions of crystal growing. After cooling virgin tetragonal sample to the liquid nitrogen temperature its structure never changed to the monoclinic system. Upon heating up to ~50°C the sample losses two out of its three water molecules and the structure changes to that of KFC monohydrate. While heating up to 120°C in air, the crystal lost the third water molecule of crystallization and converted to the monoclinic KFC. While further heating up to a temperature of ~360°C in air iron changed suddenly from ferrous to ferric and the material converts to $K_3[Fe(CN)_6]$ with a second phase of K_2O_2. If the heating process proceeds in air the second phase changes to KO_2 without a change in the structure of $K_3[Fe(CN)_6]$. The structure of $K_3[Fe(CN)_6]$ is monoclinic with lattice constants very close to those detected in the literature.

  The following sequence with temperature is believed to occur

$$\begin{gathered} KFC(3H_2O)\xrightarrow{\sim 50^\circ C}KFC(H_2O)\xrightarrow{\sim 110^\circ C} \\ KFC\cdots+O_2\xrightarrow{\sim 360^\circ C} \\ K_3[Fe(CN)_6]+K_2O_2+O_2\xrightarrow{\sim 420^\circ C} \\ K_3[Fe(CN)_6]+2KO_2 \end{gathered} \tag{4}$$

- Irradiating KFCT with γ-dose of $5\cdot10^5$ Gy changed the symmetry and dimensions of the unit cell. The effect of γ-irradiation is almost the same as heating up to 120°C, the sample lost its water of crystallization and hence it is expected that γ-irradiation with a dose of $5\cdot10^5$ Gy would inhibit spontaneous polarization in KFCT crystal.

Acknowledgements

The authors are grateful to Prof. Abousehly, Al-Azhar University, Assiut Branch and Dr. Abu-Zayed, Faculty of Science, Assiut University, Assiut, Egypt for the DTA, DSC and TG measurements. The authors wish also to thank the staff of the Radiotherapy and Nuclear Medicine Department, Assiut University, Assiut, Egypt for irradiating the samples.

References

1 R. Kiriyama, H. Kiriyama, T. Wada, N. Niizeki and H. Hirabayashi, J. Phys. Soc. Jpn., 19 (1964) 540.
2 S. Waku, H. Hirabayashi, H. Toyoda, H. Iwasaki and R. Kiriyama, J. Phys. Soc. Jpn., 14 (1959) 973.
3 S. Waku, K. Masuno, T. Tanaka and H. Iwasaki, J. Phys. Soc. Jpn., 15 (1960) 1185.
4 A.Ya. Krasnikova and I. N. Polandov, Sov. Phys. Solid State, 11 (1970) 1421.
5 H. Toyoda, N. Niizeki and S. Waku, J. Phys. Soc. Jpn., 15 (1960) 1831.
6 H. Toyoda, N. Niizeki and S. Waku, J. Phys. Soc. Jpn., 15 (1960) 10.
7 Yu. O. Punin and V. Yu. Zhogoleva, Izvestiya Akademii Nauk SSSR, Neorganicheskie Materialy, 16 (1980) 1785.
8 D. E. O'Reilly and T. Tsong, J. Chem. Phys., 47 (1967) 4072.
9 T. Tsang and D. E. O'Reilly, J. Chem. Phys., 43 (1965) 4234.
10 A. Ya. Krasnikova and V. A. Koptsik, Sov. Phys. Solid State, 10 (1968) 709.
11 D. E. O'Reilly and G. E. Schacher, J. Chem. Phys., 43 (1965) 4222.
12 J. C. Taylor, M. H. Mueller and R. L. Hitterman, Acta Crystallogr. Sect. A: Found. Crystallogr., 26 (1970) 559.
13 I. Savatinova and E. Anachkova, Phys. Stat. Sol. B, 84 (1977) 401.
14 E. Anachkova and I. Savatinova, Spectrosc. Lett., 16 (1983) 879.
15 W. C. Nieuwpoort, D. Post and P. Th. Van Duijnen, Phys. Rev. B, 17 (1978) 91.
16 Y. Hazony, D. E. Earls and I. Lefkowitz, Phys. Rev., 166 (1968) 507.

17 R. Blinc, M. Brenman and J. S. Waugh, J. Chem. Phys., 35 (1961) 1770.
18 J. J. Rush, P. S. Leung and T. I. Taylor, J. Chem. Phys., 45 (1966) 1312.
19 R. Kroon, R. Sprik and Ad Lagendijk, Phys. Rev. B, 42 (1990) 2785.
20 E. Anachkova, I. Savatinova and M. Szostack, J. Mol. Struct., 115 (1984) 83.
21 M. A. Gaffar and M. I. Abd-Elrahman, Phys. Status Solidi B, 225 (2001) 271.
22 M. A. Gaffar and M. I. Abd-Elrahman, Physica B (Condensed Matter), 304 (2001) 423.
23 S. Waku, K. Masuno and T. Tanaka, J. Phys. Soc. Jpn., 16 (1961) 1158.
24 S. Fukunishi, S. Kittaka, Y. Makita and S. Waku, J. Phys. Soc. Jpn., 23 (1967) 1181.
25 S. Waku, K. Masuno and T. Tanaka, J. Phys. Soc. Jpn., 15 (1960) 1698.
26 T. Nakagawa, S. Sawada, T. Kawakubo and S. Nomura, J. Phys. Soc. Jpn., 18 (1963) 1227.
27 I. G. Amov, K. I. Kirov and S. D. Toshev, Sov. Phys. Crystallogr., 17 (1973) 1101.
28 M. A. Gaffar and A. Abu El-Fadl, Physica B, 292 (2000) 221.
29 M. A. Gaffar, A. El-Korashy, A. M. Abdalla and M. Almokhtar, Physica B, 193 (1994) 277.
30 E. Anachkova, H. Rarajczak and I. Savatinova, Phys. Stat. Sol. B, 108 (1981) 65.
31 I. Savatinova, E. Anachkova and E. V. Chisler, Sov. Phys. Solid State, 23 (1981) 1568.
32 E. Anachkova, I. Savatinova and H. Ratajczak, J. Mol. Struct., 78 (1982) 153.
33 H. Flores Llamas, Rev. Mex. Fis. (Mexico), 44 (1998) 385.
34 A. McNaughtan, R. O. Ansell and J. R. Pugh, Sensors and their Applications VII. Proceedings of the Seventh Conference on Sensors and their Applications. Institute of Physics Publishing, 65 (1995).
35 A. McNaughtan, R. O. Ansell and J. R. Pugh, Meas. Sci. Technol., 5 (1994) 789.
36 Chun-Nan Hsu, Kwo-Ping Chang, Chia-Liang Tseng and Wei Ho, Nucl. Sci. J. (Taiwan), 30 (1993) 395.
37 P. M. De Wolff, J. Appl. Crystallogr., 5 (1968) 108.
38 G. S. Smith and R. L. Snyder, J. Appl. Crystallogr., 12 (1979) 60.
39 Yu. O. Punin and V. Yu. Zhogolevam, Izvestiya Akademii Nauk SSSR, Neorganicheskie Materialym, 16 (1980) 1785.

Received: October 5, 2004
In revised form: February 23, 2005

DOI: 10.1007/s10973-005-6823-4