Effect of Thermal Neutron Irradiation on the Growth and Structure of K_2SO_4 Crystal

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Abstract

In this work we studied the effects of K_2SO_4 crystal which is exposure to thermal neutron radiation. This crystal was grown by slow evaporation of the aqueous solution technique to the size (28 x 6x 6)mm^3.X-ray powder diffraction was used to identify the structures for before and after irradiation samples. Lattice parameter calculations revealed orthorhombic crystal system for before irradiation and monoclinic for after irradiation sample. Then we followed it by DSC which allowed us to highlight the high temperature phase transition around T_c581.9°Cfor before irradiation and at 670ºC for after irradiation .The difference in T_c at high temperature during heating run indicates for structural changed. Then IR study verifies the reduction in crystal symmetry, which indicates to the correlation between thermal neutron irradiation and structure of K_2SO_4.

Keywords: Thermal neutron, Isomorphism**,** Single crystal, Phase transition, Symmetry reduction, after irradiation.

Introduction

Potassium sulphate(PS) K_2SO_4) is a material of great interest fertilizer and many other applications, like analytical chemistry as reagent, medicine, gypsum cements, glass manufactures ,food additive(Periasamy et al 2009) and recently in biodiesel production Lipase-coated K_2SO_4 micro-crystals (Zhengetal2012)[1,2].The isomorphism structure of K_2SO_4crystals with K_2SeO_4 salt compounds are the reference ones while studying the effects of various kinds in ferroic crystals of group. There are two groups of compounds with an A_2BX_4-type chemical formula having different crystal structures. One is the group of substances having an orthorhombic structure with a space group of P_{mcn} at room temperature. The other is the group having a monoclinic structure with a space group of $P2_1/m$ at room temperature (Fuminao et al 2011)[3].K_2SO_4 crystallizes in the room temperature into orthorhombic system with space group $P_{mcn}(D^{16}_{2h})$ of lattice parameters a=5.763Å, b=10.071Å and c=7.476Å(Stadnyk et al 2013)[4]. It revealed a sequence of phase transitions that include disordered and incommensurate phases upon heating at 587°C into a hexagonal structure (commensurate ferroelastic phase) with lattice parameters a=5.921Å and c=8.182Å, of space group $P6_3/mmc(D^4_{6h})$(Arnold etal1981)[5].Upon cooling, there is probably another phase transformation, from orthorhombic to monoclinic at 56 K with space group $P2_1/b$ (C^5_{2h}) of displacive type.(Ahmed **1996)**[6].

According to nuclear theory, thermal neutron may be captured by nuclei in the irradiated material, possibly changing its identity, produces an isotope of that nucleus, that is due to focus its energy into highly localized areas and the crystal structure of the irradiated material may be modified. The most common interaction of free neutrons with the nuclei of other materials are absorption and scattering. Scattering results in the transfer of some of its energy and the neutron continues to move through the irradiated material but at a lower energy and hence lower velocity .Its velocity is equivalent to thermal motion of a material, 2200 m/sec. and the corresponding energy <E> is 0.025 eV, which is the most probable energy in the distribution at room temperature (20◦C). The average energy of thermal neutrons at room temperature is 0.038 eV. Which is the upper limit ~0.4 eV (Cadmium cutoff) and epithermal , just above 0.4 eV. As thermal neutrons are of low energy, usually only a high flux density or a long exposure induces the change in materials(James 2007) and (Myrzakhmet 20013)[7,8].Kamali and Walton1985 [9] ,attributed their electron spin resonance spectra of (PS) ,which was irradiated by gamma, electron, neutron and fission fragments due to the formation of SO^-_3, SO^-_4, SO^-_2 , and O^-_3radical ions. The most intense radical ion was due to the SO_3, and the other radicals were relatively much lower in intensity. There have been many articles published, concerning both pure and applied aspects, on the; K_2SO_4 however, the use of thermal neutron radiation to modify the properties of (PS) is relatively unreported. The present work focuses on irradiated (PS) by thermal neutron, grown single crystal to the size of(28 x 6x 6)mm^{3}then study the effect of thermal neutron irradiation on its properties. So, the Fundamental goals of irradiation are to correlate physical properties of (PS) with their crystal structures and to determine the impact of irradiation on crystal parameters and phase transitions.

2 Experimental details

2-1 Growth of the crystal

Single crystals of K_2SO_4 was grown by using slow evaporation technique from saturated aqueous solution of one molar concentration .The solution prepared by dissolving 34.86 gm of potassium sulphate powder, (Chem-

Supply PTY.LTD analytical reagent AR 99.5%) as a source of (PS) which was purified by re crystallization into 200 ml of double distilled water .The aqueous solution was mixed with magnetic stirrer for two hours at 200 rpm and 50º C . Then, we poured it into crystallization vessel, during slow evaporation process; the crystallizers were covered with perforated plastic sheet and kept in a dust free in the undisturbed oven at 40°C .After 3-5 days, small crystals were grown as a result of spontaneous nucleation in the bottom of the vessel. It appeared as singular and of regular shape with well faceted .So, we allowed it to grow larger. At the end of growth period (50 days) a crystal of dimensions(28 x 6x 6)mm^3 are obtained. Some of the grown crystal was exposed to neutron irradiation. Crystal habit for the grown crystal and its morphology will be discussed.

2-2 Sample preparation for irradiation

Powder samples are obtained from the grown crystal, then divided into two parts. One of them was kept as reference specimen and the other was irradiated.

The neutron radiation source used for the sample irradiation was produced from an^{241}Am-^{9}Be source with activity 12Ci and flux10^{5}n.cm^{-2}.s^{-1}. The sources is made by mixing the target material like Beryllium with a suitably strong α- source. When Beryllium is bombarded by α particle, it undergoes a number of reactions, which lead to the production of free neutrons according to (α n) type nuclear reaction).

$$ {}_{4}^{9}Be + {}_{2}^{4}He \rightarrow {}_{6}^{12}C + {}_{0}^{1}n + 5.7MeV $$

Taking Am^{241}as an α-source of energy to yield a neutrons beam of (6.048x10^{10} n.cm, that is used to irradiate the sample for seven days in room temperature and atmospheric pressure.

2-3 Powder XRD

The X-ray diffraction patterns were recorded in a (Shimadzu XRD-6000) using copper target (Cu K_α, 1.5418 Å), (40 kV and 30 mA). The samples were mounted an on glass sample holder. Step-scan data were collected from different ranges with a step width of 0.02° and a counting time of 5 sec/step.

3-4The mid-infrared,

FTIR Shimadzu spectrophotometer model 8400S is used to study the fundamental vibrations K_2SO_4 .The (PS) samples were finely ground for one minute, combined with oven dried KBr (2 mg K_2SO_4/200 mg spectroscopic grade KBr) and pressed into a disc .The spectrum of the sample was recorded in transmittance (%) mode with 50 scans at 4 cm^{-1} resolution between 400 cm^{-1} and 4000 cm^{-1} (2.5–25 µm),for pre- irradiated and post irradiated samples at room temperature.

4-5Differential scanning calorimetric is preformed using Linsess (STR PT-1000)

3 Results and Discussion

3-1Crystal growth and morphology

Transparent, colorless single crystals of (PS) were grown from an aqueous solution by slow evaporation for before irradiation sample .The photograph of the as-grown crystals is presented in Figure (1).

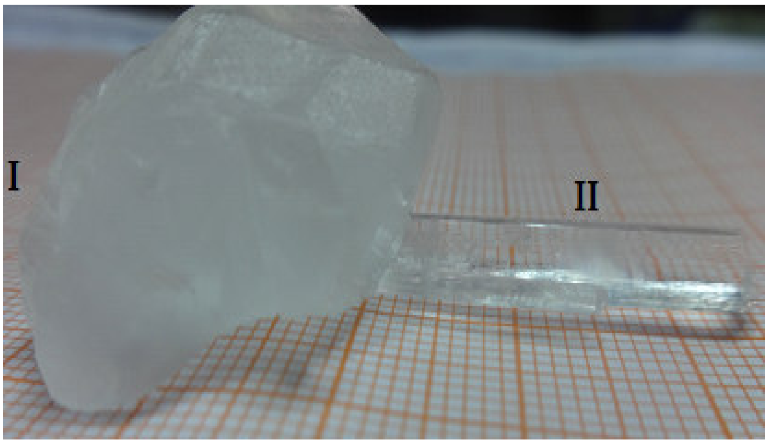
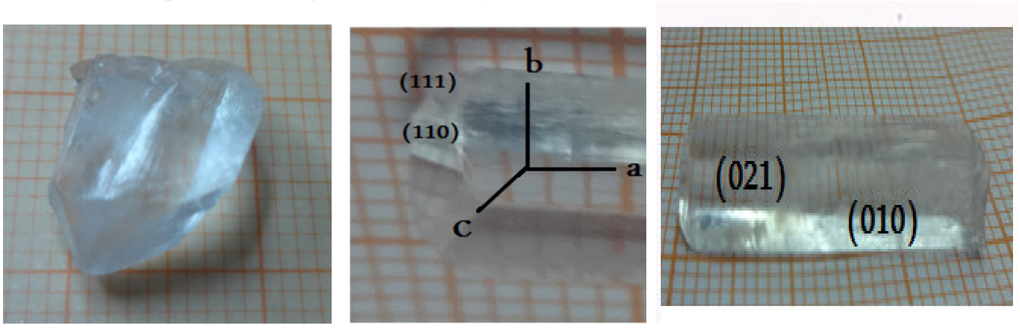


Fig.(1)Photography of the grown K_2SO_4 crystal ,(I)Dipyramidal, and (II) Elongated hexagonal pyramids.

K_2SO_4 is crystallized in two different habits of crystal belonging to orthorhombic .This is due to the effect of interactions between solute and solvents molecules at the various crystal interfaces, which may have a dominant role on the shape of the crystal morphology that is obtained from solution growth .So, preferential adsorption of solvent molecules on a particular faces delay the growth rate of other faces(Singh 2006)[10].Left side(I)shows a crystal a predominant dipyramidal or prismatic habit with dimensions (25x22x18)mm^3, with b-axis along the long axis of the pyramid and the c-axis was along one edge of the quasi-triangular basal plane. While the other one is on the right side with dimensions(28 x 6x 6) mm^3 , represent a combination crystal terminated by hexagonal pyramids from one end and with six flat parallel faces along the direction of its elongation which was with the same form as that presented by (Mullin 2001)([11]. Twinning is occurred in(PS) crystal grown from aqueous solution with three ferroelastic domains under a polarizing microscope at room temperature, and their boundary(domain walls) disappeared at 860K(Chbn and Wang 1997)[12].This means triple twin is related to three twin mirror planes or twofold twin axis .The permissible walls for any two adjacent domain pairs are derived by the symmetry approach to a crystal undergoing the structural phase transition by considering the twin structures across the domain boundaries (Dhanaraj et al 2010)[13].

Fig1 exhibits the habit of actual shape of the as grown single crystal .The difference in the two grown crystal form (I &II) appeared due to the possible of non uniformity of actual conditions of growth, like temperature gradient, concentrate and other factor. So, the actual shape does not differ drastically from the ideal. The re crystallization growth of after irradiation (PS) K_2SO_4 sample ,lead to prismatic habit to the dimensions (13x11x5) mm^3 with a flat plane as shown in fig.2a.While fig .b represents the photograph crystal (II) with more details about its planes and direction. Fig.c represents a single part from other side of part(II) with marked Miller indices for the planes of the grown K_2SO_4 crystal.

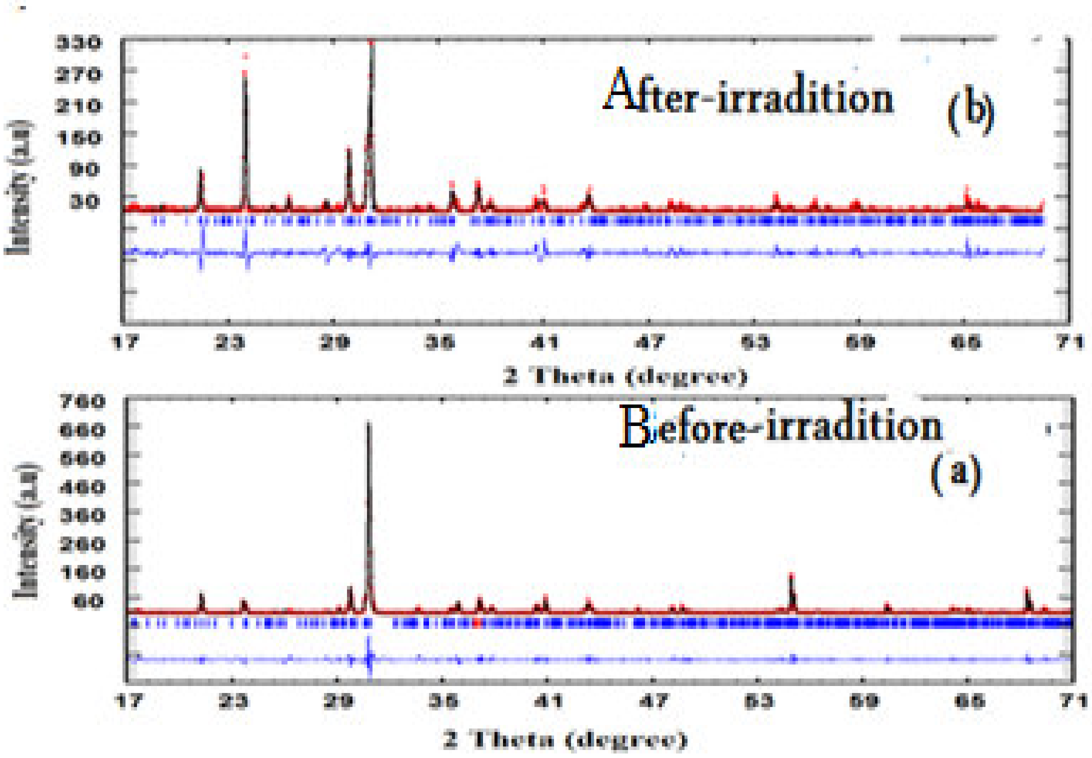


(a) (b) (c)

Fig.2. photograph grown K_2SO_4 crystal, a- prismatic habit for after irradiation growth, b &c for before irradiation crystal growth .

3-2 X-RAY diffraction analysis

Powder x-ray diffraction studies were performed on the powder of the grown crystals to identify the phase formation and degree of crystal perfection. Its pattern of before irradiation and after irradiation by thermal neutron was recorded. Figure 3a shows the diffraction peaks of before irradiation matched well with peaks that reported for (PS) crystal in the literature((Fuminao et al 2011), (Stadnyk et al 2013) (Arnold et al 1981)and (Ahmed **1996)** [3-6].That is due to the clear crystalline samples, so, the occurrence of sharp peaks at specific Bragg's angles**.** The recorded data were treated by Rietveld analysis with "full prof"(fullprof,VersionApril2014-ILL JRC(Roisnel and Rodiguez 2014)[14] shows the calculated lattice parameters are in good agreement with the reported values. It is clear from figure 3b, that the after irradiation (PS) K_2SO_4 crystals lead to a change in the intensity, shift of peaks when compared with that peaks of before irradiation. So, the irradiation has brought a change in the internal structure of crystals due to change in bond lengths or the angle. According to the data analysis of the XRD patterns presented in figure 3a, the lattice parameter $\alpha = \gamma = 90°$ and $\beta = 90.5415°$, and a(Å) = 10.01577, b(Å)= 7.47461 and c(Å)= 5.78989 with conventional unit cell volume V= 433.43Å3 are obtained. It is clear that, the angle beta (β) is not 90, this is due to the twinning of the crystal. So the possible pitfalls errors are in the space-group determination outcome. This is occurred to monoclinic crystal (b unique) with the angle fortuitously equal to ~ 90 ° (in our case $\beta = 90.5415$ °).Since there is twinning according to (100)plane , this will cause overlap of the reflections hkl and $\bar{h}kl$. So, the observed Laue symmetry is mmm (orthorhombic) crystal system rather than 2/m (monoclinic)(Theo 2005)[15] . So ,it is possible to be pseudo orthorhombic.



Figure(3);X-ray diffraction pattern for K_2SO_4(a)before irradiation,(b)after irradiation

While lattice parameters for the after irradiation sample are calculated from the data of fig.3b which revealed the crystals belong to monoclinic system as $\alpha = \gamma = 90^\circ$ and $\beta = 101.7997^\circ$, a(Å)= 10.0842 ,b(Å) =7.5810 and c (Å)= 4.6398 of space group with conventional unit cell volume V=344.45 $Å^3$. It is clear from the comparison of the unit cell calculated parameters of before and the after irradiation, that the after irradiation sample is with monoclinic crystal system rather than pseudo orthorhombic; and the volume of unit cell is reduced by 21% from that of before irradiation .In literature there are two groups of halide compounds with an A_2BX_4-type chemical formula having different structures. One is the group of substances of orthorhombic β -K_2SO_4 structure with a space group of P_{mcn} at room temperature. The other is the group having a monoclinic like Sr_2GeS_4 structure with a space group of $P2_1/m$ at room temperature. Furthermore, Cs_2CdI_4 and Cs_2HgI_4 transform from the monoclinic Sr_2GeS_4 structure (called the α -phase) to the orthorhombic β -K_2SO_4 structure (called the β -phase) at high temperatures, and this phase transition is called an α-β phase transition(Fuminao et al 2011)[3].So, thermal neutron irradiation induces a lattice change and there is possibility of (PS) crystal structure changed from pseudo orthorhombic before irradiation to monoclinic crystal system of the same as the structure of Sr_2GeS_4.

K_2SO_4 revealed a ferroelastic phase transition temperature at (T_c = 584°C) with symmetry change according to Aizu notation 6/mmm to mmm. The hexagonal structure of space group D^4_{6h} = $P6_3/mmc$(Park 1998).[16]

3-3 Differential Scanning Calorimetric

To compare the results of DSC measurements of heating and cooling run with rates of ±5K/min around T_c for both samples of the grown(PS) crystals with that published data (Anooz et al 2008) [17] .The heating run for before irradiation revealed the expected endothermic peak maximum T_c at 581.9°C,while it revealed an exothermic T_c at 577.9°C after cooling the sample. There is hysteresis of about 4°C. This behavior matched very well to the high-temperature hexagonal phase of (PS) (Park 1998)[16].

While for that for after irradiation sample, T_c is appeared at 670°C for heating and 566°Cfor cooling run(with hysteresis of about 104°C) (AL-Dhahir) [18].The hysteresis arises for first-order phase transitions because nucleation of the new phase is activated. The change free-energy positive until the nucleus reaches a critical size beyond which further growth is downhill. The transformation at 670°C leads us to suggest that crystal system of this phase is either hexagonal or orthorhombic .The result of DSC for after irradiation sample encourages us to go to Aizu notation (Aizu1970) [19] and look for a species which is matching with this transformation. Since ferroelastic hexagonal is the crystal system of high temperature phase as reported earlier (Park 1998)[16], and our room temperature structure is monoclinic as mentioned from the x-ray structure analysis. So, Aizu notation for this phase transition may be 6/mmmF2/m, or mmmF2/m .Details will be considered in future studies for ferroelatic and the crystal structure for irradiated at high temperature.

3-4 Fourier transform Infrared Transmission Spectroscopy

The FTIR spectroscopy studies are used to analyze qualitatively the presence of functional groups in the grown (PS) crystals for before thermal neutron irradiation.

Fig.(4a)presented the absorption bands in the region of 3,485.37 cm^{-1} and 3415.93 cm^{-1} are corresponding to O-H stretching vibrations of water and hydroxyls .These are due to the symmetric and asymmetric stretching of the O-H bond. The peak observed at 3485.37 cm^{-1} is due to asymmetric O–H stretching vibration present in the compound. According to the selection rules for T_d symmetry, the IR spectrum of SO_4^{-2} ion has two absorption bands υ_3 which correspond the asymmetric stretching vibrations of the S-O bonds, and υ_4 which correspond to the bending vibrations of O-S-O. Each of these frequencies are triply degenerated. These two bands triply degenerated vibrations (ν_3 and ν_4) are observed in the IR absorption spectrum of at (PS)1114.86 cm^{-1} and 617.22 cm^{-1}.The strong peaks observed at 1114.86 cm^{-1} and weak at 1160 cm^{-1} are attributed to triply degenerate of asymmetric stretching mode (ν_3) of SO_4^{-2}. Since the symmetry of SO_4^{-2} in solution is nearly tetrahedral(Ilamaran 2012)and(Satish1998)[20,21] , with a totally symmetric S–O stretching vibration at 980 cm^{-1} (v_1 ,IR inactive) and an asymmetric, triply degenerate, S–O stretching vibration at 1102cm^{-1}(v_3 ,IR active). The deformation and combination vibrations ($v_2$and v_4) for S–O occur at lower energy. If the tetrahedral SO_4^{-2} symmetry is lowered, their IR spectrum changes and becomes IR-active .The triple degeneracy of v_3 is lifted, which results in a split of the v_3 band into two or three bands depending on the symmetry of the structure formed. The spectral changes are on coordination of the sulfate anion. Therefore ,the degenerate due to T_d tetrahedral deformation leads to symmetry reduction to C_{3v} (Hug 1997)[22].The single strong peak at 617.22cm^{-1} assigned as asymmetric bending mode of SO_4^{-2} , a weak sharp peak appears at 981.77 cm^{-1} (υ_1) , corresponding to the symmetric stretching vibration of (S-O). The band observed at 482.20 cm^{-1} is assigned to the doubly degenerate (ν_2) SO_4^{-2}.

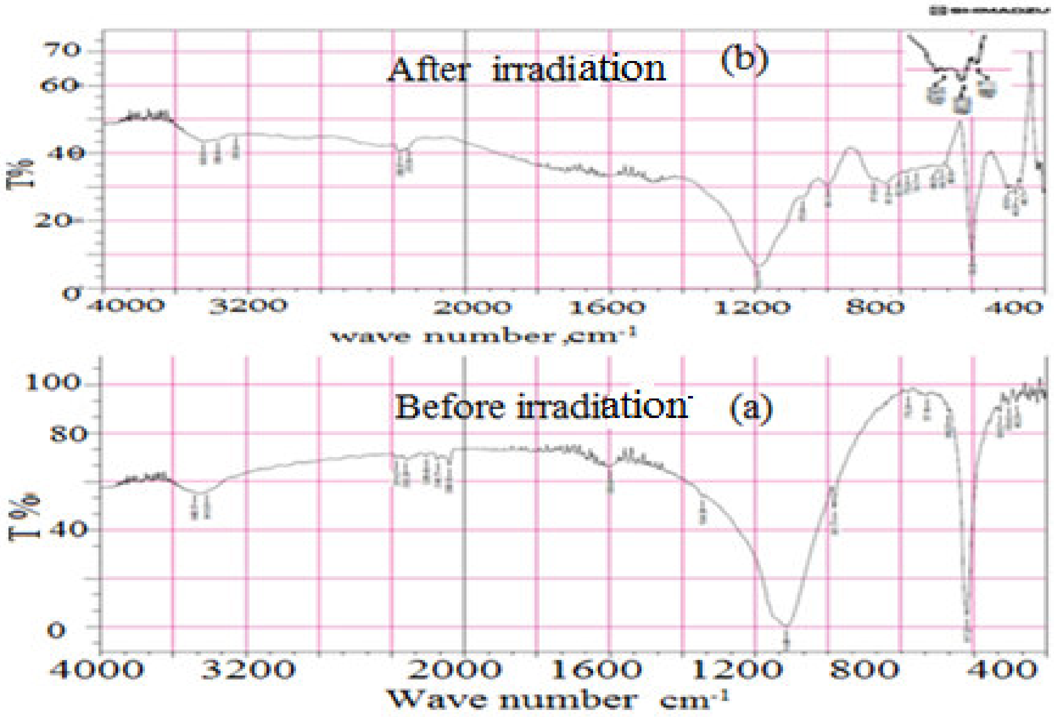


Fig.4:Fourier transform Infrared Transmission **,a-**before thermal neutron irradiation**, b-**after neutron irradiation**.**

The FTIR spectrum for the after thermal neutron irradiation is presented in fig.(4b). It showed an absorption band in the region of 3450.65$cm^{-1}$and 3369.64 cm^{-1}which are corresponding to OH stretching vibrations of water and hydroxyls ,and are due to the symmetric and asymmetric stretching of the O-H bond both are shifted to lower wave number. The bands appeared at 1192.01 cm^{-1} and 1070.49 cm^{-1}shifted to higher wave number than that appeared for before irradiation and assigned to asymmetric stretching sample. Forbidden , but occasionally be seen as a very weak band at 1000 cm^{-1}(Periasamy et al 2009) [1].So it is observed at

999.13cm^{-1}. Distortion of tetrahedral due to electrostatic effects, could shift the v_3 to higher wave number and cause the v_1 band to become IR active (Derek et al 1999)[23]. If sulfate forms a bidentate binuclear (bridging) surface complex, due to the irradiation by thermal neutron the symmetry is further lowered to C_{2v} , then the v_3 band splits into three bands between 1070.49 and 1192.01 cm^{-1}, while the v_1 band is shifted to around 1000 cm^{-1}.As the non degenerate symmetric stretching v_1 and the triply degenerate asymmetric stretching $v3$ bands are the two infrared sulfate vibrations v1 and v3 that are accessible to spectroscopic investigation(Nakamoto 1986)[24].The bands appeared below 700 cm^{-1} are assigned to the symmetric and asymmetric bending(v_2) O-S-O of SO_4 groups. Hence we have assigned the frequency 599.86 cm^{-1} to the asymmetric bending , and 497.83, 480.28 and 466.77cm^{-1} to symmetric bending of the SO_4 groups. The band observed at 669.30 cm^{-1} is assigned as asymmetric bending. The non degenerate symmetric stretching v_1 and the triply degenerate asymmetric stretching $v3$ bands are two infrared sulfate vibrations that are accessible to spectroscopic investigation.

4-Conclusion

In conclusion, the stable structure of K_2SO_4 at room temperature is orthorhombic for before thermal neutron irradiation and monoclinic structure for after irradiation. Both samples showed a high temperature first order phase transition with different T_c and different hysteresis range. Fourier transform infrared transmission spectroscopy carried at room temperature revealed a reduction in symmetry for after irradiation sample .Unfortunately, it is not clear the connection between room temperature suggested monoclinic structure phase for after irradiation sample due to unavailable of facility at high temperature X-ray scattering .So, Further structural study is needed.

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