Coloring of Topaz after Irradiation

S. Salama [(1)], A.I. Helal [(1)], M.A.M. Gomaa[(1)], L.I. Abou-Salem [(2)], H. Nafie [(2)] and E.A. Badawi [(3)]

(1) Egyptian Atomic Energy Authority
(2) Benha University
(3) Faculty of Science, Physics Department, El-Minia University, Egypt.

ABSTRACT

Raw topaz stone samples are subjected to irradiation by neutrons from the Egyptian research reactor and by γ rays from a gamma source. Changes in the color of the stones are observed which can be attributed to the formation of defects in the structure of the stones. The defects can absorb certain wave length which is observed as a change in the stone color .The absorption of light is investigated by an optical spectrophotometer technique at different irradiation and heating conditions. Raman studies of topaz stones showed a relation between the color changes with changes in the intensities of the band of scattered peaks corresponding to OH group stretching modes of vibration.Positron Annihilation Spectroscopy (PAS) technique is used to study the behavior of defect concentration in topaz in two states; pure and irradiated stones by neutrons and γ. It has been shown that positrons are trapped in imperfect locations in topaz samples and their mean lifetime can be influenced by changes in the concentration of such defects.

INTRODUCTION

The colorless topaz is changed to reddish pink after neutron irradiation in the Egyptian research reactor. The coloration is observed to be deepened with the increase in the neutron dosage which could be changed to blue by heating. Particles of high energy such as electrons or neutrons and electromagnetic ionizing radiations like gamma rays can produce color centers in the stone which can transfer it to a gem stone.

Topaz is currently the most commonly irradiated gemstone and is the best example for enhancement of color by commercial application of irradiation. Irradiation induces defects which behave as a color centers in topaz crystals. A color center involves one electron missing from a normally occupied position, leading to a 'hole color-center'. Neutron irradiation processes were carried out in the Egyptian second research reactor (ETRR-2) and also in the gamma facility of the national center of radiation research and technology at Egyptian Atomic Energy Authority (EAEA).

Three techniques were used to investigate these defects namely, spectrophotometer to study the optical absorptions, Raman studies to know the effective groups in topaz in the color changes and Positron Annihilation Spectroscopy (PAS) to study induced defects in topaz which are created by neutrons and γ irradiation.

EXPERIMENTAL

Natural topaz which has the structure of an aluminum silicate fluoride hydroxide $Al_2(Sio_4)(OH, F)_2$, and it is usually is colorless or has unattractive color. Therefore, it is not considered before irradiation treatment to be a gemstone.

Cut topaz samples were prepared from large piece of raw and treated topaz to have the size of (~ 1.0 cm x 1.0 cm x0.2 cm).

(PAS) technique is used for crystal defects detection, Spectrophotometer of a double beam to measure light intensity at different wavelengths and finally Raman spectrometer to observe spectral variations before and after treatment.

The samples are irradiated for (2,4,8 and 12) hours at 22 MW- with an average of thermal neutron flux of $2.37x$ 10^{14} $n/(cm^2.s)$. After irradiation of the stones, they have to be transferred to the auxiliary pool until their radioactivity reduces to permissible level, and then to hot cells before any treatments.

The optical absorption spectra of raw and irradiated samples were carried out with "UV/VIS8500" spectrophotometer and measured in the spectral range from 190-1100 nm at room temperature.

The Raman measurements were performed using a backscattering geometry at room temperature in the range from 400 to 4500 cm^{-1}. These measurements were done using Fourier Transform Raman Spectroscopy (FTRS) "FRA 106/S" equipped with an optional high-sensitivity "Ge" detector and a "CaF_2" beam splitter.

At Positron Annihilation Spectroscopy (PAS) The Fast-Fast coincidence technique and the positron lifetime measurement with a half maximum (FWHM) time resolution of 290 ps was used. The 1274 keV γ-rays were taken as the start signal for TPHC or the "time to pulse height converter" (TPHC), while one of the 511 keV annihilation quanta, resulting from the two photons annihilation in the material, was chosen as the stop signal. The signal from the TPHC or the "time to amplitude converter" (TAG) was fed to the multi-channels analyzer (MCA) for storage. The 1274 keV signal indicates the birth of the positron and the 511 keV annihilation energy indicates the positron death. Thus, the time interval between the above two γ-rays is the lifetime of the positron in the material.

RESULTS AND DISCUSSION

Optical absorption

The optical absorption spectra of samples were measured in the spectral range from 350 to 800nm at room temperature. As can be noticed from the figures, the band centered at 620 nm which increases with the dose. This band together with the absorption tail in the UV region is responsible for the blue color of the topaz leaving an absorption valley at about 480 nm. However, increasing the irradiation to the doubled time increases the absorption band at 620 nm by only 10%. All the samples from different regions in Brazil show the same optical absorption spectra, and the same trend on neutron irradiation, i.e., the absolute absorption is the same for all investigated samples. It means that the produced colors and color centres do not depend on the origin of samples.
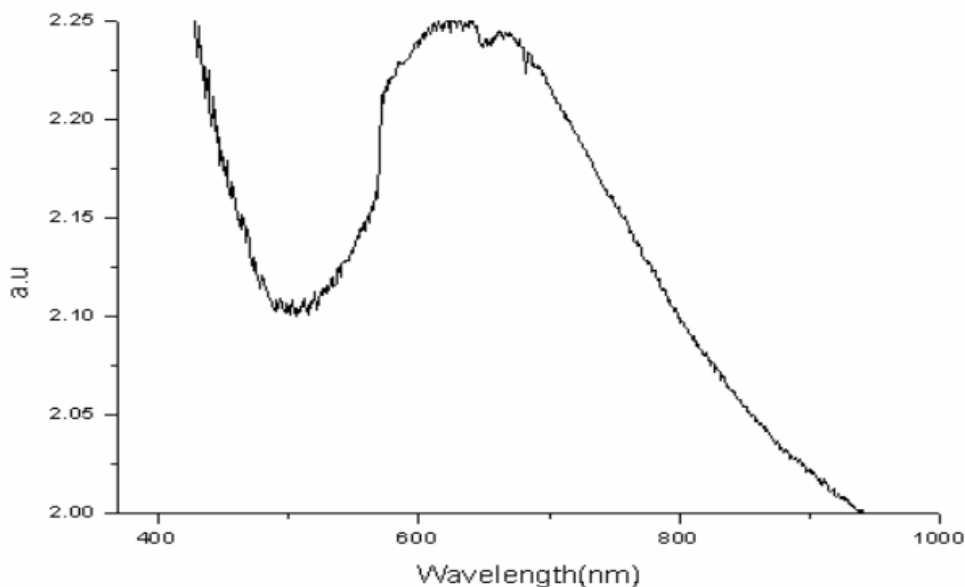
Fig(1); Optical absorption spectra of neutron irradiated topaz for 12 hours after heating at 200 ^{0}C for 4 hours
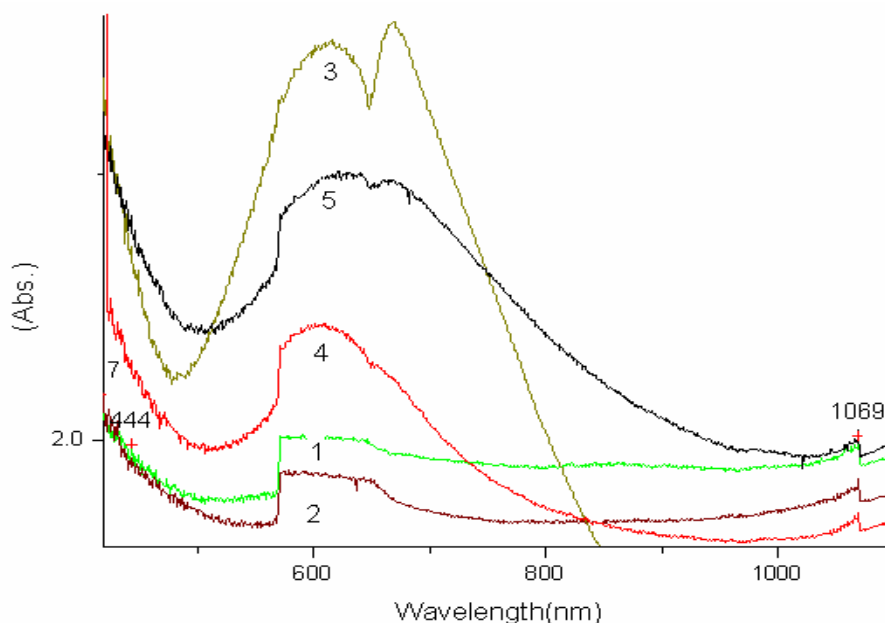

Fig (2); Topaz [1.Raw, 2. irradiated by γ, 3. irradiated by neutrons, 4. irradiated by neutrons after γ irradiation and 5. Heated gamma irradiated for 4 hours at 200C^0]

The treatment of topaz with γ rays increases the overall optical absorption giving the crystals a brown color. Applying thermal treatment at 200-250 ^{0}C, the brown component of optical absorption spectrum (~ 450-500 nm) is removed leaving a weak band at 620 nm, which gives the crystal its blue color. The apparent difference is thus the brownish color was more distinct

59

in the neutron-irradiated and annealed stones. The treatment of topaz with γ rays for months, continuously gives the blue color directly without heat treatment, but lighter than the color resultant from the reactor irradiation. It takes very long time but very low residual radioactivity, which goes to vanish quickly, through days.

Raman Spectroscopy

Topaz was subjected to intensive Raman spectroscopic studies as raw material and after treatment by irradiation with neutrons and γ. The effects of the different parameters of irradiation were considered. Spectra of all samples were recorded in the range of 4500–400 cm^{-1} at room temperature.

Raman studies of interested topaz stones showed a relation between the color changes with changes in the intensities of the band of scattered peaks corresponding to OH group stretching modes of vibrations.

Structural defects result in anomalous weak vibrations in the region between 3000 and 4000 cm^{-1}. Based on the crystal structure, which contains hydroxyl groups showing partial OH-F substitution, it is expected to observe OH-stretching vibrations in this region, although there are contradictions in the exact positions of the OH stretching vibrations where single band is observed around 3143 cm^{-1}. Typically, colorless or pale-colored topaz is heated to 300 degrees centigrade for several hours. The longer the stone is heated the deeper the color change will occur in the stone. No changes under 200 C^{o} were observed.

The stones will turn to a yellow to brownish green to a dark brown color above this degree. These colors however are not stable and will eventually fade to clear unless the stones are irradiated. The irradiation process essentially eliminates the yellow-brown and green colors and leaves a stable blue color which will not fade unless subjected to temperatures of 500 to 600 degrees centigrade at the case of γ irradiation while no effects in neutron irradiation state to highest temperatures.
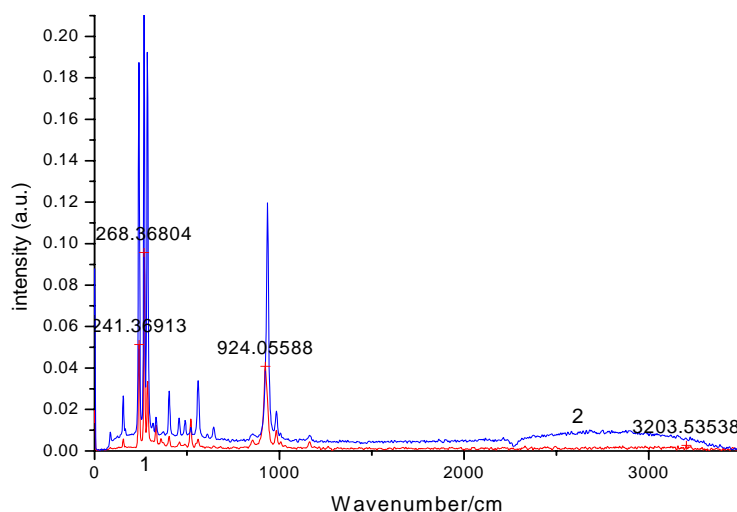

Fig (3); Raw topaz sample down and neutron irradiated topaz up

Impact of neutron flux in the range of 2×10^{14} n /cm^2 /s into topaz can cause point defects [1] due to OH mobility in the crystal structure of topaz. Longer irradiation causes clustering of these defects and more mobility of defects giving rise to a strong optical absorption in the visible region [2]. The band of raman scattered peaks between 3000 cm^{-1} and about 3500 cm^{-1} corresponding to (OH) stretching modes of vibration is recorded.

Inspection of the Raman scattered peaks at about 3000 cm^{-1} show that by increasing irradiation time and increasing the temperature can lead to an increase in the scattering peaks. This may mean that neutron irradiation helps in band cleavage of the OH group.
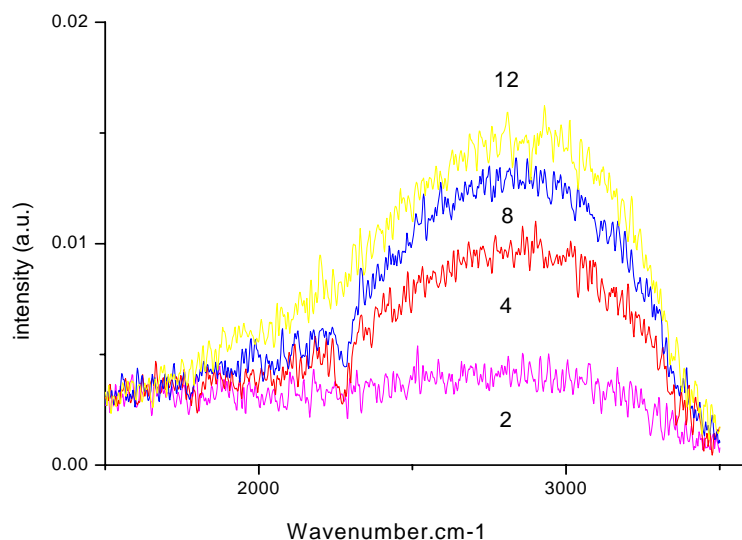

Fig (4); Neutron irradiated topaz for (2, 4, 8 and 12) hours, at OH band region

Fig (4) shows that the intensity of OH band increases by increasing the time of irradiation, which means more scattering of this band group and more collection of the cluster defects.
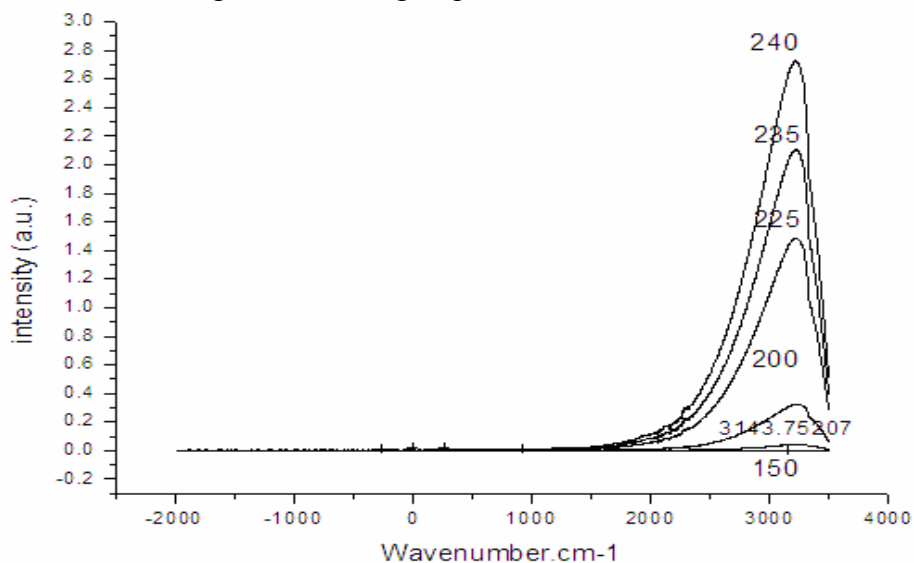

Fig (5); Topaz heating from 0 to 240 ^{0}C (for OH bands)

Inspection of Fig (5) shows that the intensity of OH group did not change by heating until 150 C^0 and it begins increasing continuously to 240 C^0. The intensity of OH band increases by heating, which means more scattering of this band group and more collection of the cluster defects.

In contrast for heating by cooling topaz sample to (-100) C^0 the variation of OH group frequency shows that the intensity of OH band decreases by cooling, which means less scattering or decreases in cluster defects. The relation between temperatures in degree centigrade with intensity is a linear relation. On the other hand the study showed that the variation of intensity of OH group frequency with irradiation time increases continuously with increasing irradiation time up to (12) hours irradiation at the reactor. No investigation for more irradiation time but it is expected that up to certain time the intensity of OH group frequency could be constant whatever the irradiation time may increase. Also the study shows that the Intensity of most bands in topaz irradiated by neutrons after γ irradiation are higher than the bands in topaz irradiated by γ because of the strong effect of neutrons which penetrates the atoms and interacts by impact with the OH groups leading to the deformations while γ cause induced with the OH groups with less effect.

Positron annihilation

The positron source is the radioactive isotope ^{22}Na which was evaporated from an aqueous solution of free carrier ^{22}NaCl with 1 mCi activity and deposited on a thin kapton foil of 7.5 μm in thickness. The ^{22}Na decays with the emission of a $β^+$ with 511 KeV followed by a 1274 Kev γ-ray.

A sandwich configuration has been used for Al alloy sample measurements. The present studies were performed using sets of couple of two identical samples of the material under investigation.
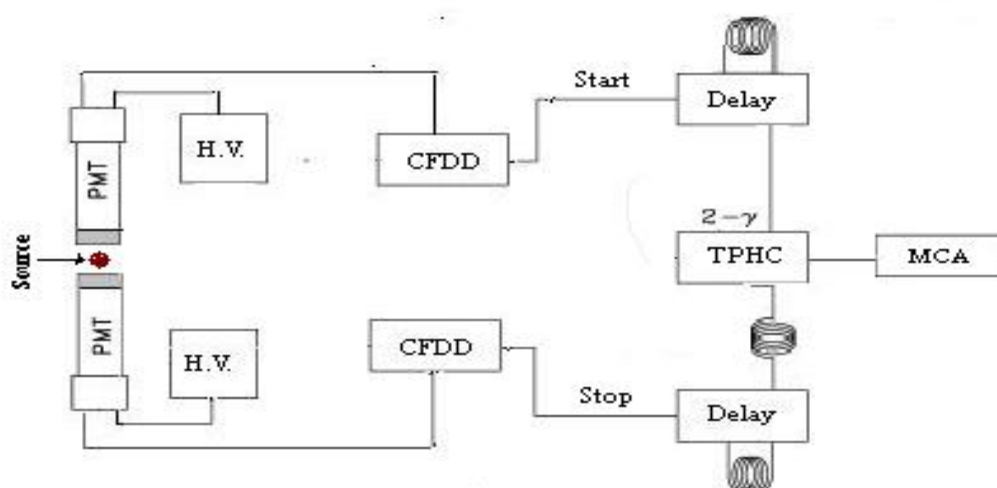

Fig (6); Schematic diagram for the detection of the 2-γ positron annihilation.

The schematic diagram for the Fast coincidence system which was used in the measurements is shown in figure (6), with time resolution of 290 ps [3, 4]. The equipment consists of a pair of scintillators and photomultipliers (PMTs) rigidly mounted. Positive high voltage power

supply provides power to the PMTs via voltage divider which allows one to vary the potential applied to the two tubes. The 1274 keV γ-ray was taken as a start signal for the time to pulse height converter (TPHC), while one of the 511 keV annihilation quanta, resulting from the 2γ-rays annihilation in the material, was chosen as the stop signal. The signal from the TPHC was fed to the multi-channel analyzer (MCA) for storage. The 1274 keV signal indicates the birth of the positron and the 511 keV indicates the positron death. Thus, the time interval between the above 2γ-rays was the lifetime of the positron or Ps in the material. The thickness of the samples is adequate to absorb emitted positrons. For most of measurements, account period at least 3 hrs were required to obtain sufficient statistics. The technique of positron annihilation (lifetime technique) is described in more details elsewhere [5].

The lifetime spectra were analyzed as 2 lifetime components (τ_1, and τ_2, with corresponding intensities I_1 and I_2 with the help of computer program PATFIT-88 [6]. The positrons source is sandwiched between two identical samples. The source-sample configuration was then wrapped in a thin aluminum foil. Each sample was measured for 10800 seconds during which about 3.17×10^5 coincidence events were accumulated.

The positron lifetime measurement of the fast-fast coincidence technique with a FWHM time resolution of 290 ps was used. The 1274 keV γ-rays were taken as the start signal for TPHC or the "time to pulse height converter" (TPHC), while one of the 511 keV annihilation quanta, resulting from the two photons annihilation in the material, was chosen as the stop signal. The signal from the TPHC or the "time to amplitude converter" (TAG) was fed to the multi-channels analyzer (MCA) for storage. The 1274 keV signal indicates the birth of the positron and the 511 keV annihilation energy indicates the positron death. Thus, the time interval between the above two γ-rays is the lifetime of the positron in the material.

The positron lifetime were measured in (3) pairs of topaz pure and irradiated. The dimensions of topaz samples were: (1 x 1 x 0.2) where thickness around 2.2 mm and 2 samples are identical. The positron source of 1mCi free-carrier ^{22}NaCl was evaporated from an aqueous solution of sodium chloride and deposited on a thin Kapton foil of 7.5 μm in thickness. The positron source is sandwiched between two identical samples.

Raw and irradiated samples were measured for the same time; 010800 seconds. The data for the lifetime spectra were analyzed by using the PATFIT88 computer program [7]. The value of the source contribution (Kapton foil) of lifetime and its intensity was subtracted during the analysis. The block diagram of the system used in measuring lifetime is described elsewhere [8].

The results of the positron annihilation experiment on topaz samples, which contain defects that trap positrons, were analyzed. The main radiation –induced defects in topaz were previously observed and identified by Petrov [3]. The dislocation density is generally expressed as length per unit volume, ρ cm^{-2} [9]. The defect density is related to dislocation density.

Table (4); Lifetime of the positron in topaz raw, irradiated by γ and irradiated by neutrons

Sample name	Lifetime (PS)	Intensity
Topaz raw	188.1	86.02
Topaz irradiated by γ irradiation	189	86.55
Topaz irradiated by neutrons	198.6	87.05

Because of the vacancy clustering the signal increases in positron lifetime and table (4) shows the variation in the lifetime of the positron in topaz as raw, irradiated by γ and irradiated by neutrons. The data means that the deformation in topaz which irradiated by neutrons has the largest effect leading to deformation and rearrangement and, consequently causing deepest and more stable color.
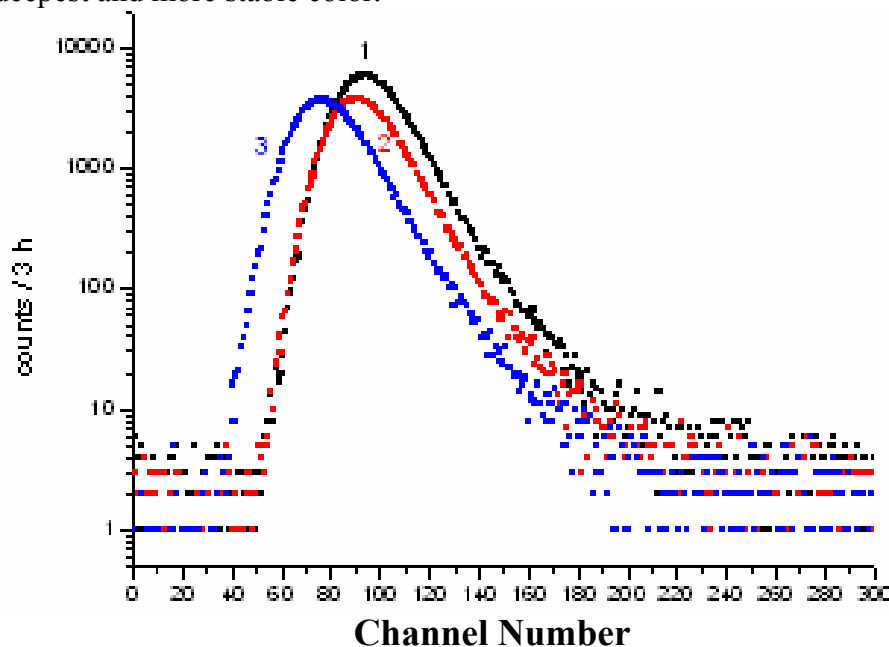

Fig (7); PAS curve of topaz [pure (1), irradiated by γ (2) and irradiated by neutrons (3)

It is possible to create more complex defects by irradiating topaz with long irradiation times. The natural color of topaz may be related to vacancies due to deformation of topaz while the vacancies are more created and distributed by irradiation could explain why these types of blue color are differently distributed while they may be caused by a similar and very stable defect consisting of multiple vacancies.

REFERENCES

1) J.A. Gadsden, Infrared Spectra of Minerals and Related Compounds, Butterworth, London, (1975).
2) D.A.Souza, J.F. de Lima, M.E.Valerio, C.Fantini, M.A.Pimevta, R.L.Moreira and L.V.Caldas, Nuclear Instruments and Methods in Physics Research Section B, 191.230 (2002).
3) M.A.Abdel-Rahman, M.S. Abdallah and Emad A. Badawi: Surface Review and Letters 11 (5) (2004) 427.
4) M.A.Abdel-Rahman, M.S. Abdallah and Emad A. Badawi: Surface Review and Letters 12 (2) (2005).
5) P. Hautojärvi, K. Rytsölä, P. Tuovinen, A. Vehanen, and P. Jauho, Department of Technical Physics, Helsinki University of Technology, SF-02150 Espoo 15, Finland, The American Physical Society, 1977.
6) P. Kirkegaard, M. Eldrup, O. Mogensen and N. Pedersen: Comp. Phys. Commun., vol. 23, 1981, P. 307.

7) P. Kirkegaard, M. Eldrup, O. Mogensen and N. Pedersen, Comp. Phys. Coramun. 23, 307 (1981).
8) E. A. Badawi, M. A. Abdel-Rahaman and E. M. Hassan, Mater. Sci. Forum 445, 45 (2004).
9) J Baram and M. Rosen, Phys. Status Solidi. A16, 263 (1973).