Gamma ray irradiation induced optical band gap variations in silica sol-gel doped sucrose

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دراسة تأثير أشعة غاما على خصائص فجوة الطاقة البصرية لسيليكا المشوَّب بالسكّر« sol- gel »

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الملخص:

تم في هذا البحث توليف مصفوفات السليكا بطريقة حديثة « sol-gel » وهي سهلة الاستخدام إذ تعتمد على الطريقة الكيميائية الرطبة باستعمال كحول الإيثانول، و محلول التترائيل اورثو سيليكات ($Si(OC_2H_5)_4$) و يقع إضافة السكَر كشائب بواسطة إذابته في حمض الكلوريد كعامل مساعد في عملية الهدرجة. ويتم بالتالي الحصول على نماذج الكتل الحجمية بعد التجفيف بدرجة حرارة الغرفة . عندها يقع تعريض هذا الزجاج المطعم لأشعة غاما (^{60}Co) حيث يصير لونه داكنا وكلما طالت فترة التعريض كلما صار اللون داكنا أكثر. لذلك قمنا بتوصيف و دراسة الخصائص الضوئية لعينات الزجاج المطعم بالسكر باستخدام مطيافية الأشعّة تحت الحمراء إلى جانب مطيافية الأشعّة الفوق البنفسجية و المرئية حيث لوحظ أن كثافته الضوئية تزداد تناسبيا مع الجرعة الممتصة ويمكن قياسها بسهولة بواسطة جهاز المطياف الضوئي. فقد تبيَن من خلال تجربة قياس الطيف الضوئي بالنسبة لكلّ الجرعات الإشعاعية في ميدان 1 و100 كيلوغراي تغييرا في عرض حزمة الطاقة الممنوعة للزجاج لمطعم بالسكر حيث أظهرت النتائج المتحصل عليها تناقصا في فجوة الطاقة البصريَّة الممنوعة من 5،8 إلى 3،5 الكترون فولط (eV) بعد عملية التشعيع. وبالتالي مكّنت عملية التشعيع من التغيير في الخصائص الفيزيائية و الكميائية للسليكا المشوَب بالسكَر و المصنوع بطريقة " sol-gel" بإضفاء خاصية شبه الموصل على الزجاج ذا صبغة العازل.

Abstract

The silica xerogels doped sucrose was prepared via sol-gel process and exposed at room temperature to different doses of high energy (^{60}Co) gamma irradiation. Changes in the UV–visible and FTIR spectra of pristine and irradiated xerogels with varying of gamma doses rays show variation in the gap energy. It was found that energy gap of the investigated silica xerogels decreases with increasing the gamma irradiation doses. Thereby the irradiated samples reveal behaviour changes, from an insulator (Eg ~5,8 eV) towards a semiconductor with (Eg~ 3.5 eV).

Introduction

During the past few years, the physical, electrical, optical and magnetic properties of glassy materials have a lot of interest [1, 2]. Actually and since sol- gel process has attracted much attention in recent years because of its simplicity and suitability for large-scale production it can be intended for the routine applications, providing in fact a new fundamental challenging solution [3, 4]. Then silica xerogels synthetized by sol-gel routes represents a potential candidate for eventual optical dosimeter application. Also the silica xerogels are considered to be an out most important material due to its high homogeneity, good purity, easy doping and cheaply cost [4].

The fundamental purpose of this study is to investigate the effect of gamma irradiation on optical properties of xerogels SiO_2 doped sucrose prepared by sol-gel process. So present work is expected to evaluate the effects of gamma irradiation on the optical properties and justify the induced defects generated in silica xerogels matrix towards gamma irradiation. We show that the gamma rays irradiation of silica networking arising from the sol-gel synthesis matrix doped sucrose plays an important role in its modification from an insulator to a semiconductor.

Materials and methods

1. Chemicals

The starting materials were tetraethylorthosilicate (TEOS), ethanol, hydrochloric acid (HCl), ammonium hydroxide (NH_4OH). All chemicals were purchased from Sigma-aldrich. Also these reagents were of analytical purity.

2. Sol–gel preparation

High purity samples have been prepared via the sol gel technique starts with a solution containing tetraethyl orthosilicate ($Si(OCH_2CH_3)_4$) as silicon precursor and using pure ethanol as a solvent. As the sol-gel process consists mainly of two steps of hydrolysis and condensation [5,6], then in the first step, solution TEOS was hydrolyzed with ethanol under stirring for 15 min at room temperature, before adding HCl used as catalyst to adjust the pH of the hydrolysis reaction [6,7], in which sucrose dopant was dissolved . After 2h stirring, the second catalysis NH_4OH was added in order to accelerate gelation reaction. Finally, the sols were cast into plastic petri dishes and kept at room temperature for several weeks to get xerogels by slow evaporation.

3. Irradiation

All samples of dried monoliths xerogels were irradiated using gamma-rays from ^{60}Co source at a dose rate of 6 $Gy.min^{-1}$. The irradiation was performed in air, at room temperature. The absorbed dose administered was 500 kGy. Coloration was observed after samples irradiation.

4. Characterization

After irradiation, the xerogels samples measurement have been effected by UV-visible Spectrophotometer Shimadzu 1800 in the wavelength range of 200–800 nm using air as the reference in room temperature. The FTIR analyses were acquired using the KBr method with a Magna-IR-560 apparatus. The related spectral resolution is 1 cm^{-1}, measured between 400 and 4000 cm^{-1}.

Results and discussion

1. FTIR spectroscopy characterization

SiO_2 xerogels were amorphous because no crystalline phase was detected by conventional X-ray diffraction (XRD). Then the XRD pattern of the xerogels materials show a typical broad peak around $2\theta=23°$, characteristic of amorphous silica SiO_2 matrix [8] (Fig.1).

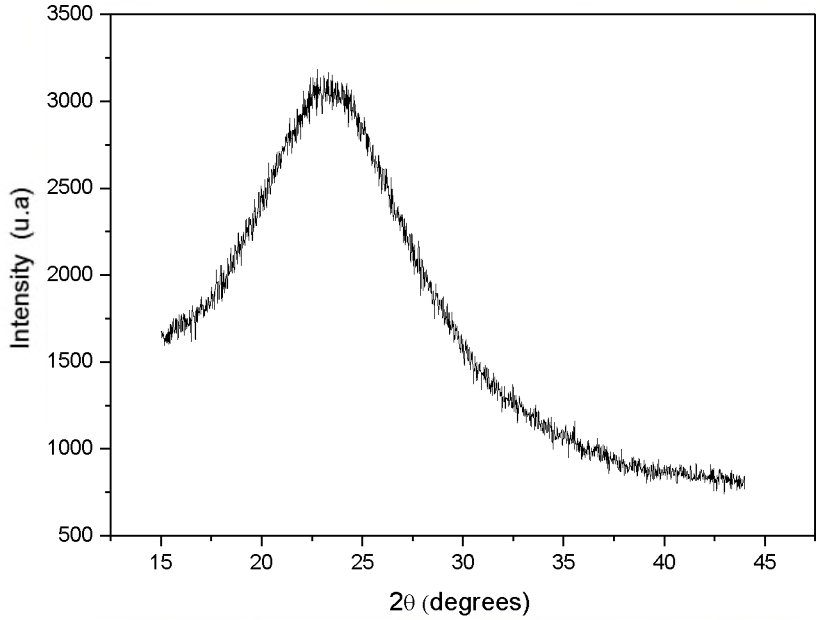

Figure 1. X-ray diffraction patterns of silica xerogels samples.

The microstructure evolution of the solid xerogels SiO_2 xerogels with gamma irradiation has been investigated with FTIR measurements in the wave number ranging from 400 to 4000 cm^{-1}. According to the spectra of irradiated xerogels matrix doped sucrose shown in Fig.2, structural bonds in xerogels are similar without significant differences as a function of dose irradiation, whereas difference was obviously shown between irradiated and those unirradiated samples. The absorption bands of surface silanols groups stretching vibrations observed at 940 cm^{-1} and 3640 cm^{-1} in unirradiated xerogels samples becomes weaker to disappear with increasing irradiation dose, suggesting the polycondensation of Si-OH bonds into Si–O–Si with water molecules evacuation near the surface [9, 10, 11]. Then, this increase in the degree of condensation may indicate the effect of the irradiation process on the xerogel silica network formation.

The dominant band observed at 1080 cm^{-1} is assigned to the asymmetric stretching vibration of the Si–O–Si bond, which confirms the silica network formation [9, 11, 12, 13].

Furthermore, an additional weak shoulder around 1190 cm^{-1}, is attributed to the stretching vibrations of carbon–oxygen bonds [14, 15]. A broad band founded at 3460 cm^{-1} due to the free molecule water, characteristic of the presence of surface hydroxylic groups physically adsorbed in the network [11], accompanied by another band at 1620 cm^{-1} of chemisorbed water which remained almost unchanged with irradiation process.

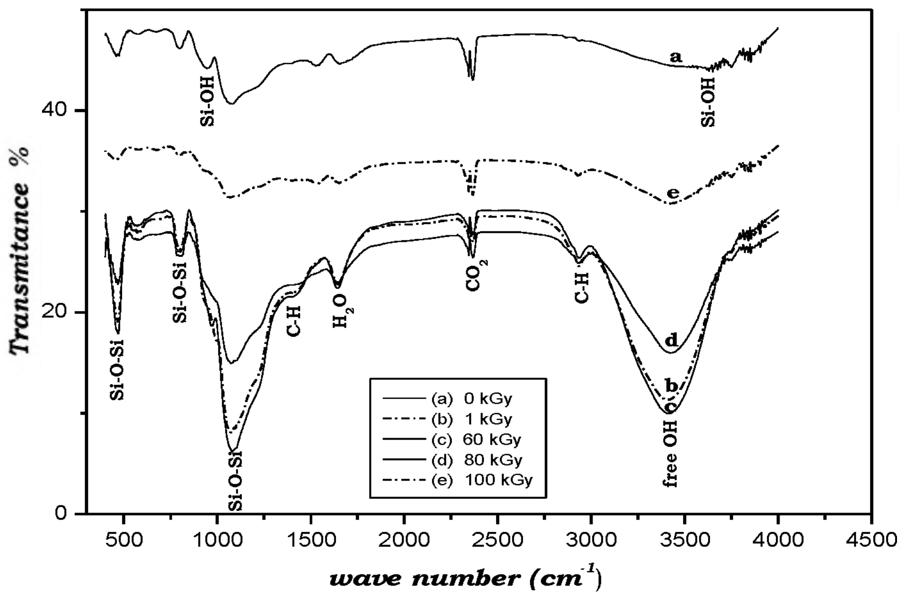

Figure 2. FTIR spectra doped xerogels plotted with absorbed dose.

Upon irradiation, and since the hydrolysis reaction of TEOS was incompleted, a C-H stretching band of ethoxy groups ($–OC_2H_5$) arises at 2930 cm^{-1} [8, 16]. Also the deformation mode of C-H presents a weak shoulder at 1420 cm^{-1} that was removed with irradiation [16, 17]. Finally, a small peak intensity of the 2360 cm^{-1} absorption band on xerogels samples, could be assigned to the C-O group, associated with uncompensated atmospheric CO_2 absorption [18, 19].

2. Optical properties

2.1. Optical band gap

The absorbance edge of the UV–vis spectra of the unirradiated and irradiated silica xerogels doped with sucrose is as shown in Fig. 3. The unirradiated sample exhibits two shoulders at 230 and 273 nm which the shoulder at 230 is corresponding to oxygen deficient centers (ODCs) [20]. Whereas those irradiated shows two or three distinct defect bands found between 261-290 nm and 214nm. Further, it is seen that the absorption edge increases gradually with increasing radiation dose, whereas only the absorption peak of carbonyl band around 270 nm decreases gradually from dose of 60 kGy. The band centred at 214 nm corresponding to E' defect type [21, 22, 23], shows a little red shift of the optical absorption edge with increasing irradiation.

The analysis of the optical absorption spectra in many amorphous materials is found to obey the Tauc relation [25], given by Eq1, which can reveal the optical energy gap Eg between the CB and VB:

$$Ah\upsilon = B\,(h\upsilon - Eg)^n \qquad (Eq1)$$

Where n(½, 2) depending on whether the transition is direct or indirect; A is the absorbance; and B is a constant [24]. So, and in order to investigate the effect of gamma irradiation, the direct optical band gap of the silica xerogels samples have been determined by plotting $(Ah\upsilon)^2$ against the photon energy (hυ). Therefore, the indirect band-gap energy can be estimated by extrapolation of the linear region of the curve $(Ah\upsilon)^2$ to the energy axis indicates as shown in Fig. 4.

The band gap of silica xerogels decreases from 5.82 (eV) for unirradiated samples to 3.56 (eV) for those irradiated to 60 kGy, while a slight increases in gap value, is observed with increasing dose up to 100 kGy. So, a noticeable decrease in the optical energy gap of silica xerogels shows that the structure of silica xerogels has been changed during irradiation from insulator to semi-conductor, which is probably due to the generation of some defects [22]. Moreover the observed red shift of the optical absorption edge with increasing dose irradiation up to 60 kGy, can be explained by the increase in the oxygen environment [25], where the decrease in the optical band gap can be related to the increment of spin density that may be related to breaking bonds [26] so related to the formation of NBOs [25], hence an increase in the formation of non-bridging oxygen is confirmed by FTIR characterization. Consequently, the density spin increasing leads to more unpaired electron in the unfilled band related to excited state from interaction between electron radiation and material molecule, which resulting at the same time to energy gap decrease and degree disorder increase confirmed by Urbach energy (Fig.5) [27, 28].

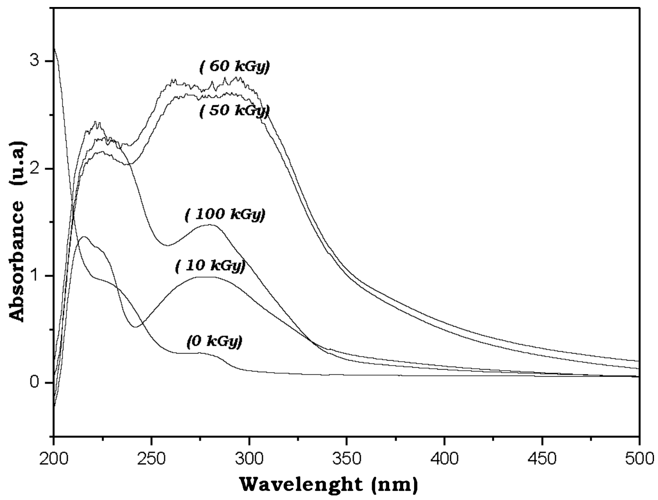

Figure 3.UV-Vis absorption of silica xerogels with different dose irradiation.

While a slight blue shift due to band gap enlargement at high energy gamma doses (> 60 kGy) is observed. This may be explained by the increasing carrier concentration and conduction band filling according to the Burstein–Moss effect [24]. Therefore, the decrease in Eg values implies an increase in conductivity of irradiated xerogels doped sucrose that proofed previously for irradiated sucrose only [29]. Also the decrease in the energy band gaps may be attributed to an increase in structural disorder of the xerogels silica when the dose is increased.

2.2. Urbach energy

Since, the Urbach energy (Eu) gives information about to presence of different types of impurities, structural disorder and point defects in the samples network [30], it was evaluated using (Eq2), and experimentally determined by taking the inverse of the slope of the linear part of the graph plotted between logarithm of the absorption and photon energy:

$$A=A0 \exp(h\nu/Eu) \qquad (Eq2)$$

As all the optical absorption spectra have been recorded at room temperature, the increase in the Eu upon gamma irradiation is supposed to be only due to the increase in structural disorder. But as seen in Fig.5 that increasing of Eu with Eg increasing let to supposed that other disordered structures such as compositional, heterogeneous, and defective tend to increase the Urbach energy [31]. Consequently, may be it will be worth noting the existing of two different behaviors of the Urbach energy versus irradiation in silica xerogels.

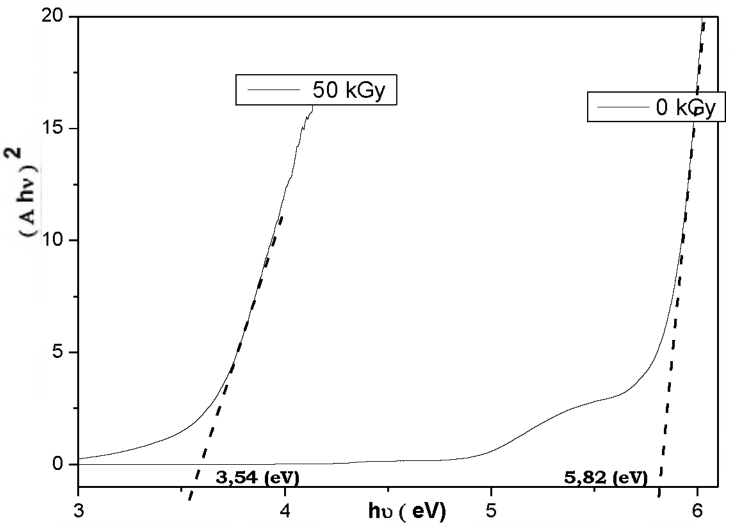

Figure 4. Tauc plots of xerogels doped sucrose before and after irradiation.

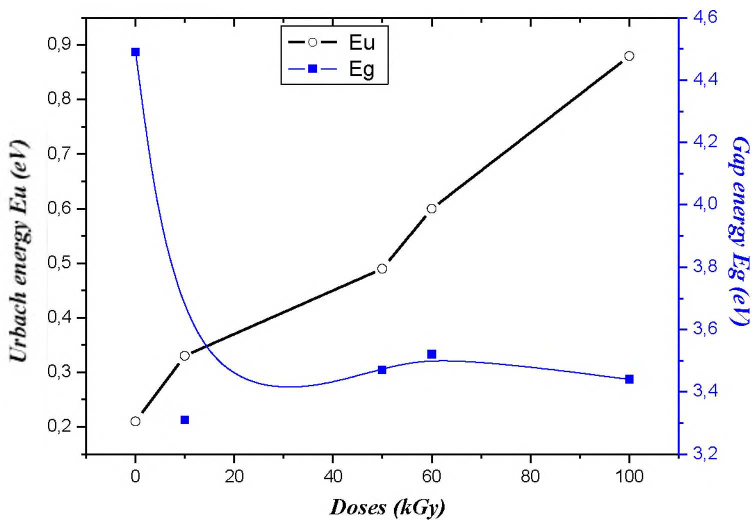

Figure 5. Variation of gap energy and Urbach energy with irradiation doses.

Conclusions

The physical properties of the xerogels before and after irradiation were characterized by using UV-VIS and FTIR techniques. It was found that the gamma irradiation influences the optical properties and modifies the network structure. Then, results indicate a decrease of band gap energy Eg values with increasing irradiation doses and have the value 5,8 (eV) before irradiation against 3,5 (eV) for samples irradiated to 50 kGy.

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