

# ‘Optical and FT Infrared Absorption Spectra of Soda Lime Silicate Glasses Containing nano Fe<sub>2</sub>O<sub>3</sub> and Effects of Gamma Irradiation

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**Abstract** The optical absorption spectra of undoped soda lime silicate glass together with two glasses doped with either (1 % nano Fe<sub>2</sub>O<sub>3</sub>) or with both (1 % Nano Fe<sub>2</sub>O<sub>3</sub> + 5 % cement dust) have been measured from 200 to 2400 nm before and after gamma irradiation with a dose of 8 Mrad. The undoped glass reveals strong UV absorption with two distinct peaks which are attributed to trace ferric iron ions present as impurity. Upon gamma irradiation, this base glass exhibits three peaks at 240, 310 and 340 nm and the resolution of an induced broad visible band centered at 530 nm. The two doped glasses show an additional small visible band at about 440 nm and followed by a very broad band centered at 1050 nm. Upon gamma irradiation, the two doped samples reveal the decrease of intensities of the spectrum. The two additional bands are related to ferric (Fe<sup>+3</sup>) ions to the band at (440 nm) while and the broad band at 1050 nm is due to ferrous iron (Fe<sup>+2</sup>) ions. The decrease of the intensities of the UV-visible spectrum upon irradiation can be related to capturing freed electrons during irradiation. Infrared spectra of the glasses reveal repetitive characteristic absorption bands of silicate groups including bending modes of Si–O–Si or O–Si–O, symmetric stretching, antisymmetric stretching and some other peaks due to

carbonate, molecular water, SiOH vibrations. Upon gamma irradiation, the IR spectra reveal a small change in the base spectrum while the IR spectra of the two doped glasses remain unchanged. The change of the IR spectrum of the base glass is related to suggested changes in the bond angles or bond lengths of the mid band structural units. The doped glasses show resistance to gamma irradiation because the nano Fe<sub>2</sub>O<sub>3</sub> can capture released electrons and positive holes.

**Keywords** Optical and FTIR spectra · Silicate glass · Nano Fe<sub>2</sub>O<sub>3</sub> · Cement dust · Gamma irradiation

## 1 Introduction

It is internationally accepted that most of the produced commercial glasses by weight is based on the soda–lime–silica ternary system with minor additions of other oxides to adjust the various physical and chemical properties for the need of specific applications [1]. Development of soda–lime–silica glass compositions represents a compromise between the outstanding properties of pure vitreous silica, and the cost of producing the massive quantities of glass required for windows, containers and electrical lighting.

Glasses containing 3d transition metal ions possess interesting optical and electrical properties which make them suitable for variable applications [2]. Iron is a 3d transition metal universally present in all oxide glasses as an unavoidable trace impurity, and is responsible for the undesirable greenish tint of many commercial window or plate glasses. It is the most important and most widely investigated of the 3d transition metals in glasses, being present in oxide glasses as either Fe<sup>2+</sup> (d<sup>6</sup>) and Fe<sup>3+</sup> (d<sup>5</sup>). Iron species in glasses have unique extended optical absorption in the ultraviolet,

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visible and near infrared spectral regions, which make them well studied for solar control [3].

When subjected to ionizing radiation, most glasses acquire radiation – induced defects which may give rise to optical and /or ESR absorption bands [4, 5]. The formation and the nature of induced color centers in many different types of glasses such as borate, silicate and phosphate glasses have received considerable recent attention and have been extensively studied by many workers [e.g. 6–9]. Glasses are continuously needed to act as radiation dosimeters, radiation shielding or for immobilization of radioactive wastes [10].

The present study aims to investigate combined optical and FT infrared absorption spectra of three soda lime silicate glasses, the first is a ternary soda lime silicate glass and the second containing the same composition with added 1 gm nano Fe<sub>2</sub>O<sub>3</sub> and the third containing added both 1 gm nano Fe<sub>2</sub>O<sub>3</sub>+5 gm cement dust. The same two collective spectral measurements were repeated after subjecting the glasses to a gamma ray dose of 8 M rad (8×10<sup>4</sup>Gy).

## 2 Experimental Methods

Table 1 shows the chemical composition of the studied glasses in this investigation.

Table 2 shows the detailed composition of the cement kiln dust used as an additive in this work and obtained from Tura cement factory Cairo (Egypt).

### 2.1 Preparation of the Glasses

The glasses were prepared from reagent grade chemical powders. Silica was introduced as pulverized purified quartz, soda and lime were added in the form of their respective anhydrous carbonates. Cement kiln dust was obtained from Tura cement factory [Tura province, Cairo] and the chemical composition of which is shown in Table 2. Nano Fe<sub>2</sub>O<sub>3</sub> was added in the doping percent (1 gm) for 100 gm glass batch. The accurately weighed batches were melted in platinum crucibles in an electric SiC heated furnace (Vecstar, United Kingdom) at 1400 °C. The melting was extended to 2½ hours to obtain clear bubble –free glasses. The crucibles were rotated at intervals to reach acceptable homogeneity for the melts. The melts were poured

into heated stainless steel molds to obtain the required dimensions. The shaped prepared glasses were immediately transferred to a muffle furnace regulated at 480 °C for annealing. The annealing muffle was switched off after one hour and the glasses were kept inside the muffle and the rate of cooling was 30 °C/h to room temperature.

### 2.2 Optical (UV–Visible) Absorption Spectra Measurements

UV-Visible absorption spectra of the glasses were measured for perfectly polished samples of equal thickness (2 ± 0.1 mm) before and after gamma irradiation using a recording double beam spectrophotometer (SHIMADZU UV–3600 Japan) covering the range of (200–2400 nm). The optical spectral measurements were repeated twice to check the accuracy of the absorption peaks position.

### 2.3 FTIR Spectral Investigation

FT infrared absorption spectra of the glasses were measured at room temperature (25 °C) in the wave number range 4000–400 cm<sup>-1</sup> using a Fourier transform infrared spectrometer type (NICOLET 6700 FT–IR, USA). Fine powder samples were mixed with KBr in the ratio 1:100 and the mixtures were subjected to a load of 5 tons/cm<sup>2</sup> in an Evocable die to produce clear homogeneous discs, the IR absorption spectra were immediately measured after preparing the discs to avoid moisture attack. The same measurements were repeated after the glass powders were subjected to gamma irradiation with a dose of 8 M rad (= 8 × 10<sup>4</sup>Gy).

## 3 Results

### 3.1 Optical Absorption Spectra

Figure 1 illustrates the optical (UV – visible) absorption spectra of the base undoped soda lime silicate glass before and after irradiation. The optical spectra before irradiation reveal that the base undoped soda lime silicate glass shows a strong UV absorption with two distinct peaks at about 210 and 235 nm and no visible absorption bands are identified. Upon gamma irradiation of the base undoped glass, the

**Table 1** Chemical composition of the studied glasses

Glass samples (No)	SiO <sub>2</sub> wt %	Na <sub>2</sub> O wt %	CaO wt %	Addition gm/ 100gm glass
S1 (base)	70	20	10	
S2	70	20	10	1 gm nano Fe <sub>2</sub> O <sub>3</sub>
S3	70	20	10	1 gm nano Fe <sub>2</sub> O <sub>3</sub> 5 gm cement

**Table 2** Composition of cement kiln dust (Tura cement factory)

Oxides	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	K <sub>2</sub> O	SO <sub>3</sub>	Cl	Na <sub>2</sub> O
wt %	13.69	4.03	3.51	61.03	2.40	5.01	9.58	4.62	1.43

spectrum exhibits extension of the UV absorption revealing three strong peaks at 240, 310 and 340 nm and a broad band centered at 530 nm.

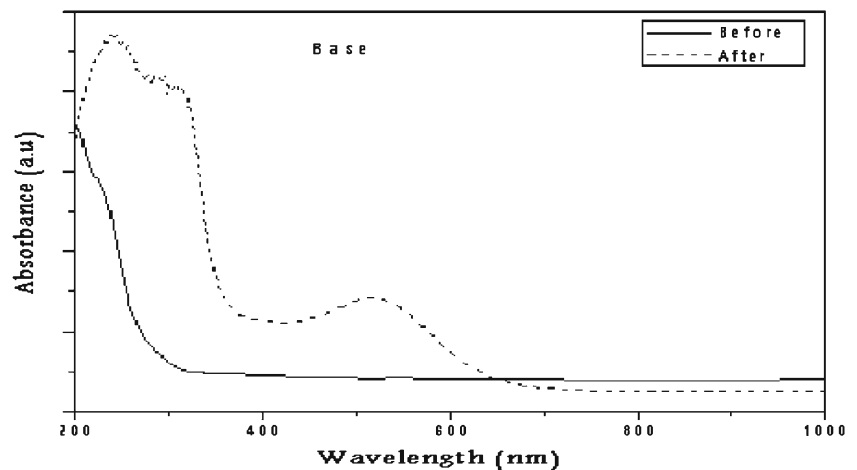
Figure 2 shows that the glass containing additional 1 gm nano Fe<sub>2</sub>O<sub>3</sub> shows a broad and strong UV absorption with peaks at 220 and 335 nm beside two other small bands at about 380 nm and at about 443 nm and with a very broad band extending from about 800 to 1600 nm and centered at 1050 nm. Figure 3 shows the spectrum of the third glass containing two additives (1 gm nano Fe<sub>2</sub>O<sub>3</sub>+5 gm cement dust) reveals an intense UV absorption with peaks at 220 and 280 nm and with two small peaks at 380 and 443 nm and a very broad visible near IR band centered at about 1050 nm. Figures 2 and 3 reveal that upon gamma irradiation, the optical spectra of the two glasses exhibit lower intensities in both the UV and visible regions.

### 3.2 FT Infrared Absorption Spectra

Figure 4 illustrates the infrared absorption spectra of the three glasses before irradiation. The base soda lime silicate glass shows the following characteristic IR vibrational bands:

- A first sharp band is observed at 454 cm<sup>-1</sup>.
- A second medium band is identified at 775 cm<sup>-1</sup>.
- A third broad band is observed with a peak at about 1049 cm<sup>-1</sup>.
- A small peak is observed at the descending lobe of the third band at 1458 cm<sup>-1</sup>.

**Fig. 1** Optical absorption spectra of the base undoped soda lime silicate glass



- A small broad peak near IR band centered at about 3450 cm<sup>-1</sup> is identified.

Figure 4 also shows that the glass No.2 containing only additional nano Fe<sub>2</sub>O<sub>3</sub> and the glass No.3 containing two additives exhibit the same spectral characteristics as the base glass with minor changes. The first far IR band and the third band reveal broadening to a measurable extent while the middle band at 775 cm<sup>-1</sup> remains unchanged.

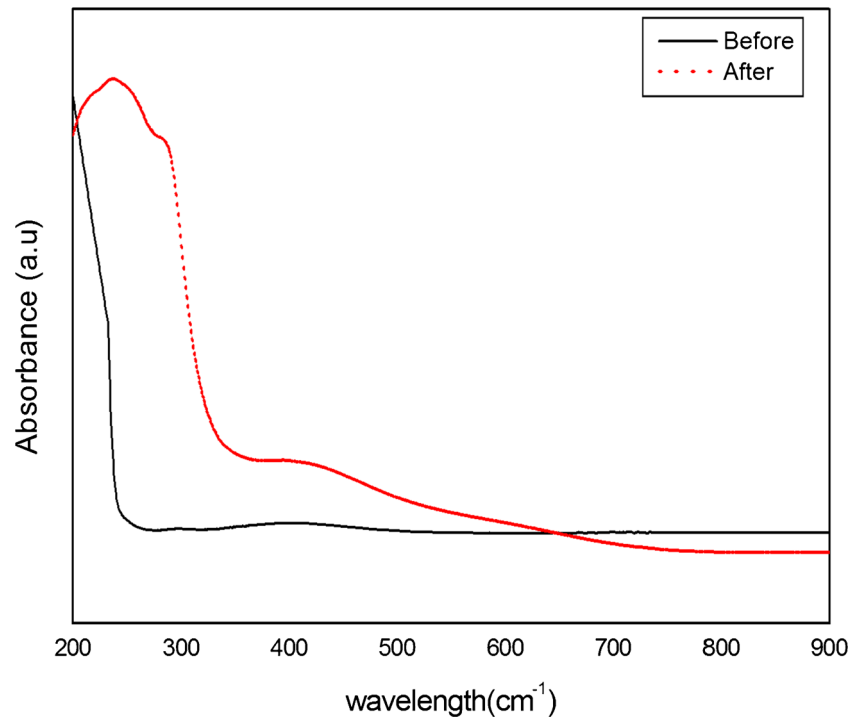
Figure 5 illustrates the FTIR spectra of the three studied after gamma irradiation. The spectra show that the main broad band of the base glass becomes broader revealing two peaks at 973 and 1073 cm<sup>-1</sup> while the spectra of the doped glasses remain unchanged after gamma irradiation.

## 4 Discussion

### 4.1 Origin of Ultraviolet Absorption Spectrum from Base Soda Lime Silicate Glass

The optical spectrum of the base glass (Fig. 1) reveals strong UV absorption and no further visible bands are identified. Some glass scientists [11–13] had previously observed that various undoped commercial silicate glasses exhibit intense ultraviolet absorption bands. They assumed that such strong UV bands originated from unavoidable trace iron impurities (mainly Fe<sup>3+</sup> ions) within the raw materials used for the preparation of such commercial glasses or from

**Fig. 2** Optical absorption spectra of soda lime silicate + 1 % nano  $\text{Fe}_2\text{O}_3$  before and after gamma irradiation



contamination of the molten glasses with refractories of the furnaces during the industrial melting of glasses.

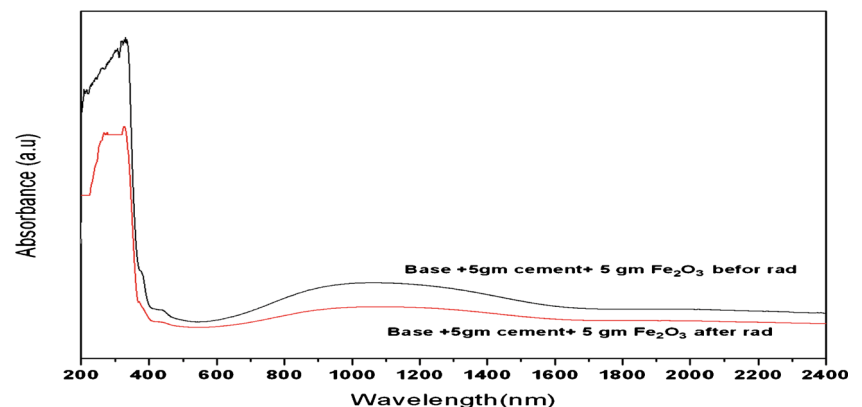
Duffy and Ingram [14] and Duffy [15] have classified differently originated ultraviolet absorption bands in various glasses. They have assumed that certain transition metal ions [e.g.  $\text{Fe}^{3+}$ ,  $\text{Cr}^{6+}$ ] exhibit characteristic charge transfer UV absorption spectra in glasses even if present in the ppm level. Such metal ions in glass owe their UV absorption to an electron transfer mechanism.

Ehrt et al [16] and ElBatal et al [17] have confirmed in a series of optical absorption spectral studies on silicate,

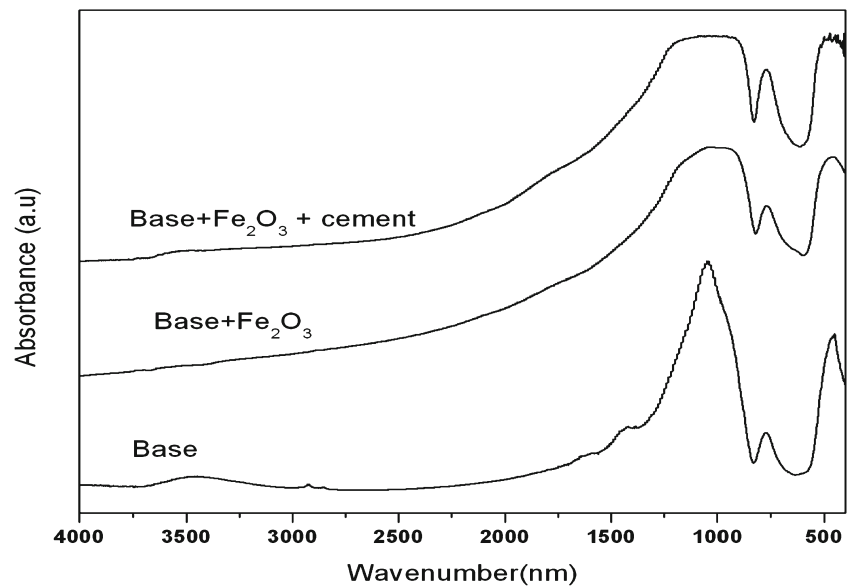
borate and phosphate glasses that small amounts of transition metal ions (especially trace ferric iron even in the ppm level) cause deterioration of the UV transmission in optical glasses. They have claimed the need for ultrapure chemicals for the preparation of special optical glasses for recent applications.

On the basis of this consideration, it is suggested that the observed strong UV absorption bands obtained from the base soda lime silicate glass are due to absorption from trace iron impurities ( $\text{Fe}^{3+}$  ions) contaminated within the raw materials used for its preparation.

**Fig. 3** Optical absorption spectra of soda lime silicate containing additional 1 % nano  $\text{Fe}_2\text{O}_3$ +5gm cement dust before and after gamma irradiation



**Fig. 4** FT infrared absorption spectra of the studied glasses before gamma irradiation



#### 4.2 Interpretation of the Effect of Gamma Irradiation on the Spectra of the Undoped Glass

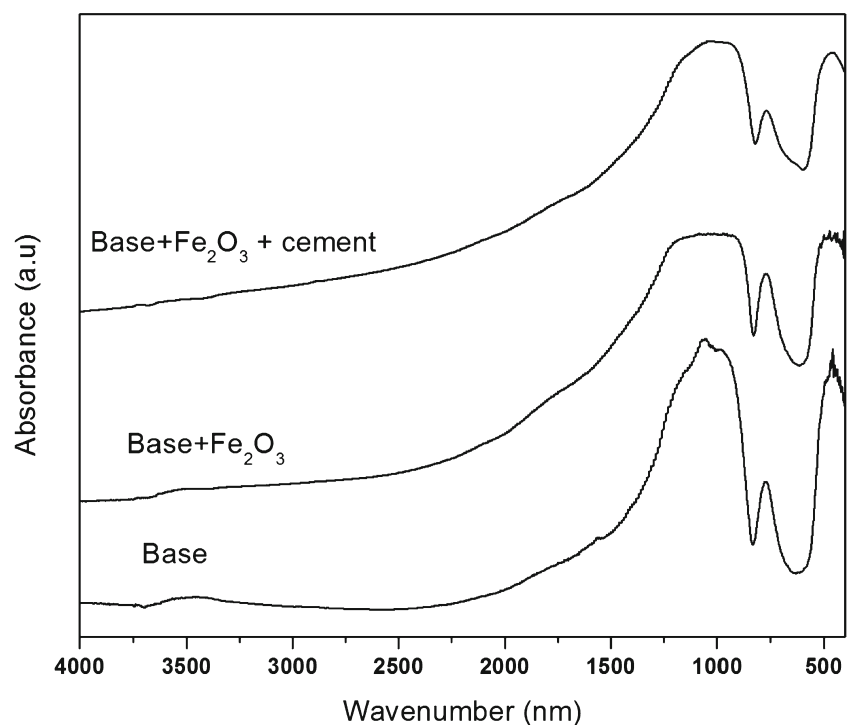
When ionizing radiation such as gamma rays, X-rays, UV radiation impinges on or reacts with the glass, electrons are initially excited from the valence band and travel through the material. They will either react with positively charged holes, or become trapped in specified sites to form color centers.

Glass is not a perfect material but also contains preexisting flaws in the glass matrix, such as oxygen vacancies or nonbridging oxygens, or flaws caused by the high – energy electrons themselves.

The experimental optical results indicate that gamma irradiation causes the extension of the UV absorption of the base undoped glass forming new UV bands and the creation of an induced broad visible band.

Such previous results can be explained as follows

**Fig. 5** FT infrared absorption spectra of the studied glasses after gamma irradiation (8 Mrad)



- (a) The newly formed UV absorption bands with gamma irradiation is assumed to be due to the reaction of the few ferrous ions present as impurities with positive holes to form additional ferric iron ions producing the excess UV absorption bands.
- (b) The formation of an induced broad visible band is related to the formation of a silicon oxygen hole center (SiOHC) or nonbridging oxygen hole center (NBOHC) as suggested by various authors [19, 20].

#### 4.3 Interpretation of the Optical Spectra of Doped Glasses

Figures 2 and 3 reveal two additional peaks from the glasses 2 and 3 at 380 and 440 nm peaks than that observed from the base undoped glass, beside a very broad band centered at 1050 nm. The two peaks at about 380 and 440 nm are attributed by various authors [18–20] to be due to  $\text{Fe}^{3+}$  ions and the precise coordination is controversial with different views as either being octahedral or tetrahedral. The broad visible band centered at 1050 nm is correlated with ferrous ( $\text{Fe}^{2+}$ ) ions [19, 20].

#### 4.4 Interpretation of the Effect of Gamma Irradiation on the Optical Spectra of the two Doped Glasses

Optical spectra of the two doped glasses after gamma irradiation reveal a decrease of the entire UV-visible spectra. This different response towards irradiation is related to the additions of nano iron oxide and cement dust. The close resemblance of the two spectra for the two samples points out that the addition of 1 gm (1 %) nano iron oxide is the most effective in the observed change in the optical spectra by irradiation.

Bishay [4] and Friebele [5] have assumed that transition metal ions are a readily effective component in the irradiation process. TM ions compete for negative electrons and positive holes during the irradiation and can readily change their valencies. Also it has been observed by ELBatal et al [18] that some transition metal ions (e.g.  $\text{Cr}^{3+}$ ,  $\text{Cu}^{2+}$ ,  $\text{V}^{3+}$ ) possess the ability to suppress or shield the effect of irradiation.

Similarly, in the present case the presence of nano iron oxide (1 %) produces some shielding of the effect of irradiation and causes the observed decrease of the absorption throughout the entire UV-visible spectrum as iron ions possess this possibility.

#### 4.5 Interpretation of the Infrared Absorption Spectra

The realization and interpretation of the observed IR spectra from studied multicomponent silicate glasses must take into consideration the following parameters:

- a– The agreement with the concept previously introduced by Tarte [20] and Condrate [21] about the free independent vibrations of the different structural building units in glasses.
- b– The basic characteristic structural units of silicate glasses have been agreed upon [18, 22, 23]. The fundamental building block in the glassy network is the basic  $\text{SiO}_4$  tetrahedral units in which all oxygens are shared between two tetrahedra and form a fully polymerized network. Alkali cations (e.g.  $\text{Li}^+$ ,  $\text{Na}^+$ ) or alkaline earth cations (e.g.  $\text{Ca}^{2+}$ ) act as network modifiers, breaking building oxygen bonds to form non-bridging oxygens (NBOs) and residing in sites interstitial to the tetrahedral network in the vicinity of the negatively charged NBOs.
- c– The principal absorption frequencies of silicate glasses can be classified to occur in two regions:
  - i)– The mid region of the IR spectrum extended from  $400\text{--}2000\text{ cm}^{-1}$  and is characterized by the appearance of the characteristic absorption bands of the silicate chains ( $\text{SiO}_4$  groups) including bending, symmetric and antisymmetric stretching of the silicate units.
  - ii)– The near -IR region of the spectrum extends from  $2000$  to  $4000\text{ cm}^{-1}$  and comprises the absorption bands or peaks due to vibrations of water, hydroxyl and silanol ( $\text{SiOH}$ ) groups.

Based on these considerations, the interpretation of the IR bands of the studied glasses can be summarized as follows [18, 22, 23, 27, 28]:

  - (a) The peaks at  $450\text{--}500\text{ cm}^{-1}$  can be attributed to bending modes of Si–O–Si or O–Si–O.
  - (b) The medium band at  $720\text{--}780\text{ cm}^{-1}$  can be assigned to Si–O–Si symmetric stretching vibrations of bridging oxygens between tetrahedra.
  - (c) The strong broad band extending from  $850\text{--}1200\text{ cm}^{-1}$  can be related to Si–O–Si anti-symmetric stretching of bridging oxygen within the tetrahedra. This broad band reveals a peak at  $920\text{--}980\text{ cm}^{-1}$  which can be related to Si–O– stretching with non-bridging oxygens.
  - (d) The weak peak at  $1350\text{--}1450\text{ cm}^{-1}$  is related to a carbonate group and the peak at  $1620\text{--}1650\text{ cm}^{-1}$  is due to molecular water.
  - (e) The broad near-IR band at  $3430\text{--}3460\text{ cm}^{-1}$  is related to a water group while the small peak at  $3740\text{--}3750\text{ cm}^{-1}$  is related to the SiOH group.

- (f) The far IR band at 420–450  $\text{cm}^{-1}$  is related to modifier cations in their residing sites as bridging and nonbridging types (e.g.  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ).

#### 4.6 Interpretation of the Effect of Gamma Irradiation on the FTIR Spectra

Experimental IR data indicate that gamma irradiation causes only a change of the main silicate band revealing the broadness and appearance of two peaks at 973 and 1073  $\text{cm}^{-1}$  while the IR spectra of the two doped glasses remain unchanged. The observed change in the IR spectrum of the base glass can be related to the change of bond angles or bond lengths of the silicate groups with irradiation. The same assumption was previously introduced by several authors [24–26] and adopted by ELBatal et al [7–9].

### 5 Conclusion

Undoped soda lime silicate glass together with two samples of the same composition but doped with 1gm nano  $\text{Fe}_2\text{O}_3$  or 1gm nano  $\text{Fe}_2\text{O}_3$ +5gm cement dust have been prepared and characterized by dual optical and FTIR spectral analysis before and after gamma irradiation (8 M rad). The undoped sample exhibits strong UV absorption due to trace  $\text{Fe}^{3+}$  ions impurity and the two doped sample glasses show additional UV-Visible bands due to the doping with nano  $\text{Fe}_2\text{O}_3$  containing  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  ions. Gamma irradiation produces noticeable induced defects which are related to photochemical reactions in the UV region and the generation of an induced visible positive hole band due to a silicon-oxygen-hole center (SiOHC) or a non-bridging-hole center (NBOHC). The glasses containing nano  $\text{Fe}_2\text{O}_3$  show resistance to radiation.

Infrared absorption spectra reveal characteristic vibrational modes due to silicate groups and nano  $\text{Fe}_2\text{O}_3$  or gamma irradiation show minor variations due to proposed changes in the bond angles and /or bond lengths of the structural silicate units.

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