

Structural Modification of Silica on Addition of P₂O₅

Md. Arifur Rahman Khan¹, A. H. M. Azadur Rahman¹, Anika Benozir Asha¹, Manzila Islam Tuheen¹,
Md. Miftaur Rahman¹

Department of Materials and Metallurgical Engineering, Bangladesh University of Engineering and Technology,
Dhaka, Bangladesh¹

ABSTRACT: P₂O₅ is added to SiO₂ to reduce its softening temperature which occurs by the breaking of strong Si-O-Si bridging bonds. The aim of this work was to observe this structural change of SiO₂ with the addition of P₂O₅, varying its amount and varying the sintering temperature and holding time at that temperature. In this work, SiO₂ was doped with 5 weight per cent and 10 weight per cent of P₂O₅ by mixing SiO₂ powder with (NH₄)₂HPO₄, heating the mix at 500⁰ C to remove NH₃ and after pelletisation, the pellets were sintered at 1100⁰ C for 2 hours and 1200⁰ C for 8 hours. The sintered pellets were then characterized by Fourier Transform Infrared (FTIR) spectroscopy to determine the effect of P₂O₅ addition on the structure of SiO₂. FTIR spectra reveals that addition of P₂O₅ causes new peaks to emerge at about 500-550 cm⁻¹ and 794 cm⁻¹ after sintering at 1100⁰ C for 2 hours with a decrease in the per cent absorbance of Si-O-Si stretching, bending and rocking vibration modes. After sintering at 1200⁰ C for 8 hours bands at 1020-1040 cm⁻¹ for Si-O-NBO (Non Bridging Oxygen) have appeared which reveals the breaking of Si-O-Si bridging bonds. This is the indication of the degradation of crystalline structure and formation of amorphous structure.

KEYWORDS: P₂O₅, SiO₂, Sintering, FTIR Spectroscopy, Non bridging Oxygen, Amorphous Structure.

I. INTRODUCTION

SiO₂ has wide application in the microelectric devices as a gate and as field effect oxides in metal-oxide semiconductor field-effect-transistors (MOSFETs), as passivation layers because of its high electrical resistivity that can be as high as 10¹⁸ ohm-cm [1,2]. Also, the structure of SiO₂ consists of interconnected SiO₄ tetrahedra that are connected by highly flexible Si-O-Si bridging bonds. This flexibility results in many possible crystalline structures of SiO₂ to transform into amorphous structure which does not crystallize upon annealing at normal temperatures. This amorphous SiO₂ gets sufficiently flowable at higher temperature which is a requirement for planarization in IC processing. This makes SiO₂ suitable for integrated circuit application. But the temperature to achieve this flowability is about 1300-1400⁰C for pure SiO₂ which is too hot for other features on the wafer to tolerate [3]. Moreover, small positive ions like Na⁺ and K⁺ ions can migrate through the open structure of the amorphous SiO₂ under the influence of electric field which is detrimental to microelectronic devices [3, 4]. That is why, dopants like phosphorus, boron or a combination of the two is added to SiO₂. Phosphorus after doping into SiO₂, getters these alkali ions [4, 5] and makes SiO₂ to soften and flow at 950⁰C to 1150⁰C [3]. This phosphorous doped silicate glass is used as a premetal dielectric layer between polysilicon and metal in logic devices. Also, they have potential applications in Raman fiber lasers and amplifiers [6], biomedical research, catalysis, drug delivery and imaging [7-9].

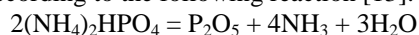
Many processes for producing phosphosilicate glasses have been used like sol gel processing [7, 10], modified chemical vapor deposition [6] and plasma enhanced chemical vapor deposition [11]. Sol gel processing possesses a disadvantage of large volume changes during fluid removal, pyrolysis, and/or densification. Columnar grain growth and uneconomical deposition rates are some major disadvantages of vapor condensation methods [12]. In this present study we have used a facile route of powder processing which is more economical than the other processing routes and the most widely used processing techniques for the processing of ceramic powder. This powder processing technique includes the following steps - powder manufacture, powder preparation for consolidation, consolidation of powder to

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 5, Issue 1, Januray 2016

an engineering shape and sintering. In this work, we have added 5 weight percent and 10 weight percent of P_2O_5 into high purity SiO_2 powder by the powder processing technique. Due to the highly hygroscopic nature of P_2O_5 , we have used Di-ammonium Hydrogen Phosphate, $(NH_4)_2HPO_4$ powder as the source of P_2O_5 which dissociates into P_2O_5 according to the following reaction [13]:



Our main aim is to observe the structural modifications of SiO_2 by varying the amount of P_2O_5 , the sintering temperature and the holding time at that temperature by using the Fourier Transform Infrared Spectroscopy (FTIR) technique and then obtain an optimum sintering temperature at low cost.

II. EXPERIMENTAL PROCEDURES

HDPE(High density Poly Ethylene) container, ZrO_2 balls, beaker and sieve all were first washed with detergent and then cleaned ultrasonically. Then Calculated amounts of diammoniumhydrogenphosphate, $(NH_4)_2HPO_4$ and SiO_2 were weighed to produce 10 gm sample of SiO_2 doped with 5% P_2O_5 and SiO_2 doped with 10% P_2O_5 each. These were then mixed inside the HDPE container by ball milling process using ZrO_2 balls in the acetone for 24 hrs. Mixed powder was then collected in a beaker with acetone and dried in a drying oven at about $100^{\circ}C$. Sample was then preserved in an air tight container.

Powders prepared from both of these processes were then put inside a furnace. These were then heated up to $500^{\circ}C$ at rate of about $4^{\circ}C/min$. At $500^{\circ}C$ temperature, these samples were then held for about 7 hours. Samples were then furnace cooled.

Heat treated powder was then mixed with 2.5% binder in an agate mortar to produce a powder mixture of 1 gram to produce a pellet of 1 gram weight for each of the compositions. The binder composition is 81% C, 13.5% H, 2.9% O, and 2.6% N. This 1 gram of binder mixed powder is then poured into the die cavity of the pressing machine. Compaction pressure is kept at 40KN and was held for about 1 minute. The compact was then ejected from the die using the lower punch. This process was repeated to produce required numbers of pellets.

Pellets sintered at about $1100^{\circ}C$ and $1200^{\circ}C$. The sintering cycle constitutes first heating the pellets to about $500^{\circ}C$ at a heating rate of about $2^{\circ}C$ per minute, holding there for about one hour to remove the binder content, then again heating at the rate of $5^{\circ}C$ per minute to two sets of temperatures with different holding time. Holding time for sintering at $1100^{\circ}C$ was 2 hours and $1200^{\circ}C$ was 8 hours after that the samples were furnace cooled.

Fourier Transform Infrared Spectroscopy of pure silica powder and SiO_2 doped with 5% and 10% P_2O_5 and sintered at $1100^{\circ}C$ for about two hours in the wave number range of $400 -1400\text{ cm}^{-1}$ and $1200^{\circ}C$ for about eight hours in the wave number range of $400 -4000\text{ cm}^{-1}$, were performed in the Nicolet 380 FTIR machine. Potassium bromide (KBr) powder was used as a standard material to measure the background.

III. RESULTS AND DISCUSSION

Figure 1 shows the FTIR spectra of pure SiO_2 . In this figure, band located at 1082.2 cm^{-1} , represents the Si-O-Si stretching vibration [14] in pure SiO_2 . Band located at 454 cm^{-1} [14], represents the Si-O-Si rocking vibration and band at 776.8 cm^{-1} represents the Si-O-Si bending vibration [14, 15].

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 5, Issue 1, Januray 2016

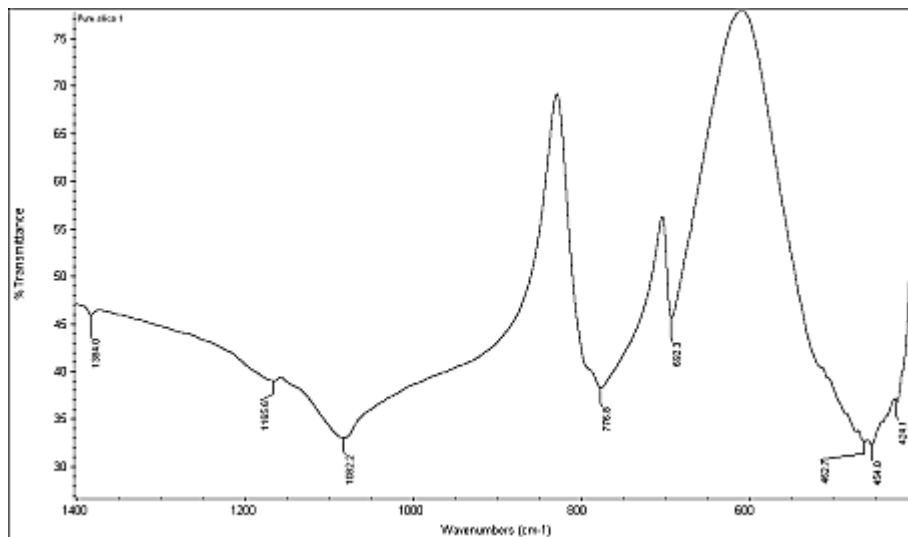


Fig. 1. FTIR spectra of pure SiO₂

After addition of P₂O₅ and by sintering at 1100⁰ C for two hours, some strong peaks were observed from figure 2 and figure 3 other than those observed for pure SiO₂. Some peaks of low intensity in the range of 500-550 cm⁻¹ were observed for 5% P₂O₅ addition and for 10% P₂O₅ some strong peaks were also observed at 500.3 and 513.7 cm⁻¹. These peaks between 500 and 600 cm⁻¹ represent the PO₄³⁻ bending vibration [14].

The strong peaks at 794.8 cm⁻¹ for 5% P₂O₅ and 793.6 cm⁻¹ for 10% P₂O₅ represent the P-O-P asymmetric stretching of the bridging oxygen atoms bonded to a phosphorus atom in a phosphate tetrahedron [16]

The comparison of % Transmittances for the Si-O-Si stretching, Si-O-Si bending and Si-O-Si rocking vibrations of pure silica, 5% P₂O₅ and 10% P₂O₅ added silica are tabulated and plotted in Table 1 and Fig 4 respectively.

Table 1: Comparison of % transmittances for various vibrational modes

Vibrational Mode	Pure SiO ₂	SiO ₂ -5%P ₂ O ₅	SiO ₂ -10%P ₂ O ₅
Si-O-Si stretching	28	34	36
Si-O-Si bending	33	51	51
Si-O-Si rocking	26	40	40

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 5, Issue 1, Januray 2016

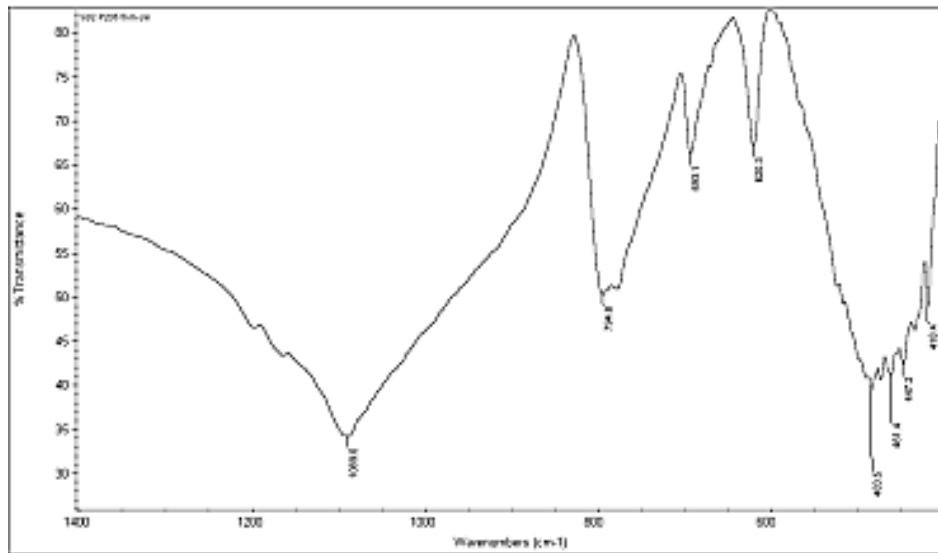


Fig. 2FTIR spectra of SiO₂-5% P₂O₅ after sintering at 1100⁰ C for two hours

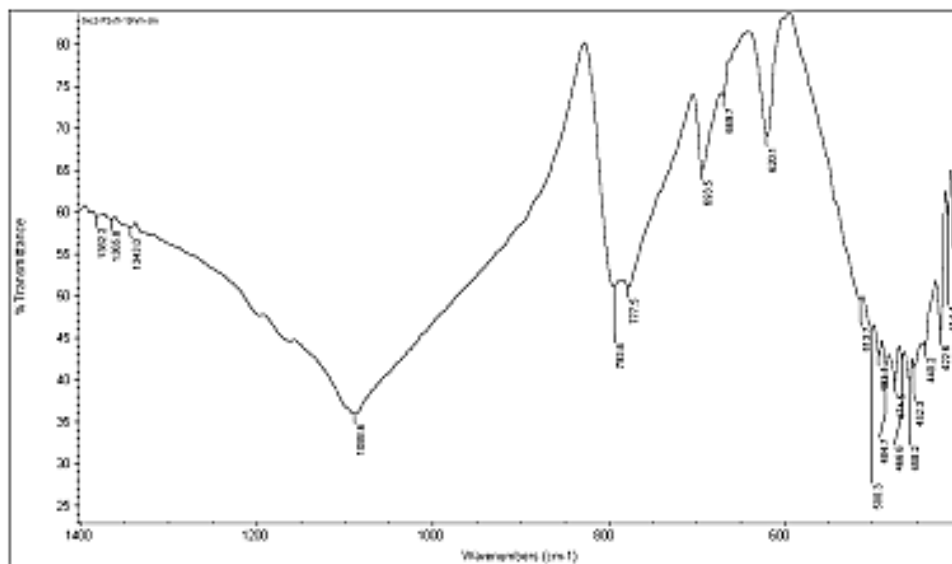


Fig. 3FTIR spectra of SiO₂-10% P₂O₅ after sintering at 1100⁰C for two hours

Fig 4.shows the comparison of % Transmittances for the Si-O-Si stretching, Si-O-Si bending and Si-O-Si rocking vibrations of pure silica, 5% P₂O₅ and 10% P₂O₅ added silica.

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 5, Issue 1, Januray 2016

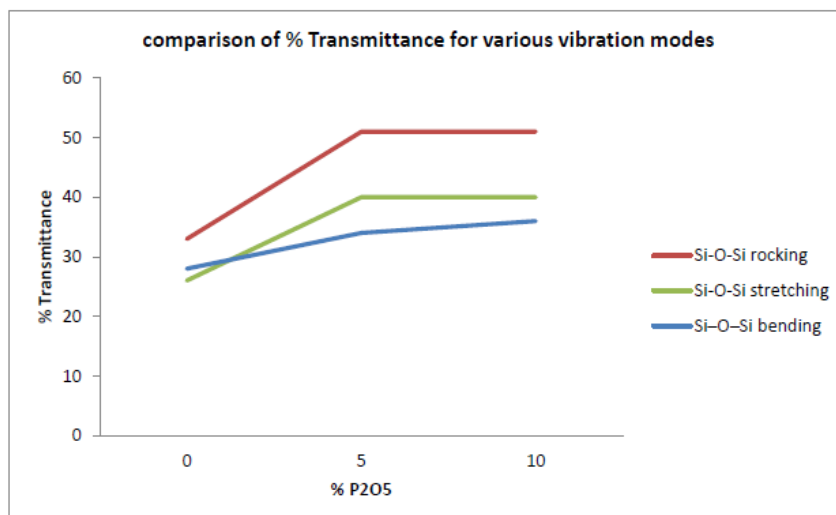


Fig. 4 Comparison of % Transmittance with addition of P₂O₅ for various Si-O-Si vibration modes

This shows that % transmittance increases which means % absorbance decreases as P₂O₅ is added. Breaking of some bridging oxygen bonds due to P₂O₅ addition may attribute to this increment.

FTIR spectra of the SiO₂-10% P₂O₅ after sintering at 1200⁰ C for about 8 hours is shown in the figure 5.

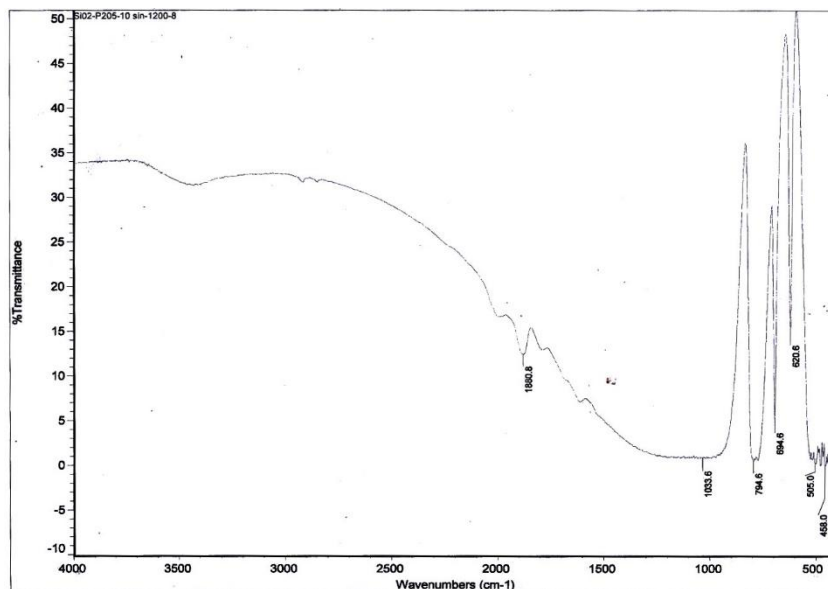


Fig. 4 FTIR spectra of SiO₂-10% P₂O₅ after sintering at 1200⁰C for eight hours

In this figure, a broaden peak ranging from 900 – 1300 cm⁻¹ were observed with very low transmittance value. This is due to the formation of PO₄³⁻ symmetric stretching, Si-O-NBO Stretching, PO₄³⁻ asymmetric stretching vibration modes which causes the breakage of bridging oxygen bonds of Si-O-Si stretching to transform into non-bridging oxygen. The presence of Si-O-NBO Stretching causes a great amount of distortion in the crystallinity pure silica and the formation

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 5, Issue 1, Januray 2016

of amorphous phase in the sintered product. The reference regions of these special interests in FTIR spectra are listed in Table 2

Table 2: IR frequencies of some functional groups

Vibration Mode	Reference wavenumbers (cm ⁻¹)
PO ₄ ³⁻ symmetric stretching	900-970 [14,17]
Si-O-Si stretch	1080 [14]
Si-O-NBO stretching	1020 to 1040[14,18]
PO ₄ ³⁻ asymmetric stretching	1000-1100 [19]

This broaden peak was not appeared at previous figures for different sintering programs. So previous heating schedules in this work was unable to make sufficient breakage of giant crystalline structure of pure silica as we got no peak in the range of 1020-1040cm⁻¹ wavenumber showing the evidence of presence of Si-O-NBO stretching except for sintering at 1200^oC for 8hrs.

IV. CONCLUSION

This work investigated the structure modification of SiO₂ after addition of P₂O₅ in its network structure. Varying the amount of P₂O₅ addition, the sintering temperature and the holding time we got the alluring result of the first appearance of Si-O-NBO (Non Bridging Oxygen) for sintering at 1200^oC temperature for 8 hours from the FTIR spectroscopy. The appearance of this Si-O-NBO (Non Bridging Oxygen) band proves the crystal distortion of SiO₂ which leads to the formation of amorphous phase. This degradation in crystallinity increases the flowability of SiO₂ which is highly required in integrated circuit processing.

ACKNOWLEDGEMENTS

The authors sincerely thank Dr. Md. Fakhurul Islam, Professor and Head, Dept of Glass & Ceramic Engineering, (GCE, BUET) for allowing us to perform the entire work in GCE, BUET.

REFERENCES

- [1] Nam C. W., Woo S., "Characterization of spin-coated silicate and phosphosilicate thin films prepared by the sol-gel method", Thin Solid Films, vol. 237, pp. 314-319, 1994.
- [2] Pierret R. F., Semiconductor Device Fundamental, Addison-Wesley Publishing Company, 1996.
- [3] Dobkin D., Zuraw M.K., Principles of Chemical Vapor Deposition, first ed., Kluwer Academic Publishers, 2003
- [4] Hsiao W.C., Liu C.P., Wang Y.L., "Influence of thermal budget on phosphosilicate glass prepared by high-density plasma chemical-vapor deposition", Journal of vacuum science & technology, vol. 23, pp. 2146-2150, 2005.
- [5] Modelli A. and Manzini S., "Dielectric relaxation in chemical vapor deposited phosphosilicate glasses, Journal of Applied Physics", Vol.71, pp.5123-5129, 1992.
- [6] Plotnichenko V.G., Sokolov V.O., V.V. Koltashev, E.M. Dianov, on the structure of phosphosilicate glasses, Journal of Non-Crystalline Solids, Vol.306, pp.209-226, 2002.
- [7] Elnahrawy A. M., Ali A.I., "Influence of Reaction Conditions on Sol-Gel Process Producing SiO₂ and SiO₂-P₂O₅ Gel and Glass", New Journal of Glass and Ceramics, Vol.4, pp. 42-47,2014.
- [8] Portales H., Mattarelli M., Montagna M., Chiasera A., Ferrari M., Martucci A., Mazzoldi P., Pelli S., Righini G.C., "Investigation of the Role of Silver on Spectroscopic Features of Er³⁺ Activated Ag-Exchanged Silicate and Phosphate Glasses", Journal of Non-Crystalline Solids, Vol.351, pp. 1738-1742, 2005.
- [9] Anderson, C. and Bard, A.J. "An Improved Photocatalyst of TiO₂/SiO₂ Prepared by a Sol-Gel Synthesis", Journal of Physical Chemistry, Vol.99, pp. 9882-9885, 1995.
- [10] Kannan A.G., Choudhury N.R., Dutta N.K., "Electrochemical Performance of Sol-Gel Derived Phospho-Silicate-Methacrylate Hybrid Coatings", Journal of Electroanalytical Chemistry, Vol.641, pp. 28-34, 2010.
- [11] Shioya Y., Maeda M., Takasaki K., Takagi M., "Method of plasma enhanced chemical vapor deposition of phosphosilicate glass film", Patent US4394401, 1983.
- [12] Lunge F.F., "Powder Processing Science and Technology for Increased Reliability", Journal of the American Ceramic Society, Vol.72, pp. 3-15, 1989.
- [13] Odinma S.C., Okoye N.H., Okoro, V.E., "Comparative Study on the Effect of Three Flame Retardant Compounds on Flame Behaviour of a Roofing Thatch", International Journal of Engineering Science Invention, Vol.2, pp. 56-60, 2013.
- [14] Aguiar H., Serra J., González P., León B., "Structural study of sol-gel silicate glasses by IR and Raman spectroscopies", Journal of Non-Crystalline Solids, Vol.355, pp. 475-480, 2009.

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 5, Issue 1, Januray 2016

- [15] Serra J., Gonzalez P., Liste S., Serra C., Chiussi S., Leon B., Perez-Amor M., Ylanen H.O. , Hupa M., “FTIR and XPS studies of bioactive silica based glasses”, Journal of Non-Crystalline Solids, Vol.332, 20–27, 2003.
- [16] Battisha I., Nahrawy A.E., “Physical Properties of Nano-Composite Silica-Phosphate Thin Film Prepared by Sol Gel Technique”, New Journal of Glass and Ceramics, Vol.2, pp. 17-22, 2012.
- [17] Carta D., Knowles J.C., Smith M.E., Newport R.J., “Synthesis and structural characterization of P₂O₅-CaO-Na₂O sol-gel materials”, Journal of Non-Crystalline Solids, Vol.353, pp.1141-1149, 2007.
- [18] Kawashita M., Miyaji F., Kokubo T., Takaoka G.H., Yamada I., Suzuki Y., and Inoue M., “Surface structure and chemical durability of P+-implanted Y₂O₃-Al₂O₃-SiO₂ glass for radiotherapy of cancer”, Journal of Non-Crystalline Solids, Vol. 255, pp.140-148, 1999.
- [19] Pryce R.S., Hench L.L., “Tailoring of bioactive glasses for the release of nitric oxide as an osteogenic stimulus”, Journal of Materials Chemistry, Vol.14, pp. 2303-2310, 2004.