Dependence of Spectroscopic Properties of Copper Oxide Based Silica Supported Nanostructure on Temperature

S. H. Tohidi[1], A. J. Novinrooz[2*], M. Derhambakhsh[3,1], G. L. Grigoryan[3]

1- Materials Research School, (NSTI) , Karaj, I. R. Iran
2- Physics Group, Islamic Azad University, Takestan branch, Takestan, I. R. Iran
3- Yerevan State University, Yerevan, Armenia

(*) Corresponding author: novinrooz@yahoo.com

Abstract:
Various concentrations of copper were embedded into silica matrix to xerogel forms using copper source $Cu(NO_3)_2 \cdot 3H_2O$. The xerogel samples were prepared by hydrolysis and condensation of Tetraethyl Ortho-Silicate (TEOS) with determination of new molar ratio of the components by the sol-gel method. After ambient drying, the xerogel samples were heated from 60 to 1000˚C at a slow heating rate (50°C/h). The absorption and transmittance spectra of the gel matrices were heat treated at different temperatures. The loss of water and hydroxyl group from the silica network changed the spectral characteristics of Cu^{2+} ions in the host silica. The shift observed for the broad band of the absorption spectrum of the samples heated up to 600°C was attributed to the legend field splitting and partial removal of the hydroxyl group from the silica matrix. Absorption spectrum of the samples heated to 1000°C confirmed the conversion of Cu^{2+} ions to Cu^+ ions. The effects of thermal treatment were characterized by Fourier Transmission Infrared (FTIR) and Raman spectroscopy at different temperatures. Also, the Transmission Electron Microscope (TEM) micrographs confirmed the average pores size of about 50 nm.
Keywords: *Copper oxide, Nano-composite, Thermal treatment, Silica, Sol-gel.*

1. INTRODUCTION

Sol-gel processing is a relatively new technique for the preparation of glasses which is primarily to get potentially high purity and homogeneity as well as low processing temperatures compared with the traditional glass melting techniques [1]. One of the best methods used for making sol-gel of silica monolith is the hydrolysis and poly-condensation of alkoxide precursors followed by aging and drying [2]. The monoliths processed by the sol-gel method allow the incorporation of transition metal ions and rare earth ions in their matrix. Introducing transition metals into hydrolysable precursors through sol-gel method permits the formation of numerous novel

materials that exhibit important optical and/or catalytic properties [3,4]. Copper or copper oxides in oxide matrixes have attracted sustained interest due to their unusual properties [5]. Mohanan and Brock [6] have studied copper oxide silica aero-gel composites by varying pH values, copper precursor salts and treatment temperatures. They found that based-catalyzed gels underwent a gradual change from bonded Cu^{+2} ions to segregated CuO at different heating conditions. Parler et al. [7] observed silicon-oxygen-metal bond formation during both the synthesis and drying stages at low temperatures with relatively high copper concentrations. Host matrices embedded with copper have been produced to study their properties

as tunable visible light solid-state lasers and colored coatings [8, 9]. The optical properties of Cu-doped silica gels in the form of xerogels, coatings and powders have been extensively studied [10]. The structural evolutions of copper-doped porous silica gels treated at different temperatures have also been studied [11]. So far, no reports have been seen on the spectroscopic studies of CuO-doped monoliths heated at different temperatures. The present work aims at understanding the effect of thermal treatment on the spectroscopic properties of different copper concentrations (2, 5 and 10 wt.%). The characterization of the xerogel samples was done by UV-Vis, FTIR, Raman spectroscopy and TEM micrograph at different temperatures [12].

2. EXPERIMENTAL

2.1. Sample preparation

In this work, raw materials including tetraethyl ortho-silicate (TEOS) (Fluka, 98%), ethanol absolute (EtOH) (Merck), and copper nitrate tri-hydrated ($Cu(NO_3)_2.3H_2O$) (Merck) were exploited as the initial solution, and nitric acid (HNO_3) (Merck, 65%), and acetic acid (CH_3COOH) (Merck, 99-100%) were used as the catalysts.

Three samples of CuO/SiO_2 nanocomposites in xerogel form were prepared by the sol-gel method and the forth sample was prepared as a blank using TEOS hydrolyzed with HNO_3, CH_3COOH, EtOH and de-ionized (DI) water with the new total molar ratio of TEOS:ETOH:H_2O=1:1.3:6.2 [12]. Appropriate amounts of tri-hydrated copper nitrate were added to the solution, such that the concentrations of copper oxide in the final products reached to 2, 5 and 10 wt.% (labeled as A, B and C, respectively). Then the solutions were mixed by magnetic stirrer for 1.5 h to make them more homogeneous. The solution acidity (pH) was measured by a pH-meter as 2.4. The samples were kept in a close container at 25-30°C. The soft gel was prepared when a dark-blue color appeared within 84 h via gelatin treatment. Next, the gel samples were dried in an oven at 60-100°C in air for 1 h to complete the gelatin process [13]. The gel samples were subjected to annealing in the temperature range of 100-1000°C at 50°C/h for 2 h, using electric furnace in order to form a condensed nanocomposites [14, 15]. The blank solution was prepared using the above mentioned procedure, but without addition of $Cu(NO_3)_2.3H_2O$.

2.2. Characterization

Characterization of ultra violet-visible (UV-Vis) spectra of samples prepared under experimental conditions was done by UV spectrophotometer of model BEKMAN (DU-600).

Fourier transmission infrared spectroscopy (FTIR) spectra, were done by a Gensis system, model ATI, using 0.05 g of the powder sample and 0.3 g of KBr.
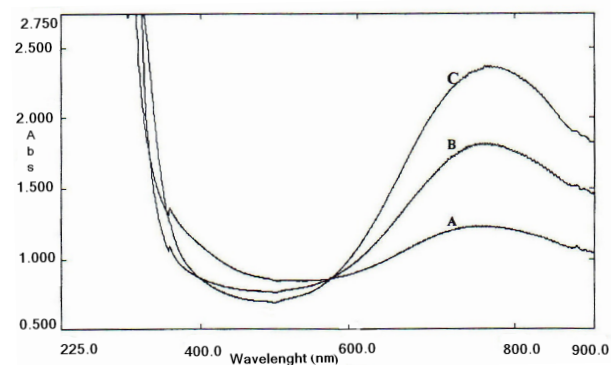
Figure 1: *Absorption spectra of the samples A, B, and C heated at 200°C.*

Raman spectrum was obtained at room temperature using a Labram-Dilor micro-Raman system, in which the samples were exited with a He-Ne laser and the signals were analyzed by a low noise charge-coupled device detector. To study the possible changes in the samples induced by laser heating, the laser spot diameter was arranged in the 1-10 μm range and the power density was supplied using neutral density filters.

A transmission electron microscope (TEM), Em208S series (Phillips Company), operating at 100 kV was used to investigate the micro structural images. The dry samples were ground suspended in dry cyclohexane and sonicated for 30 minutes. Then the solutions were allowed to settle and a droplet of the resulting supernatants was placed on a holey carbon film and dried.

Tohidi, *et al.*

The condensation and annealing of the samples were performed in a heat furnace with high thermal capacity (1500°C).

3. RESULTS AND DISCUSSION

3.1. Spectroscopy characteristics

Figure 1 exhibits the absorption spectra of the samples A, B and C heated at 200°C. As shown in this figure, all of the doped gel samples present an absorption band around the 780 nm wavelength, indicating the presence of Cu^{+2} ions in the gel matrix [16]. This absorption intensity increases for higher concentrations of copper ions in volume unit. Figure 2 shows the absorption spectra of the sample A (2 wt. %) at different temperatures of 30°C (sol), 60°C (Ref), 60°C (gel), 200°C, 500°C and 700°C. It is inferred from this figure that the broad absorption band is shifted toward the shorter wavelengths due to the temperature rise.

It is well known that diluted copper (II) ions in silica matrix exhibit broad optical absorption band in around 780 nm related to the electronic transfers caused by *d* level splitting of copper (II) ions in a legend field [10]. This broad absorption band is in the Near Infrared (NIR) region for the samples heated at 60-700°C. The band wavelength was shifted from the 750-790 nm regions and the broad band was shifted from 700-900 nm to 600-800 nm regions, i.e., the edge of red absorption energy decreases from 700 to 600 nm. There are *d-d* electronic absorption transmissions in every diagram, and the broad band in around 780 nm is related to the electronic transmission of the d orbital [16].

The absorption edge shift is referred to the charge transfer agent between the copper ions and the legends of matrix. It was reported that, the broad absorption in around 750 nm in xerogel is attributed to the presence copper (II) ions in the internal position of silica matrix [16]. The shift of broad absorption toward lower wavelengths indicates that by increasing the temperature up to 200°C, the water molecules are removed and the shrinkage of the legend field increases.
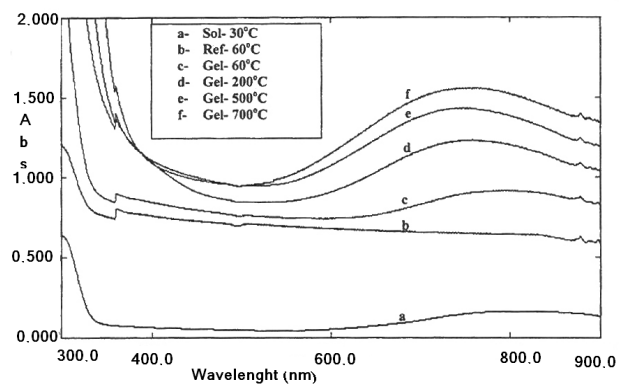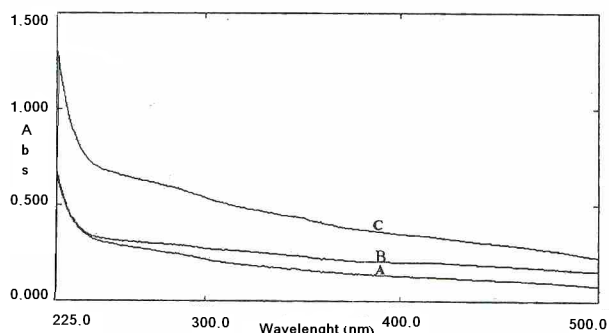

Figure 2: *Absorption spectra of the sample A heated at different temperatures.*

It is known that, impurity of water in oxides appearing in the form of hydroxyl groups produces absorption band in the NIR region [16]. It was observed that an absorption band in the violet region (400 nm) exhibits CuO colloidal particles in the matrix [16]. But it is surprising that no absorption band has been seen in this range due to low concentration of the copper ions and low acidity of the samples. Figure 3 presents the transmittance spectra of the sample B (5 wt. %) heated at different temperatures (200°C, 500°C and 700°C). The blue color of gel samples is related to the transmittance spectrum indicating maximum transmittance in the 400-600 nm range. Because of high purity and low volume of water, these composites show high transmittance. These observations indicate that the samples have filtering effect in the 400-600 nm range [17].
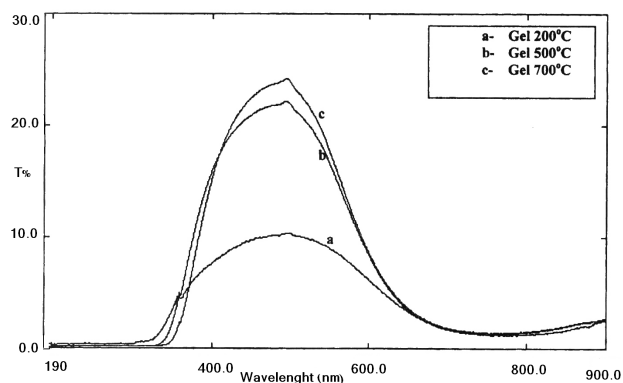
Figure 3: *The transmittance spectra of the sample B heated at different temperatures.*

Figure 4 shows the absorption spectra of the samples A, B and C heat treated at 1000˚C. The powdered samples showed similar absorption spectra to that of Cu^+ ions. The broad absorption around 780 nm was completely disappeared for all the samples. Therefore, it seems that at 1000˚C, the Cu^{2+} ions might be converted into Cu^+ ions or Cu_2O. Thus, the reaction of copper metal and oxygen initially yields CuO, which is then converted into Cu_2O during the longer reaction times or at higher temperatures [18].

Figure 4: The absorption the spectra of the samples A, B and C heated at 1000 °C.

The bonding and molecular structure properties of CuO/SiO_2 (sample C, 10 wt.%) nano-composite which were in bonding vibration mode were studied by FTIR spectrum. Figure 5 shows the FTIR absorbance spectra in the range of 500-4000 cm^{-1} for SiO_2:CuO in the powdered sample. Each of the three major features related to the transversal optical (TO) absorption bands (shown in Figure 5) could be characterized in terms of a particular vibration mode of the Oxygen (O) atom with respect to the Silicon (Si) atom. Rocking (R) of the (O) atom about an axis through the two Si atoms characterizes the vibration behavior of the lowest frequency to the bond centered at 475-490 cm^{-1}. Bending (B) of the (O) atom along a line bisecting the axis formed by the two Si atoms characterizes the vibration mode of the middle TO band centered at 780 cm^{-1} [14]. The remaining TO bands and their high frequency shoulder are due to an asymmetrical stretch (S) motion, in which the (O) atom moves back and forth along a line parallel to the axis through the two Si atoms [19]. The main band of the SiO_2 IR spectrum corresponds to the asymmetric stretching (S) mode

at 1086 cm^{-1}. It has been reported the IR spectrum with a shoulder, in the frequency range of 1150 to 1250 cm^{-1}, has an amplitude comparable or bigger than the main stretching band at 1186 cm^{-1} [20]. This has been achieved in various SiO_2 samples prepared by the sol gel method under specific preparation conditions. Also as Figure 5 shows a band at 850-990 cm^{-1} assigned to the vibration of the [Si—OH] groups, shows a noticeable evolution and change with the annealing temperature. There is an overlap of this band and the bending of Si—O (S) band that appears to spread peak type and lead to a shoulder in vibration of stretching frequency Si—O (S) [21].
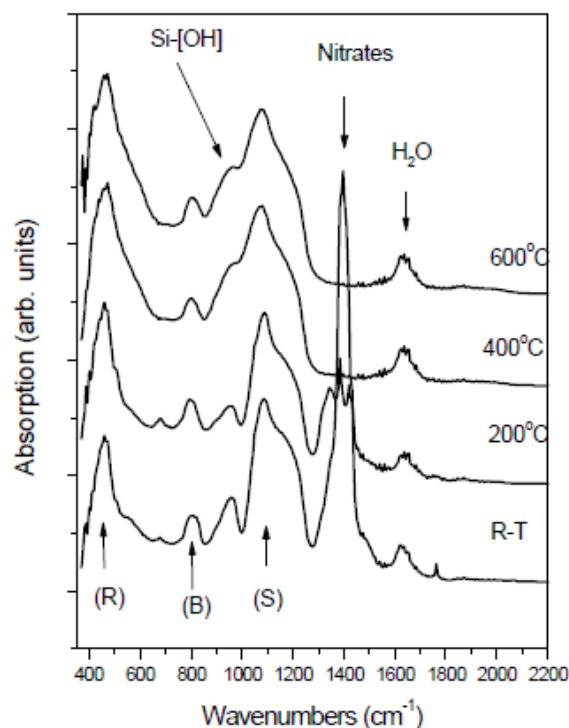
Figure 5: The FTIR spectra of CuO/SiO_2 (C) powdered samples at different temperatures.

The Si-O stretching (S) band at about 1078 cm^{-1} seems to suffer with temperature. There are two additional bands at about 1450 cm^{-1} and 1650 cm^{-1}, these bands are related to the nitrate groups and free molecular water vibrations, respectively [16]. The band assigned to the nitrate vibration decreases due to annealing at 200°C and diminishes after the 400°C annealing, indicating the evolution of nitrogen compounds probably in the form of nitrogen oxides.

Tohidi, *et al.*

We can see that at temperatures higher than 200°C, the Si-OH band starts decreasing, accompanied by the diminishment of the nitrate band, given as result an evident modification. Hence, a noticeable reduction of the bond at 950 cm^{-1} is observed [17]. Figure 6 represents the Raman spectra of the un-doped and the sol-gel samples doped with copper oxide heat treated at the temperature range of 100-600°C. The spectra of the un-doped sample show three main features at about 490, 800 and 980 cm^{-1}. But the spectra of the sample (C) treated at 100 °C, has as the main Raman feature with an intense and sharp peak at about 1050 cm^{-1}, which corresponds to the vibrations of the NO_3^- ions or forming of nitrates.
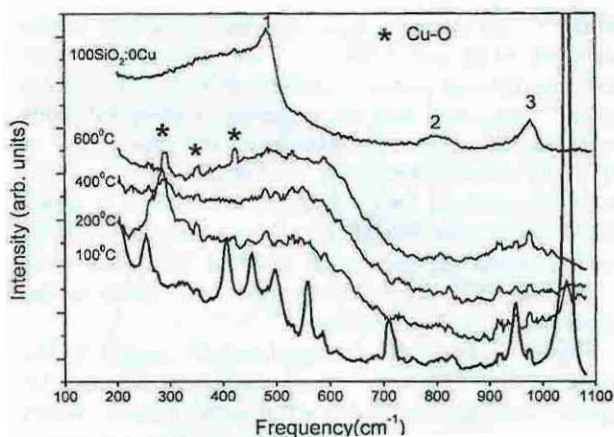

Figure 6: *Raman spectra of un-doped and copper oxide doped (C) samples treated at different temperatures*

The other peaks in the range of 250 and 950 cm^{-1} have the same origin. Notice that, in agreement with the FTIR results, the intensity of this bond was strongly reduced after the annealing at 200°C so that disappeared when annealed at the temperature above 400°C. Also, in the Raman spectra of the samples treated at 200°C there appeared a band at approximately 290 cm^{-1}, and also two weak peaks at about 350 and 430 cm^{-1}. These features are attributed to the vibrations of Cu-O bonds in cupric oxide [22]. In the same spectrum, two broad bands appear, one in the region of 400 to 700 cm^{-1} and the other at above 850 cm^{-1}. On the top of this latter band, weak peaks at 920, 950 and 980 cm^{-1} can be observed. As, shown in Figure 6 by increasing of the annealing temperature, the nitrate groups were decomposed and converted to oxide groups. This result is in agreement with our observation in FTIR measurements studies.

The nano-structural characterization of the xerogel was studied by TEM. Powder samples with 10 wt% copper, after ambient drying and thermal treatment at 400°C in air for 1 h, were objected to TEM using bright field, and the resulted images are shown in Figures 7 (a, b). No crystalline species were detected without thermal treatment, and the bright field image shows a typical amorphous xerogel. Figure 7 (a) exhibits un-doped silica matrix that is a network of pours with different sizes. Also, Figure 7. (b) presents the copper ions doped into pours of silica matrix after annealing at 400°C. In these figures, different pores with average size of about 50 nm that doped and completed the pores of silica matrix are seen. After heating at 400 °C, copper species start to segregate.
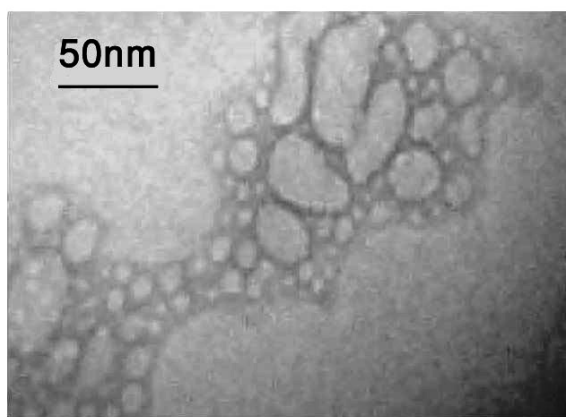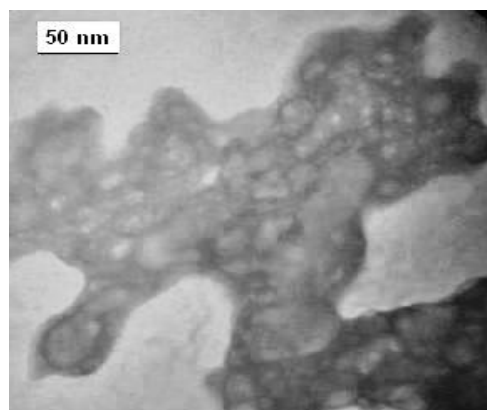
(a) (b)

Figure 7: *TEM micrograph of (a) un-doped silica and (b) CuO/SiO$_2$ nano-composite at 400°C.*

4. CONCLUSION

The incorporation of copper ions in the matrix up to 700˚C was confirmed by the absorption spectra. The broad absorption band of Cu^{2+} ions in around 780 nm was related to the legend field splitting of d levels. The partial removal of hydroxyl groups was confirmed by shifting of the broad band to the higher energy region. The transmittance spectra of high temperature treated copper ions doped into silica matrix indicates the broad bond with filtering effect. The FTIR measurements confirmed the removal of hydroxyl (OH) groups from the samples at beyond 600˚C.

The evolution of the copper species goes from copper nitrate to copper oxide species by thermal treatment. The FTIR results showed that the copper ions were mainly incorporated into the SiO_2 matrix in copper nitrate form, and there was no copper oxide (CuO) particle, or their concentration was too low. After decomposition of the copper nitrate, the CuO particles were formed and interacted with the SiO_2 matrix via the hydroxyl groups. Also, the TEM micrographs confirmed the formation of colloidal particles of about 50 nm. The comparison of Raman spectra of the un-doped and the sol-gel samples doped with copper oxide showed that they are different from each other. It is concluded that, there is a correlation between the existence of copper oxide particles embedded into the silica matrix, and the overlapping of the silanol and siloxan (Si-O) stretching bonds. This overlapping might be associated to the interaction between the guest particles and the matrix host. According to the findings of this study, the exact composition of clusters depends on the annealing temperatures and the choice of appropriate copper source.

REFERENCES

1. H. L. Larry, J. K. West: Chem. Rev. Vol. 90, (1990), p. 33.

2. K. C. Lisa: Ann. Rev. Mater. Sci. Vol. 23, (1993), p. 437.

3. D. R. Rolison, D. R., Dunn: J. Mater. Chem. Vol. 11, (2001), p. 963.

4. I. Tseng, W. Chang, C. S. Wu: Appl. Catal. Vol. 203, (2002), p. 37.

5. M. A. Karakassides, A. Bourlions, D. J. Petridis: Mater. Chem. Vol. 10, (2000), p. 403.

6. J. L. Mohanan, S. L. Brock: Chem. Mater. Vol. 15, (2003), p. 2567.

7. C. M. Parler, J. A. Ritter, M. D. Amiridis: J. Non-Cryst. Solids. Vol. 279, (2001), p. 119.

8. K. Ikoma, S. Kawakita, H. Yokio: J. Non-cryst. Solids. Vol. 122, (1990), p. 183.

9. O. DeSanctis, L. Gomez, A. Curan, C. Parodi: J. Non-cryst. Solids. Vol. 121, (1990), p. 338.

10. J. F. Perez-Robles, J. Gonzales-Hernandez,: J. Phys. Chem. Solids., Vol. 60, (1999), p. 1729.

11. E. M. B. De Sousa, A. O. Porto, P. J. Schilling, M. C. M., Alves, N. D. S Mohallem: J. Phys. Chem. Solids., Vol. 61, (2000), p. 853.

12. J. R. Martinez, S. Palomares-Sanchez, G. Ortega-Zarzosa, F. Ruiz, Y. Chumukov: Materials Letters., Vol. 60, (2006), p. 3526.

13. S. H. Tohidi, A. J. Novinrooz: Inter. J. Eng. Vol. 19, (2006), p. 53.

14. J. R. Martinez, F. Ruiz, Y. V. Vorobiev, J. Gonzalez-Hernandez: J.Chem. Phys. Vol. 109, (1998), p. 7511.

15. Z. Wang, Q. liu, J. Yu, T. Wu, G. Wang: Applied Catalysis A. Vol. 239, (2003), p. 87.

16. S. H. Tohidi., G. L. Grigoryan., A. J. Novinrooz: Inter. J. Mater. Res, Vol. 102, No. 10, (2011), p. 1247.

17. F. Ruiz, J. R. Martinez, J. Gonzalez-Hernandez: J. Mater. Res. Vol. 15, No. 12, (2000), p. 2875.

18. R. R. Conry, D. K. Karlin, Encyclopedia of Inorganic Chemistry (England: John Wiley & Sons) Vol. 2, (1994), p. 829.

19. J. R. Martinez, F. Ruiz, M. M. Gonzalez-Chavez, A. Valle-Aguilera: Rev. Mex. Fis. Vol. 44, (1998), p. 575.

20. J. A. Calderon-Guillen, L. M. Aviles- Arellano, J. F. Perez-Robles, J. F. Gonzalez-Hernandez: J. Surface & Coating Technology. Vol. 190, (2005), p. 110.

21. S. B. Ogale, P. G. Bilukar, N. Mate, S. M. Kanetkar, N. Parikh, B. Patnaik: J. Appl. Phys., Vol. 72, (1992), p. 3765.

22. S. H. Tohidi: Int. J. Nanosci. Nanotechnol., Vol. 7, No. 1, (2011), p. 7.