Available online at www.scholarsresearchlibrary.com

Scholars Research Library

Archives of Physics Research, 2011, 2 (1): 6-14
(http://scholarsresearchlibrary.com/archive.html)

Archives of Physics Research
Scholars Research Library
ISSN 0976-0970
CODEN (USA): APRRC7

Novel processing of silica gel with inner reactant

G. Mangalam[1] and S. Jerome Das[2]*

[1]*Department of Physics, Dr. MGR University, Chennai, India*
[2]*Department of Physics, Loyola College, Chennai, India*

ABSTRACT

Pure silica gel samples of various pH were prepared using sodium metasilicate and ortho phpsphoric acid. The prepared well set gel samples were characterized by powder XRD, FTIR, UV and EDAX. Amorphous nature of silica gel sample was cofirmed by powder XRD spectrum. The gel was subjected to EDAX to analyze the elemental and atomic percentage of the elements present in the sample. The presence of various functional groups in the grown crystals was identified by performing FTIR studies. The UV absorption study reveals the transparency of the silica gel in the entire visible region.

Keywords: X-ray diffraction, relative density, amorphous nature, EDAX, diffused spectrum.

INTRODUCTION

A world wide research effort has been directed towards crystal growth. Over the past decade, a great deal of work has been carried out in crystal growth to grow good quality crystals. In general, single crystals are expected to be of higher perfection in crystalline structure. The crystalline perfection of all the single crystals whether organic or inorganic depends strongly on the growth conditions, annealing, reduction, solvents, dopants etc [1, 2]. The quest for highly efficient inorganic, nonlinear optical (NLO) ferroelectric single crystals is growing at a rapid pace to meet the demands in the field of electronics, mechatronics and optics. In this context, the design and growth of single crystals suitable for such requirements, assumes centre stage. The first place of such criteria is satisfied when single crystals are grown under most favorable conditions. A number of experiments were carried out with an objective to establish the conditions conducive for growth of better quality single crystals [3]. Normally, crystals grown at ambient temperature have lower concentration on nonequilibrium defects than those grown at elevated temperature [4]. Growth from gel at room temperature leads to better quality single crystals. When gels are used, the requirements for the crystallization process are less rigid, due to its

unique characteristic of suppressing nucleation centers [5, 6]. By preventing convection currents and remaining chemically inert, the gel medium itself provides a soft three dimensional network in which the crystal nuclei are delicately held in the position of their formation [7]. Its softness and uniform nature of constraining forces that it exerts upon the growing crystals, encourages orderly growth. Crystals of substance with low solubility and low thermal stability are difficult to grow by conventional methods, which in turn can be easily grown by gel method since it involves diffusion of two reagents at a reasonably slow and controlled rate that yields sparingly soluble reaction product [8, 9].

Over the past decade, variety of crystals required for the purpose of research and application have been grown by silica gel method. Silica gel is an attractive amorphous material which can be regarded as loosely interlinked polymer [10]. In order to have a clear idea regarding the function of silica gel, the sodium metasilicate solution prepared under various parameters are considered [11]. The gel formation depends on the concentration of ionic species inside the gel, gel pH, and temperature of the gel [12, 13] Different parameters such as concentration of reactants, pH of gel, gel age, gel density, and molarity of lower and upper reactants have considerable effect on growth rate [14]. These factors insist that it is important to understand the properties of base silica gel material. The present work is focused on the preparation and characterization of silica gel material. Even though crystals can be grown in a variety of gels, the general observation is that silica gel is the most suitable base to grow, as it does not require any heating effects and also any additional acids or alcoholic substances. It is comparatively cheap and best also.

MATEIALS AND METHODS

2.1 Preparation of stock solution

The silica gel, also known as water glass, was used in the present work. SMS (AR-sodium metasilicate powder) was added to double distilled water in 1:1 ratio, mixed and then stirred well. It was then kept in undisturbed condition for few days to allow sedimentation. Then, the clear top solution was filtered and stored in a light protected glass container with air tight cork so that the solution may not be affected by oxygen in air and light. This is known as stock solution. Relative density, or specific gravity, is the ratio of the density (mass of a unit volume) of a substance to the density of a given reference material. Specific gravity usually means relative density with respect to water.

$$RD = \frac{W_{air}}{W_{air} - W_{water}} \qquad (1)$$

Where, W_{air} is the weight of the sample in air. W_{water} is the weight of the sample in water.

2.2 Preparation of gel solution of definite density

The density of the stock solution is determined by specific gravity bottle method. The different quantities of stock solution (i.e.) 10, 15, 20 and 30 ml are mixed with double distilled water and the quantities of the final solution are made equal to 100 ml.

Specific density of these solutions are determined by the following formula,

$$Specific\ gravity = (A - C)/(A - B) \qquad (2)$$

Where, A is the weight of empty bottle, B is the weight of water in the bottle and C is the weight of sodium metasilicate in the bottle. A graph is drawn between the quantities of stock solution mixed with water and their corresponding densities. Figure 1 shows the graphical method to determine the density of the gel solution.

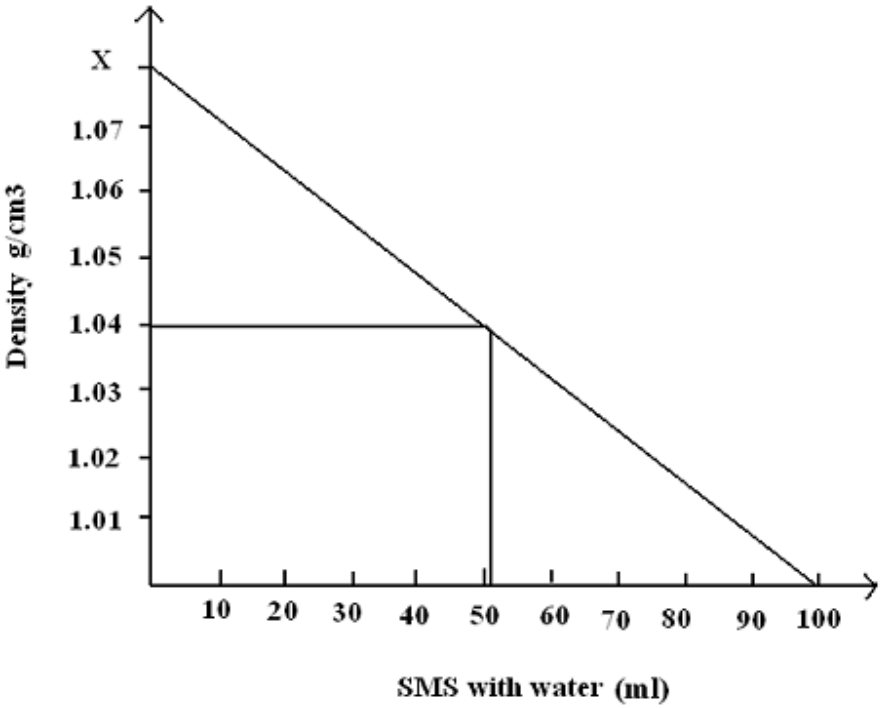

Fig.1 Graphical method to determine the density of gel solution

The control of nucleation is very important in the gel growth and it was taken care of by controlling various gel parameters such as gel density, concentration of reactants, pH of the gel, intermediate neutral gel column, gel aging etc. A large number of nucleation sites were observed in the gel column, if proper gel aging was not adopted. By adopting gel aging technique, the nucleation sites can be controlled by placing the overhead solution after a predefined period (2 to 7 days) onto the set gel. The optimized value of gel density kept in this work was 1.035 g/cc. At higher gel densities, the crystallization is restricted appreciably and the number of well defined crystals reduced considerably. A greater gel density implies, smaller pore size and poor communication among the pores, thus decreasing the nucleation density [15].

3. Characterization

In the present work, various concentrations of gel solutions were used with orthophosphoric acid as pH reducing agents. The pH value of sodium metasilicate (Na_2SiO_3) solution having density 1.035 g/cm^3 was reduced by using 1 M of orthophosphoric acid. Various pH values of 4, 5 and 6 of the gel solution were prepared and kept at room temperature in an undisturbed condition, which makes the solution to set. The characterization of silica gel was carried out with a number

of experimental approaches in order to investigate all the relevant features. The prepared well set gel samples were characterized by powder XRD, FTIR, UV and EDAX.

3.1 Powder X-ray diffraction analysis

Sintered silica gel granules were powdered and powder X-ray diffraction spectrum of the grown crystal was also recorded on a REICH SIEFERT X-ray diffraction instrument using CuKα (1.540 Å) radiation at 55 kV and 40 mA. Figure 2 shows X-Ray diffraction patterns of the silica gel sample of pH 4 at 40 ^{o}C temperatures. No peaks are observed in the sample at 40 ^{o}C except for the harrow like pattern at 2θ degree between 12 °C and 24 °C attributed to amorphous silica gel. The diffused powder XRD spectrum shows the amorphous nature of silica gel. The absence of any crystal formation was tested by XRD studies. XRD is also used to determine the qualitative and quantitative phase analysis of silica gel mixture [16, 17].

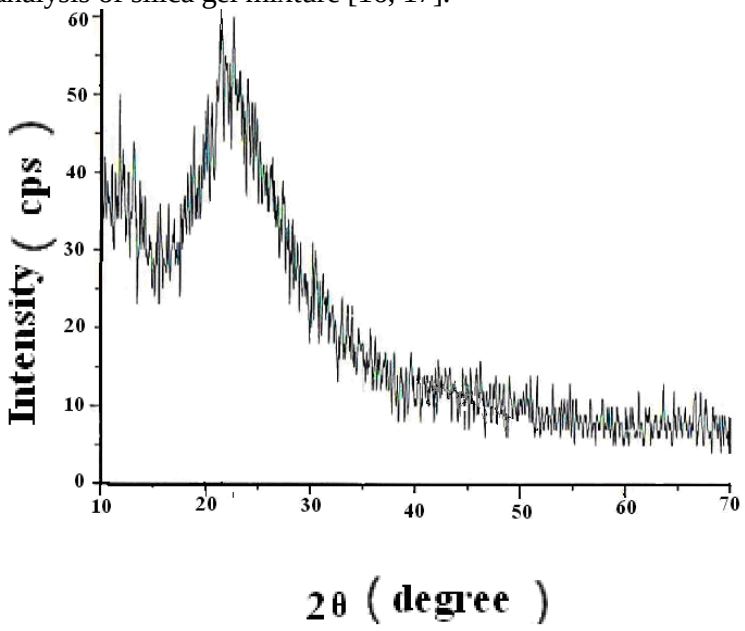

Fig. 2 Powder X-Ray diffraction patterns of silica gel

Table 1 Data from EDAX analysis for pure silica gel

Gel pH	Elements	Elemental %	Atomic %
pH 4	Na	8.00	9.90
	Si	58.95	59.73
	P	33.06	30.37
pH 5	Na	5.19	6.39
	Si	67.44	68.40
	P	27.37	25.17
pH 6	Na	5.86	7.22
	Si	72.07	72.62
	P	22.07	20.16

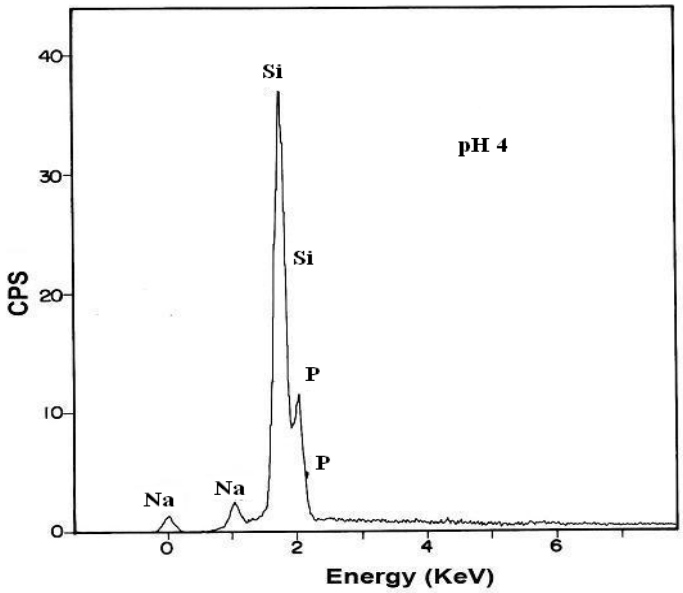

Fig. 3 EDAX spectrum of the set gel of pH 4

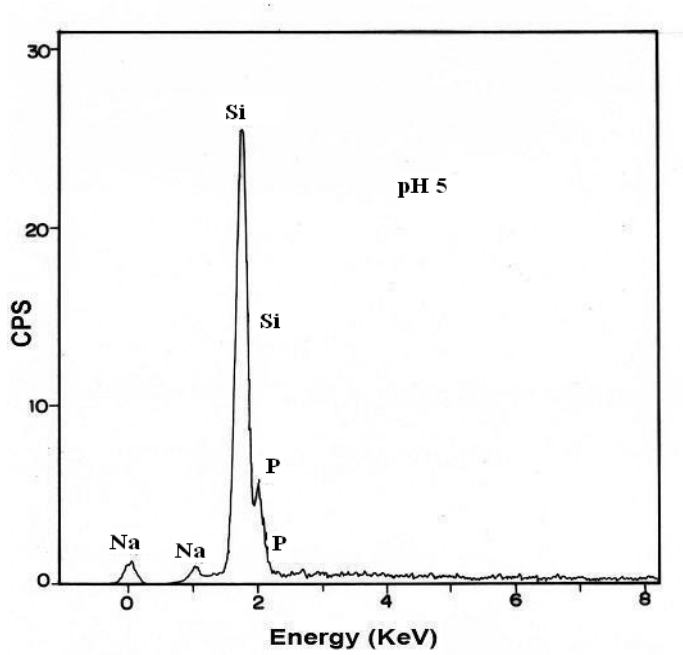

Fig.4 EDAX spectrum of the set gel of pH 5

3.2 Energy Dispersive X-ray Analysis

It was performed to know the chemical composition of the element that is present in the set gel. The prepared well set gel was subjected to EDAX in order to analyze the chemical composition (or) elemental presence in the sample. Figures 3, 4, 5 show counts per second against energy of the EDAX spectrum for the set gel of pH 4, 5 and 6 respectively. These peaks show the presence of sodium, silicon and phosphorous in the set gel. The higher a peak in the spectrum, the more concentrated is the element in the specimen. Table 1 shows the elemental and atomic percentage of the elements Na, Si, P in the silica gel of various pH values.

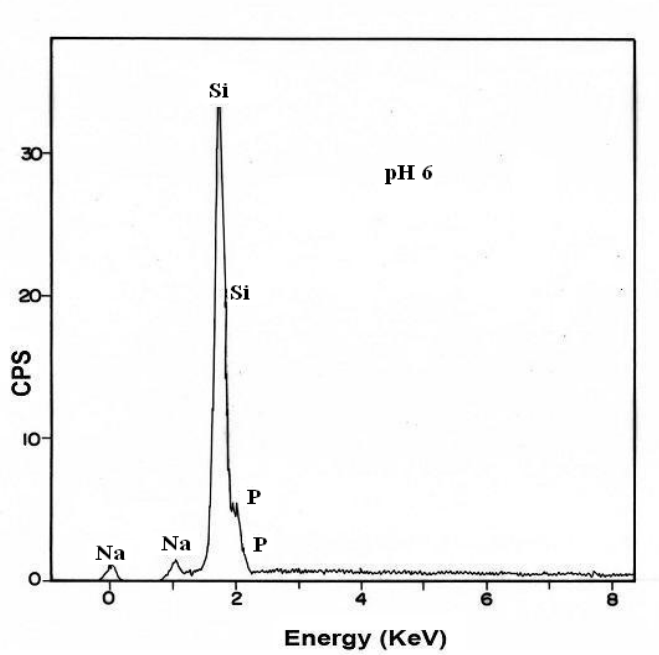

Fig.5 EDAX spectrum of the silica gel of pH 6

3.3 Fourier Transform Infrared Spectroscopy

The pelletized silica gel sample was analyzed for its vibrational spectra with the aid of Fourier transform infrared spectroscopy using Perkin Elmer 1800 model instrument in the range 400-4000 cm^{-1}. The FTIR spectrum was recorded for the sample of pH 4 is shown in fig.6 and the functional groups were identified. Further, the occurrence of the above elements in the aforesaid adsorbents given by EDAX was confirmed by FTIR study. The coupled vibrations are appreciable due to the availability of various constituents.

A strong band at 3938.9 cm^{-1}, 3784.2 cm^{-1} and 3487 cm^{-1} indicate the possibility of the hydroxyl linkage. The two vibrations in the range of 1060-1220 and 985 cm^{-1} are assignable to Si-O-Si and Si-O vibration modes of isolated Si-OH groups respectively. However, the broad band at 3487 cm^{-1} and at 1609.1 cm^{-1} in the FTIR spectrum of silica gel suggests the possibility of water of hydration in the adsorbent. The peak at 1609.1 cm^{-1} is due to water bonding. Inner layer hydrogen bonding in gel is assigned by a characteristic band at 3784.2 cm^{-1}. The broad absorption peak between 3506-3400 cm^{-1} is due to O-H stretching vibration. The sharp peak at 1146 cm^{-1} is assigned to symmetric stretching vibration mode of Si-O. The stretching mode of Si-OH is observed at 1067 cm^{-1}. The peak at 985 cm^{-1} is ascribed to the Si-O-Si bending vibration. Similar bands were observed by [18, 19]. The sharp peak at 585.9 cm^{-1} are also assigned to symmetric bending mode of $(PO_4)^{3-}$. The sharp peak at 1107 cm^{-1} is assigned to stretching mode of P-O and plane bending mode of $(PO_4)^{3-}$. The PO_4^{2-} stretching mode is positioned at 1017 cm^{-1}. These peaks of phosphate show the incorporation of orthophosphoric acid in the sample. FTIR spectra elucidates the bonding system of the constituent atoms and groups such as Si, O and OH that throws light to the expected structure intense.

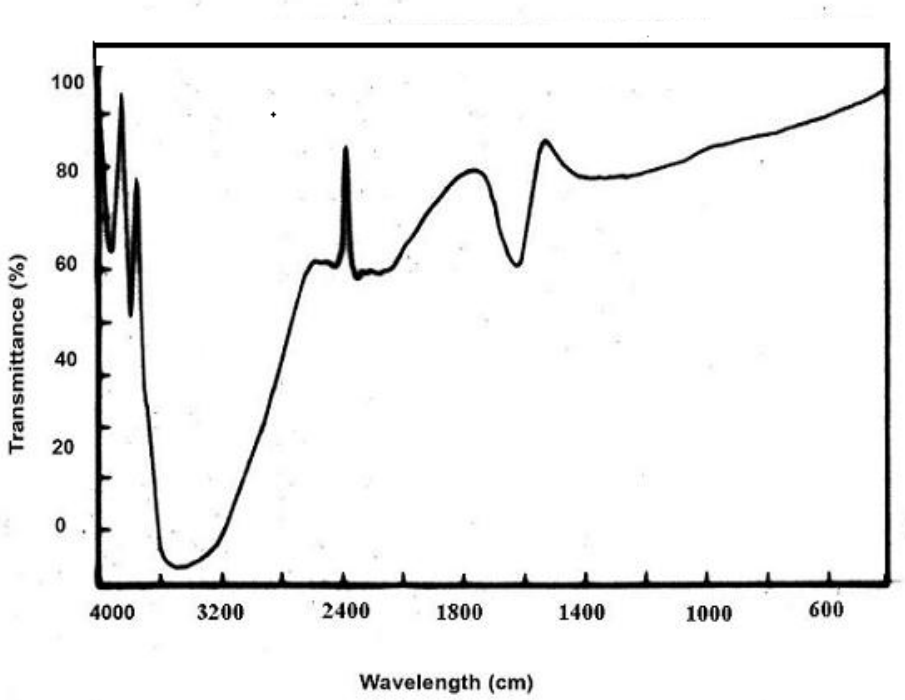

Fig.6 FTIR spectrum of the silica gel of pH 5

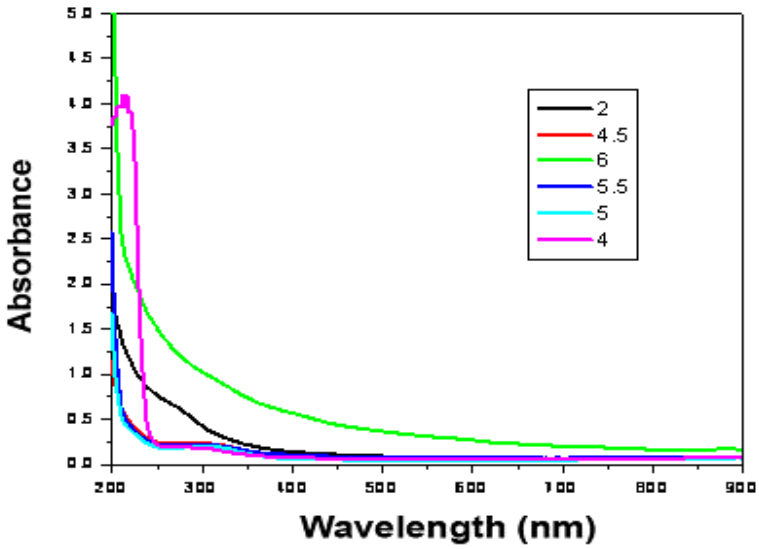

Fig.7 Optical absorption spectrum of set gel of various pH

3.4 Optical absorption spectral analysis

The UV-Vis-NIR spectrum for the grown crystal was carried out between 200 – 2000 nm using VARIAN CARY 5E spectrophotometer and is shown in fig.7. The optical absorption spectral analysis of the samples of pH 2, 4, 4.5, 5, 5.5 and 6 at 40° C for more than 10 days were recorded in the wavelength region ranging from 200 to 900 nm using UV-visible spectrometer and the results were compared. From the spectrum shown in fig.7, the transmittance was found to

be very high in the entire visible region and it shows minimum absorption in the UV region. The prepared pure silica gel was colourless. It was observed that pure prepared samples at 40 °C for more than 10 days have high transmission. For all the samples, no peaks were observed in the UV visible region. For the sample of pH 4.5, 5, 5.5 the UV absorption curves are approximately the same.

CONCLUSION

Pure silica gel samples of pH 2, 4, 4.5, 5, 5.5 and 6 were prepared. The prepared well set gel samples were characterized by powder XRD, FTIR, UV and EDAX. The diffused powder XRD spectrum shows the amorphous nature of silica gel. The gel was subjected to EDAX to analyze the elemental and atomic percentage of the sodium, silicon and phosphorus present in the sample. FTIR spectra elucidates the bonding system of the constituent atoms and groups such as Si, O and OH that throws light to the expected structure intense. The UV absorption study reveals that the transmittance was found to be very high in the entire visible region and it shows minimum absorption in the UV region.

Acknowledgements
The encouragement rendered by the authorities of *Dr. M.G.R Educational and Research Institute,* Maduravoyal, Chennai-95, is gratefully acknowledged.

REFERENCES

[1] Bhagavannarayana G., Budakoti G.C., Maurya K.K. and Kumar B., *J. of Cryst. Growth*, **2005**, 282, 394-401.
[2] Bhagavannarayana G., Parthiban S. and Meenakshisundaram S., *J. Appl. Cryst*. **2006**, 39, 784-790.
[3] Garud S.L., Maharajan N.K. and Saraf K.B., (2009), *Bull. Mater. Sci*., **2009,** 32, 187-192.
[4] Chauhan K. M., Arora S. K., *Cryst. Res. Tech*., **2008**, 44, 189-196.
[5] Patel. A.R. and Venkateshwara Rao A., *Bull.Mater. Sci*., **1982**, 4, 527-548.
[6] Govinda Bhat S. and Dharmaprakash S. M., *Indian J. Pure & Appl. Phys*. **2003**, 41, pp. 627–629.
[7] Rathi F.A.P., Dinakaran S., Robert R., Mahalakshmi R., Yogam F., and Jerome Das S.,(2008), *Cryst. Res. Technol*., **2008**, 43, pp. 729 – 732.
[8] Mayer K., Woermann D., *J. of Cryst. Growth*, **1996**, 169, 317-324.
[9] Arora. S. K., Vipul Patel, Brijesh Amin and Anjana Kothari (2004), *Bull. Mater. Sci*., **2004**, 27, 141-147.
[10] Valarmathi. D, Leela Araham and Gunasekaran S., *Indian J. Pure & Appl. Phys*. **2010**, 48, 36-38.
[11] Ajeetha N., *Bulg. J. Phys*., **2007**, 34, 108-115.
[12] Desai C. C. and Ramana M. S. V., *J. Crystal Growth*, **1990**. 102, 191–196.
[13] Nallamuthu D., Selvarajan P., Freeda T.H., *Physica B Condensed matter*, **2010** 405, 4908-4913.
[14] Vinay Hangloo, Sanjay Pandita, Bamzai K. K., Kotru P. N., and Neera Sahni, , *Crystal Growth & Design*, **2003**, 3, 753–759.
[15] Ambujam K., Rajarajan K., Selvakumar S., Madhavan J., Gulam Mohamed, Sagayaraj P., *Optical Materials*, **2007**, 29, 657 – 662.

[16] MacKenzie K. J. D. and T. Kemmitt, *Thermochimica Acta.*, **1999**, 325, 13-18.
[17] Battisha I. K., *J. Sol.*, **2001**, 24, pp. 51-65.
[18] Brinker C.J., Tallant D.R., Roth E.P., Ashley C.S., *J. Non- Crystalline Solids*, **1986**, 82, 117-126..
[19] Zhi Hua Cheng, Akemi Yasukawa, Kazuhiko Kandori and Tatsuo Ishikawa, *J. Chem. Soc., Faraday Trans.*, **1998**, 94, 1501-1505.