Front. Optoelectron. China 2010, 3(3): 328–331
DOI 10.1007/s12200-010-0096-7

RESEARCH ARTICLE

Aged rare earth doped silicates as optoelectronic material

Vandana RANGA (✉)[1], H. N. ACHARYA[2], R. K. KHANNA[3], Anirudh KUMAR[4]

1 Department of Physics, Government College, Ajmer 334001, India
2 Emeritus Scientist, Department of Physics, Indian Institute of Technology, Kharagpur 721302, India
3 Principal, BMIT, Jaipur 302022, India
4 Chino Scientific Instruments Manufacturing, Ajmer 305004, India

© Higher Education Press and Springer-Verlag Berlin Heidelberg 2010

Abstract Samples of various concentrations were prepared and kept unsintered for a period of three years to study the consistency of composition prepared and structural evolution of glass. The expanded peaks in the Raman spectra arise due to thermal agitation, and a Boltzmann type of distribution was expected in the silicate gels. The behavior of the gels during the dehydroxylation and dehydration is conditioned by its microstructure, which depends upon the physical conditions, i.e., pH, and drying conditions.

Keywords silicates, aged, rare earth, sol-gel, breathing mode

1 Introduction

Rare earth doped glasses are in much demand due to the potential applications in photonics. Samples of various concentrations had been prepared and left unsintered for a period of three years to study for consistency and the change in structural evolution of glass. The micro-Raman spectra of the samples exhibited the fundamental vibrations of dry SiO_2 near 430, 800, 1060, and 1200 cm^{-1} prominently [1–4]. In addition to these, defect bands were also observed at 490 and 600 cm^{-1} in some of the spectra [5–7]. The behavior of the gel during the dehydration and dehydroxylation is conditioned by its microstructure, which in turn depends upon the physical conditions prevailing at the time of the hydrolysis. The factors responsible are mixture components, pH of medium, and drying conditions.

Received February 19, 2010; accepted March 22, 2010

E-mail: a.vandana20@gmail.com

2 Materials and methods

Analytical grade tetraethyl orthosilicate (TEOS), $ErCl_3 \cdot 6H_2O$, $YbCl_3 \cdot 6H_2O$, HCl, NH_4OH, and de-ionized water were the starting materials for sol-gel glasses. Molar ratios of 1:14:0.01 were taken for TEOS:H_2O:HCl and magnetically stirred till a clear liquid formed. At this time, calculated and carefully measured dopants (using sartorious, single-pan electronic balance) were added and stirred again to mix the salts. Strips were used to check the pH of the solution, and NH_4OH was added to yield a pH of 3.5. The sols were poured into Petri dishes and covered with polythene sheets tied tightly with rubber bands with several pin-holes. They were then kept for seven days at room temperature and then baked in an oven for three weeks at 55°C and were separated into two set of samples.

Sample A was sintered just after baking for three weeks, and sample B was stored for three years to study the effect of aging and then sintered. Figure 1 shows the crystalline phase of silicate samples in the Raman spectra.

3 Raman spectra measurements

All the data were measured using a Renishaw micro-spectrometer, RM1000. The 514.5 nm of an Ar^+ laser had been used to excite the Raman scattering. The lasers output power was 30 mW. The micro-Raman peaks were observed at 417, 799, 1056, and 1215 cm^{-1}. The 430 cm^{-1} is allotted for the motion of oxygen, popularly called the symmetric ring breathing mode. Symmetric Si-O-Si stretching mode is represented by 800 cm^{-1}. The band at 1056 cm^{-1} is due to the C-H stretching vibrations of unhydrolysed species. The band at 1215 cm^{-1} arises due to Si-O asymmetric stretching vibrations [8–11]. Figure 2 shows the micro-Raman spectrum of a typical sample B which stored for three years to study the effect of aging.

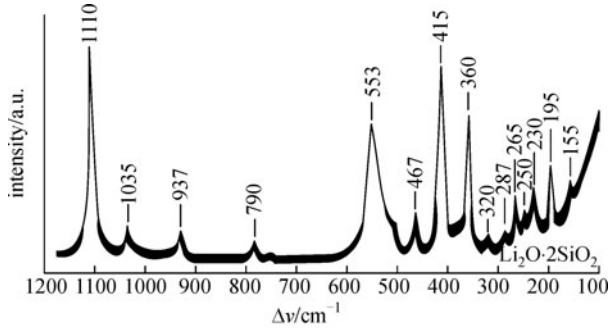


Fig. 1 Raman spectra of crystalline silicate samples

3.1 Effect of sintering on various peaks of Raman spectra

3.1.1 1180 cm^{-1} band: longitudinal asymmetric stretching modes of Si-O-Si

This band arises due to the stretching vibrations of the Si-O-Si. This peak is almost negligible in the spectrum of the unsintered sample as the sintering temperature increases, the peak emerges as shown in Fig. 3, and it also shifts toward the higher wavenumber. As shown in Fig. 4, it indicates that this is the most intense band as far as the Raman spectra of silicate glasses are concerned. Thus, the silicon atom probably has higher bond length as compared to fresh silicate samples.

3.1.2 430 cm^{-1} band: stretching or vibrational modes of ring structures [10]

Figure 3 shows the breathing mode of silicate gels. The effect of sintering on aged samples on the spectra is to reduce the intensity with increase in temperature. This band is asymmetric due to the superposition of two bands near 270 and 380 cm^{-1}. The change in intensity exhibits lesser stretching of silicate gels as sintering temperature increases.

4 Results and analysis

Figure 1 shows the crystalline phase of silicate samples in the Raman spectra. There are more peaks in the crystalline phase as compared to the glassy phase. In the glassy phase, the peak height of the defect bands is governed by the maximum temperature of sintering. The effect of increasing the sintering temperature was to lower the peak height at 600 cm^{-1}. The peak at 1100 cm^{-1} exhibited asymmetricity. This indicated a phase separation within the glassy phase due to storage for the period mentioned. An attempt had been made to study the effect of sintering temperature, concentration, and nature of dopants. The asymmetric peak

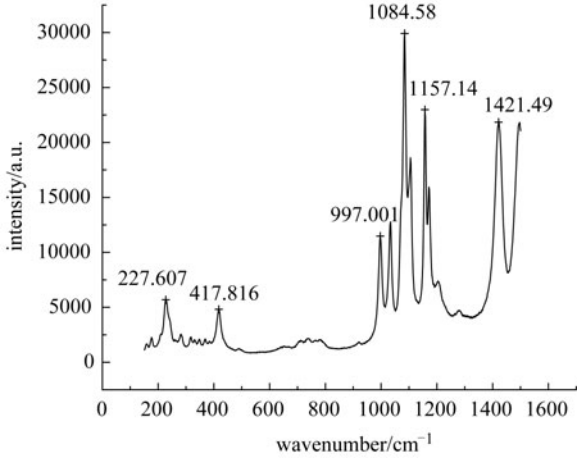


Fig. 2 Micro-Raman spectrum of a typical sample B (stored for three years to study the effect of aging)

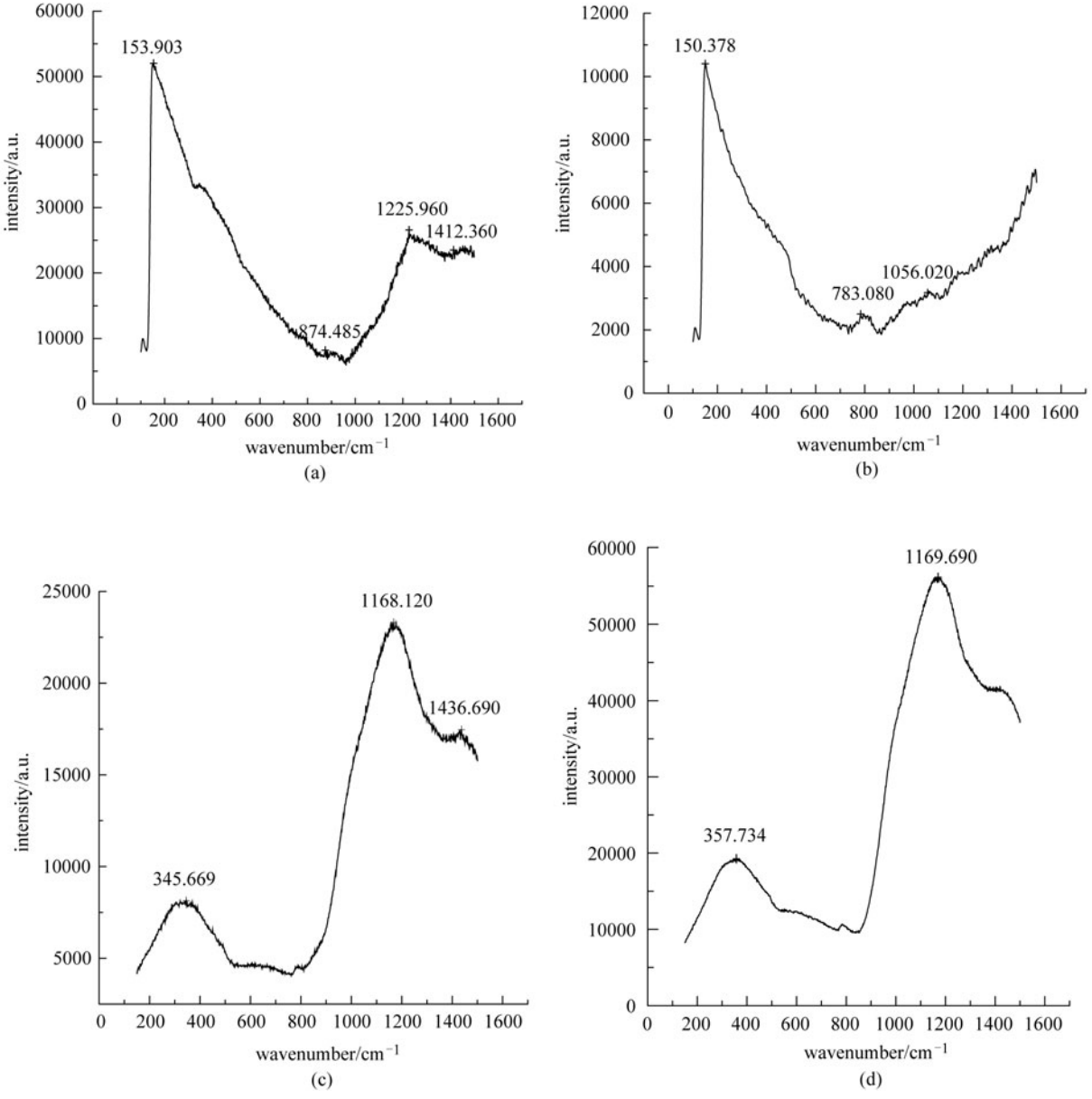


Fig. 3 Micro-Raman spectrum of samples B that were stored for three years to study the effect of sintering temperature at (a) 55°C; (b) 500°C; (c) 900°C; (d) 1100°C, respectively

is also attributed to superposition of peaks. An attempt is made to isolate the superposed peaks. The relative height of 900 cm^{-1} peak also shows degree of disorder [12–14]. Raman spectra of the samples are compared with the data in the literature, as shown in Fig. 2. Another interesting feature emerging out of the study indicates a shift of high intensity bands toward higher wavelength in aged samples. Thus, the structure of silicate gels evolved is different from the spectra of fresh samples.

It is also observed that when the shifting of the wavenumber of the high intensity band is plotted against the unsintered sample, the graph is a straight line. This indicates a linear relationship between the sintering temperature and the intensity of the peak under consideration.

5 Conclusion

The peak at 1100 cm^{-1} exhibited asymmetricity in contrast to the crystalline phase, as shown in Fig. 1. This indicated a phase separation within the glassy phase due to storage for the period mentioned. The asymmetric peak is also

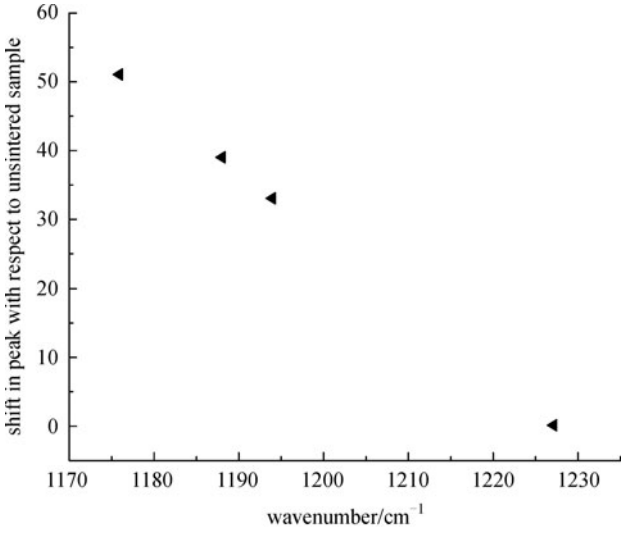


Fig. 4 Micro-Raman spectrum of samples B that were stored for three years to study the effect of sintering temperature

attributed to superposition of peaks. An attempt is made to isolate the superposed peaks. The effect of increasing the sintering temperature was to lower the peak height at 600 cm^{-1}.

Acknowledgements The experimental work was supported by the facilities of Indian Institute of Technology Kharagpur (W.B.) and the Regional Research Laboratory Bhubneshwar (Orissa). The samples were analyzed at the Central Research Facility, Indian Institute of Technology Kharagpur (W.B.). Thanks to the Principal Government College Ajmer for providing some of the facilities for research.

References

1. Brawer S A, White W B. Raman spectroscopic investigation of the structure of silicate glasses I: the binary silicate glasses. Journal of Chemical Physics, 1975, 63(6): 2421–2432
2. Walrafen G E, Stolen R H. Water and its relation to broken bond defects in fused silica. Journal of Chemical Physics, 1976, 64(6): 2623–2631
3. Walrafen G E. Raman spectral studies of mineral structure. Journal of Chemical Physics, 1964, 40(11): 3249–3256
4. Hollander A, Williams J W. The molecular scattering of light from amorphous and crystalline solids. Physical Review, 1931, 38(9): 1739–1744
5. Galeener F. Planar rings in vitreous silica. Journal of Non-Crystalline Solids, 1982, 49(1–3): 53–62
6. Mysen B O, Virgo D, Harrison W J, Scarfe C M. Solubility mechanisms of H_2O in silicate melts at high pressures and temperatures: a Raman spectroscopic study. American Mineralogist, 1980, 65(9–10): 900–914
7. Mysen B O, Finger L W, Virgo D, Seifert F A. Curve fitting of Raman spectra in silicate glasses. American Mineralogist, 1982, 67 (7–8): 686–695
8. Davis K M, Tomozawa M. An infrared spectroscopic study of water-related species in silica glasses. Journal of Non-Crystalline Solids, 1996, 201(3): 177–198
9. McMillan P F. Structural studies of silicate glasses and melts-applications and limitations of Raman spectroscopy. American Mineralogist, 1984, 69(7–8): 622–644
10. McMillan P F, Poe B T, Stanton T R, Remmele R L. A Raman spectroscopic study of H/D isotopically substituted hydrous aluminsilicate glasses. Physics and Chemistry of Minerals, 1993, 19(7): 454–459
11. McMillan P F, Remmele R L. Hydroxyl sites in SiO_2 glass: a note on infrared and Raman spectra. American Mineralogist, 1986, 71(5–6): 772–778
12. McMillan P F, Holloway J R. Water solubility in aluminosilicate melts. Contributions to Mineralogy and Petrology, 1987, 97(3): 320–332
13. Brinker C J, Scherer G W. Sol-Gel Science, the Physics and Chemistry of Sol-Gel Processing. Boston: Academic Press, 1990, 572–588
14. Phillips J C. Microscopic origin of anomalously narrow Raman lines in network glasses. Journal of Non-Crystalline Solids, 1984, 63(3): 347–355