International Journal of Technical Innovation in Modern Engineering & Science (IJTIMES)
Impact Factor: 5.22 (SJIF-2017), e-ISSN: 2455-2585
Volume 4, Issue 7, July-2018

Hydrothermal synthesis of zeolite by locally available clay and their characterization

[1]Ambadas G. M(AGM), [2]Veeresh P. Mallapur

Material Science and Technology

ABSTRACT

Zeolite A was produced by using locally available clay in the Gulbarga region of Karnataka, India, via a method of alkali fusion – hydrothermal synthesis procedure. The clay used as a source material was initially converted into metakaoline by calcinating it at 800˚C for 2h. Calcined clay was treated with sodium hydroxide to carry out fusion reactions at 850˚C; later aging was done, finally the aged sample hydrothermally treated to get the end product. The product (zeolite) obtained was characterized by Powder X-ray Diffraction (PXRD), Fourier transmission Infrared Spectroscopy (FTIR) and Scanning Electron Microscopy (SEM). This work showed that a locally available clay in the Gulbarga region can be easily converted into zeolitic type material by following user friendly method like Alkali fusion followed by Hydrothermal treatment and the synthesized zeolite can be used effectively as an adsorbent for purifying the contaminated water.

[Key words: Clay, Metakaoline, clacination and hydrothermal treatment]

1. INTRODUCTION

Zeolites are crystalline, micro porous, hydrated aluminosilicates of alkaline or alkaline earth materials which produces a system of pores and a cavity showing molecular dimensions [1]. The structure of zeolite is composed of $[SiO_4]^{-4}$ and $[AlO_4]^{5}$ tetrahydra, which 'corner share' to form different open structures [2]. $M_{x/n}[(Al_2)x(SiO_2)_y].zH_2O$ is the general formula used to indicate zeolite, where 'n' represents the charge of cation M, the values of x,y and z depend according to the type of zeolite [3,4].This structure gives excellent performance of ion exchange, catalysis and adsorption, especially Zeolite-A can be widely applied for water purification, in fields like petrochemical industry and for environmental protection [5].

Zeolites can be synthesized by using a gel of sodium aluminosilicate, however they can also be synthesized by using chemical precursors of silica and alumina but the precursors are very expensive. In order to reduce the cost of production different types of zeolites the investigators are looking for a very cheaper and easily available clays like kaolinite [6-8], halloysite [9], illite, smectite, interstratified illite-smectite [10], montmorillonite [11]and bentonite [12-13] for the synthesis of zeolitic type materials. Silica and alumina are the two rich compositions in clay minerals are found as very imperative source material to synthesize precious materials like zeolites.

In the present work we account the synthesis of zeolite A by using local clay following synthesis route alkali fusion-hydrothermal procedure. The synthesis method undertaken by using one of the effective alkali reagent sodium hydroxide. The synthesized end product were characterized and discussed by PXRD, FTIR and BY SEM analysis.

2. MATERIALS AND METHOD

2.1 Materials:

Clay used in the work collected from Sulepeth a village in Gulbarga district Karnataka, India. The clay was initially in the lumpy and hard state, was crushed, dried, sieved and chemically analysed. Table 1 gives the chemical analysis details of the clay used.

Sodium hydroxide used as a mineraliser, activator and an alkali reagent which was purchased from Venkatesh chemicals Gulbarga, Karnataka, India.

Distilled water used in the synthesis procedure was collected from a distillation unit in the Department of Ceramic and Cement Technology P D A College of Engineering, Gulbarga, Karnataka, India.

2.2 Method:

A conventional method was used for the synthesis of zeolite, which includes mainly two steps.

1) Alkali fusion- to dissolve silica and alumina into sodium aluminosilicate.
2) Hydrothermal treatment- to crystallize the fused sample after ageing.

Fig. 1 Indicates the processing steps used for the synthesis of zeolite from the clay.

2.3. Synthesis of zeolite from clay:

The clay after size reduction was sieved by using 75µ and stored in a clean and dried Nickel crucible. Initially clay has been heated to 800˚C in order to make it free from volatile and to increase its reactivity. About 20 grams of treated clay was then mixed with 24grams of sodium hydroxide and the mixture was mixed thoroughly and was carried for alkali fusion in a Muffle furnace heated to a temperature at 850˚C for 5hrs. The fused material was cooled to room temperature, powdered and mixed with distilled water to carryout ageing operation for 24hrs.The sample formed after ageing was finally hydrothermally treated in a water bath. The residue after hydrothermal treatment was washed thoroughly, filtered, and dried over night in an air oven.

Oxides	Weight %
SiO_2	48.523
Al_2O_3	9.682
Fe_2O_3	18.809
CaO	17.042
MgO	3.971
K_2O	1.768
Na_2O	0.139
SO_3	0.065

Table 1: Oxide composition of Clay

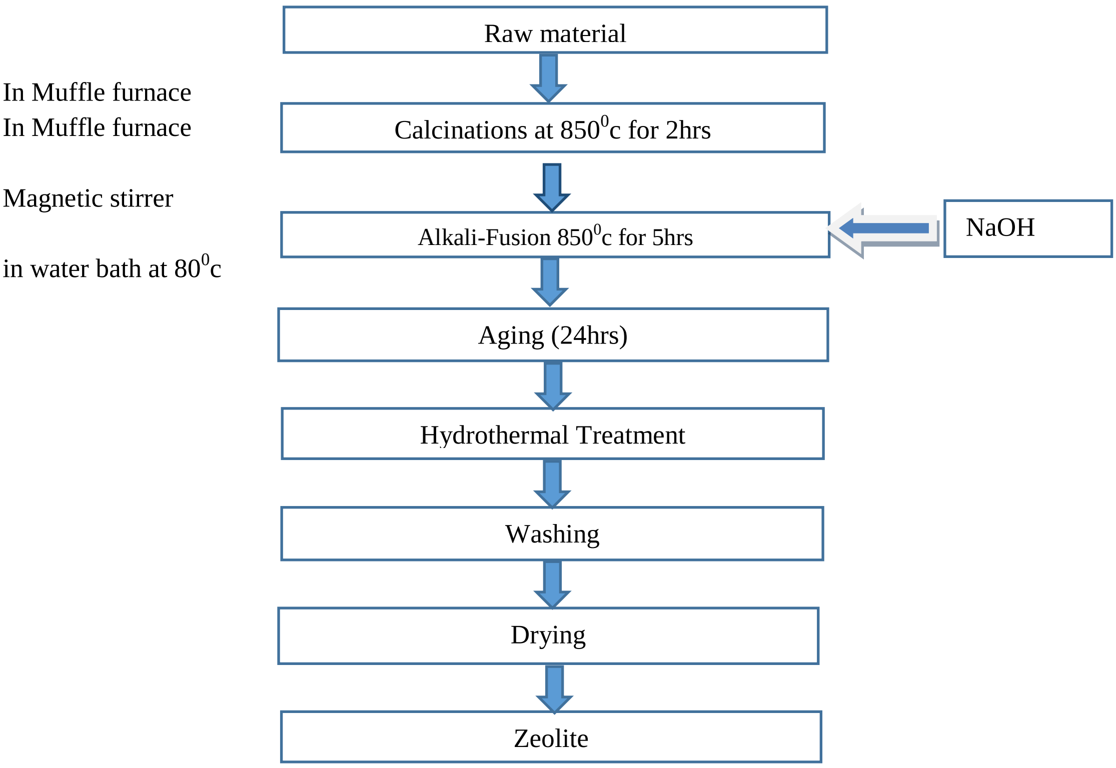

Fig 1: processing steps involved in the synthesis of zeolite

3. RESULT AND DISCUSSIONS

The clay used in the work and the end product formed was characterized by XRD for the phase analysis, SEM for surface topography and FTIR to determine internal and external vibrations in the inorganic material.

3.1 Powder X-ray diffraction (PXRD) analysis:

The Phase analysis of raw clay, aged and final product was done by PXRD, at Omerga, Maharashtra, India. Fig. 2 shows the XRD of raw clay, aged and final product (zeolite) obtained. The black coloured graph shows XRD of raw clay which shows the presence of crystalline phases of silica montmorillonite in the raw composition after initial treatment. The red colour graph shows XRD of raw clay which under gone alkali-fusion and of 24 hours ageing. The green coloured XRD is of the end product i.e. zeolite, showing the conversion of aged material into product zeolite (crystalline). Figure 2.1 shows the XRD of zeolite-A, obtained from clay and it was confirmed by JCPDS Card No. 860185, ICSD: 080880. The zeolite formed shows System: Cubic, Lattice: Primitive, Chemical composition: $Al_{12}Si_{12}O_{48}$ and chemical name: Sodium cobalt Aluminium silicate sulphur.

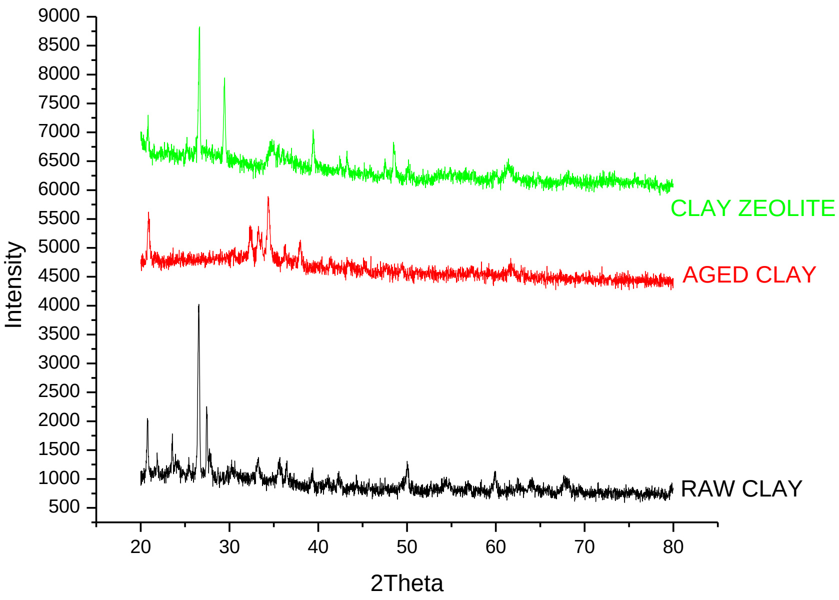

Fig. 2: PXRD of Raw Clay, Aged and Zeolite.

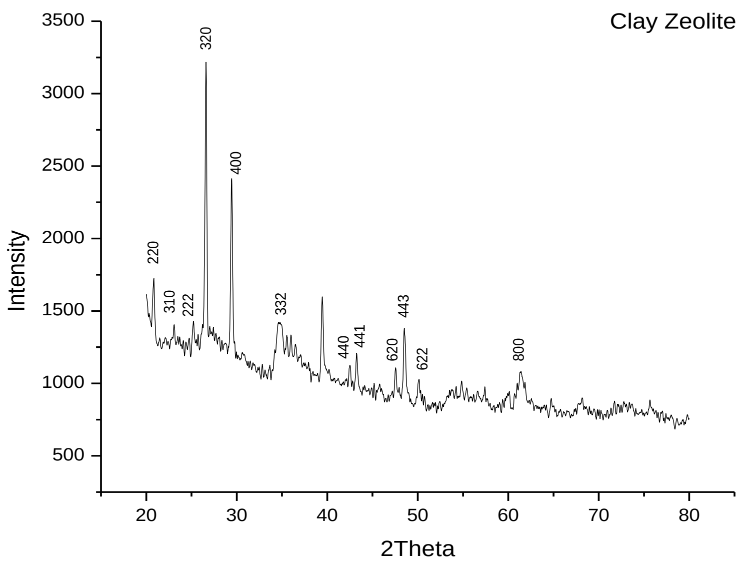

Figure 2.1: XRD of Zeolite from clay

3.2 Fourier Transform Infrared Spectroscopy Analysis (FTIR analysis):

The FTIR analysis of clay, treated clay was carried in P.D.A college of Engineering, Materials Science and Technology Department, Kalaburgi, Karnataka, India. Fig.3 shows the FTIR analysis of raw clay and of Zeolite A. The IR spectrum of synthesized zeolite was observed at 564 cm^{-1} is because of external vibration of double four rings, similarly at 968 cm^{-1} is because of internal vibration of (Si,Al)-O asymmetric stretching. The band at 564cm^{-1} is of zeolitic frame work. The broad peak at 2159 cm^{-1} indicates the presence of zeolitic water [14,15,16].

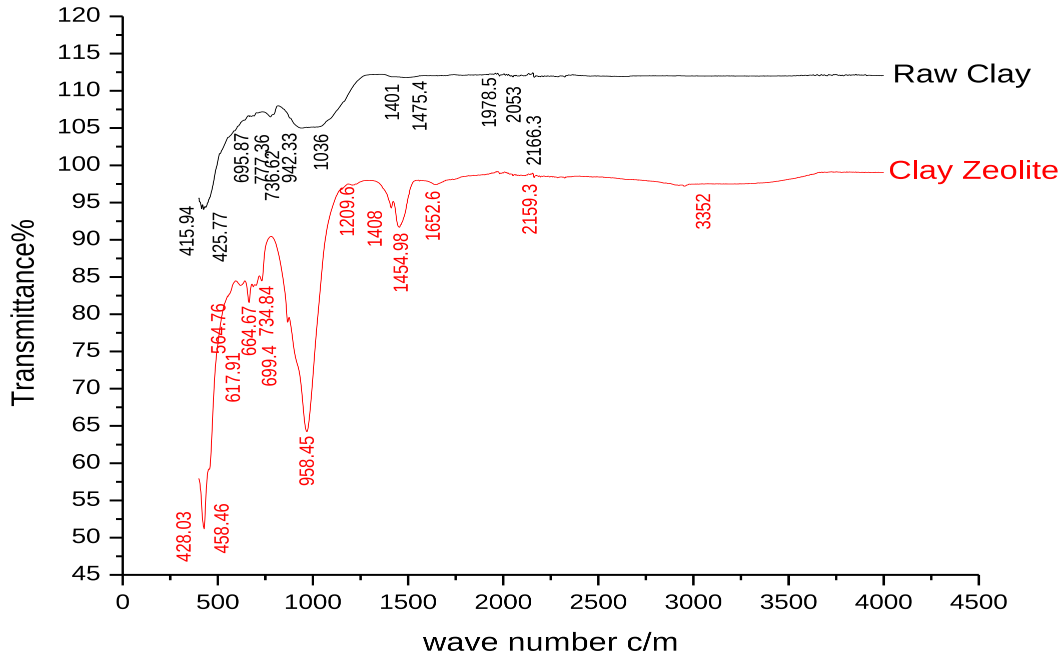

Fig 3: FTIR spectra of raw clay and product zeolite

3.3: SEM analysis of raw and treated clay: The SEM analysis of raw clay as well as of treated clay was carried in SAIF STICK, Kochin, Kerala, India.

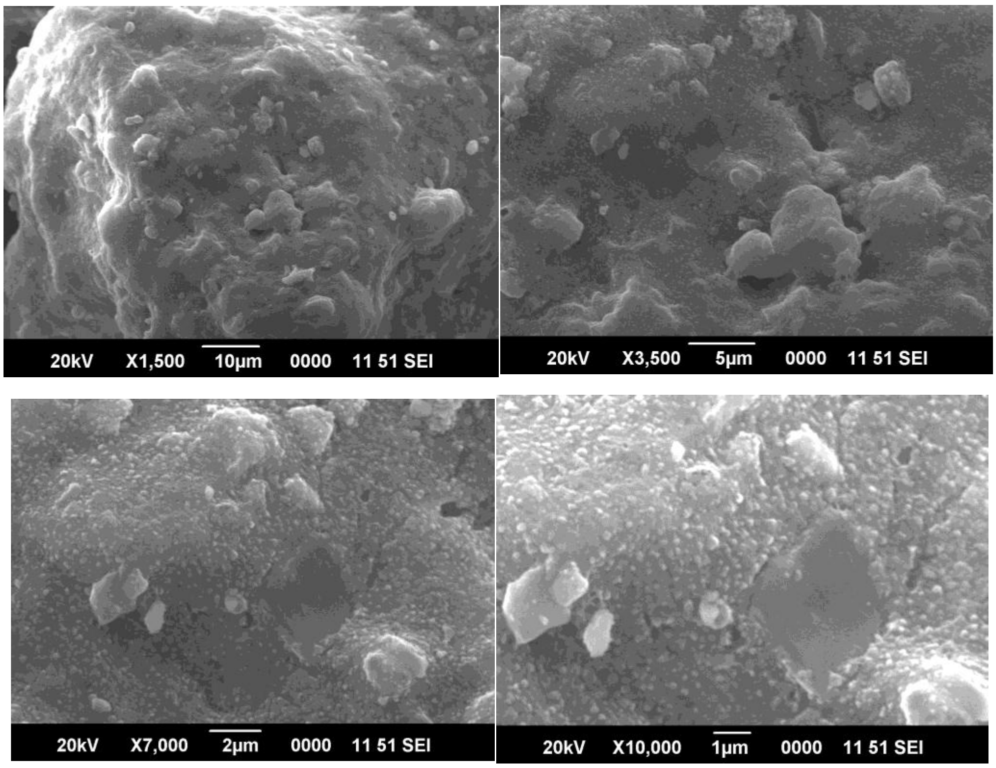

Fig.4: SEM images of raw clay

Fig.4 shows the SEM images of raw clay, according to the images it was observed that the particles are irregular in size and shape and their surface is somewhat hollow and broken.

Fig. 4.1 shows the SEM images of clay zeolite, which reveals randomly oriented silicate crystals on the surface of end product with a clear dispersed porosity.

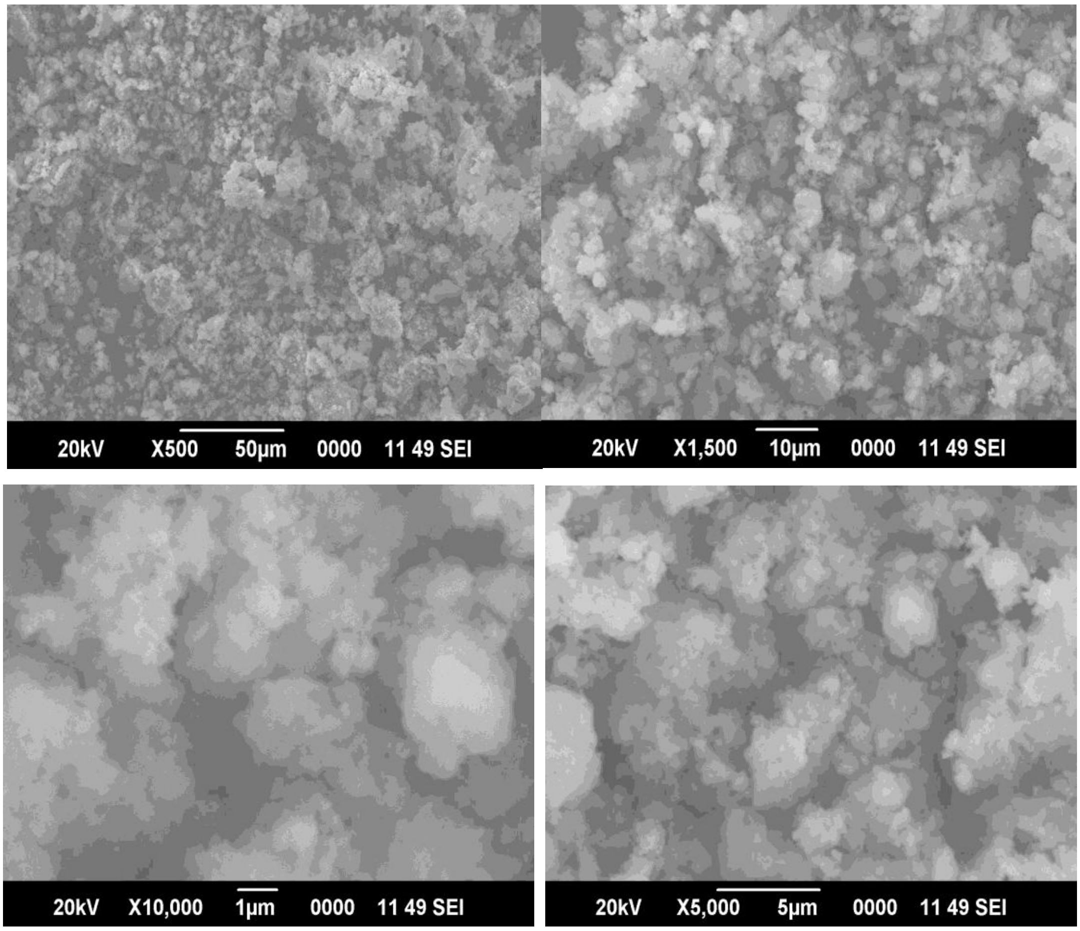

Fig 4.1: SEM images of Clay Zeolite.

4. CONCLUSION

A zeolitic material identified as zeolite-A was successfully synthesized in this work by using local clay by following easy low cost processing steps. The zeolite formation was confirmed by PXRD and the result of which compared to JCPDS card no.860185.

The FTIR peaks at 560±5 cm^{-1} shows the external vibrations and similarly 968±5 cm^{-1} are because of internal vibrations of (Si-Al)-O asymmetric stretching which confirms the formation of Zeolite-A.

The SEM images of the raw material reveals particles variation in size, shape, agglomeration in the final product, showing a randomly oriented, well dispersed porous particles distribution.

ACKNOWLEDGEMNTS

We express our appreciation towards P D A college of engineering Kalaburgi,Karnataka,India for motivating, inspiring and giving research facilities at the institute. First author Ambadas G. M(AGM) take this opportunity to express deep sense of gratitude to Prof. Veeresh P. Mallapur, Dr.John U. Kennedy and Dr.Amaresh.R for their support and helping in this work.

REFERENCES

1. Baccouche, A., Srasra, E. And Maaoui, M.E. (1998), Preparation of Na-Pl and sodalite octahydrate zeolites from Inter- stratified Illite-smecite, Applied clay sciences, Volume 13, Pages 255-273.
2. C.A. Ríos, C.D. Williams, M.A. Fullen, Nucleation and growth history of zeolite LTA synthesized from kaolinite by two different methods, Applied Clay Science, Volume 42, Issues 3–4, January 2009, Pages 446-454.
3. M.A.Ismail, M.A.Z . Eltayed and S.A. Abdel Maged. Synthesis of Zeolite A from Sudanese Montmorillonite Clay to remove Nickel and Copper ions from Aqueous Solutions. International journal of chemical and Biochemical Sciences, Volume 4, July 2013, pages 45-56.
4. Ugal, Jalil. R., Hasan, Karim, H. Ali, Inam H. Preparation of Type 4A Zeolite from Iraqi Kaolin: Characterization and properties measurements. Journal of the Association of Arab Universities for Basic and Applied Sciences, Volume 9, 2010, pages 1-8.
5. He Qian, Sun Hongjuan, PengTongjiang& Li Tao "Synthesis of Zeolite A from Natural Ca-Bentonite Using a Direct Alkali Hydrothermal Approach" (2014)
6. Breck, D.W. Zeolite Molecular Sieves: Structure, Chemistry and Use, 1st Ed., John Wiley, New York, (1974).
7. Barrer, R.M. and Marcilly, C. Hydrothermal chemistry of silicates. Part XV. Synthesis and nature of some salt-bearing aluminosilicates, Journal of Chemical Society (A) 1970.
8. Boukadir, D., Bettahar N. and Derriche, Z. Synthesis of zeolites 4A and HS from natural materials, Annales de Chimie - Science des Materiaux 2002.
9. Klimkiewicz, R. and Drąg, E.B. Catalytic activity of carbonaceous deposits in zeolite from halloysite in alcohol conversions, Journal of Physics and Chemistry of Solids 65,2004.
10. Baccouche, A., Srasra, E. and Maaoui, M.E. Preparation of Na-P1 and sodaliteoctahydrate zeolites from interstratified illite-smectite, Applied Clay Sciences 13, 1998.
11. Cañizares, P., Durán, A., Dorado, F. and Carmona, M. The role of sodium montmorillonite on bounded zeolite-type catalysts, Applied Clay Science 16,2000.
12. Ruiz, R., Blanco, C., Pesquera, C., Gonzalez, F., Benito, Zeolitization of a bentonite and its application to the removal of ammonium ion from waste water, Applied Clay Science 2002.
13. Boukadir, D., Bettahar N. and Derriche, Z. Synthesis of zeolites 4A and HS from natural materials, Annales de Chimie - Science des Materiaux 27, 2002.
14. Li, G.H. (2005) FT-IR Studies of zeolite materials: Characterization Applications. Ph. D Thesis, Graduate college, The University of Iowa, Iowa city, 162.
15. G. Lusvardi, G.Malavasi, L., Malavasi,L., Menabue, M.C.Menziani, A.Pedone. U.segre, A computational tool for prediction of crystallization phase obtained from controlled crystallization of glasses. J. Phys. Chem. B 109 (2005) 21586-21592.
16. P. Pisciella, M. Pelino, Thermal expansion investigation of iron rich glass-ceramics, J. Eur. Ceram. Soc. 28 (2008) 3021-1026.