SYNTHESIS OF HIGH PURITY -SiC AND -Si_3N_4 FROM RICE HULLS

B. TREVIÑO[1], I. GÓMEZ[1]*, R. COLÁS[2]

[1]*Centro de Laboratorios Especializados, Facultad de Ciencias Químicas, Universidad Autónoma de Nuevo León, México.*
[2]*Facultad de Ingeniería Mecánica y Eléctrica, Universidad Autónoma de Nuevo León, México. Av. Pedro de Alba s/n, Cd. Universitaria, San Nicolás de los Garza, N.L., México, C.P. 66400. *E-mail: mgomez@fcq.uanl.mx*

Abstract

Silicon carbide and silicon nitride were synthesized from ashes obtained by heating rice hulls at 800C for 3 hours in argon. -SiC was produced from the ashes by reheating them at 1400C for 8 hours in argon, whereas -Si_3N_4 was obtained by heating the ashes at temperatures ranging from 1250C to 1400C for periods of 3 to 6 hours in a nitrogen rich atmosphere. The products were characterized by infrared spectroscopy, X-ray and scanning electron microscopy. High purity -SiC and -Si_3N_4 compounds with whisker type morphology were obtained. It was possible to obtain -Si_3N_4 without SiC by heating the ashes for 6 hours at 1250C.

Keywords: Rice hulls, silicon carbide, silicon nitride, synthesis.

1. Introduction

Rice hulls offer a very high potential for their use as raw materials in the synthesis of compounds of great interest for industry due to their high silicon oxide content, abrasive properties, high degradation resistance, among many other characteristics. Examples of such use are cement, solar cells, SiC, Si_3N_4, etc. [1-7]. SiC and Si_3N_4 are of particular interest in this study, as they are classified as ceramic materials with promising future at high temperatures applications due to their excellent mechanical properties [8-11]. SiC and Si_3N_4 can by synthesized by catalysis, but their purity is limited to a mere 20% [12].

The reactions involved in the synthesis of SiC, as Lee and Cutler reported [13], can be summarized by:

$$SiO_{2(s)} + 3C_{(s)} \quad SiC_{(s)} + 2CO_{(g)} \qquad \textbf{(1)}$$

Dissociation of SiO_2 is critical for obtaining SiC, and it is required to use an inert atmosphere to inhibit oxidation and enhance the possibility for producing SiC [7,13].

Rice husks can be processed by carbothermal nitration using pyrolysis to obtain Si_3N_4, for which the final reaction is [14]:

$$3SiO_{2(s)} + 6C_{(s)} + 2N_{2(g)} \quad Si_3N_{4(s)} + 6CO_{(g)} \qquad \textbf{(2)}$$

Again, dissociation of SiO_2 is the critical factor.

Rahman and Riley [15] obtained silicon nitride by nitriding pyrolyzed rice hulls in an atmosphere containing a mixture of 95% nitrogen and 5% hydrogen. They found that hydrogen is beneficial to accelerate the rate of nitride formation. However, the rate of reaction diminishes when the process is carried out at temperatures above 1450°C.

Hanna et al. [16] impregnated rice hulls with a ferrous sulfate solution; these hulls were later soaked in an ammonia solution and heated them at 700°C for 30 minutes in the absence of air. Silicon nitride was formed by firing the treated hulls at temperature ranging from 1200 to 1500°C in a nitrogen rich atmosphere. It was found that the amount of silicon nitride increased with iron content until an optimum value was reached, as further increase in iron promoted the formation of silicon carbide. Ventura et al. [17] reported the synthesis of SiC from rice hulls by pyrolysis at temperatures above 1400°C, however some impurities, SiO_2 among them, were found to occur.

The aim of this work is to present the results of the synthesis of silicon carbide and silicon nitride using rice hulls as raw material. It was possible to determine the conditions for obtaining silicon carbide avoiding the formation of any other type of byproducts. It was also possible to find the route to synthesize silicon nitride avoiding the formation of silicon carbide.

2. Experimental Procedure

Various types of rice hulls were characterized before deciding to conduct the research with hulls from a hybrid Indic species widely grown in the Mexican State of Tamaulipas. Characterization was made by different analytical techniques such as atomic absorption (AA), X-ray diffraction (XRD), differential thermal analysis (DTA), and differential thermogravimetric analysis (DTG), infrared spectrometry (FTIR), and scanning electron microscopy (SEM) with elemental microanalysis (EDS).

The rice hulls were cleaned with a mixture of HCl:H_2O in a 1:1 proportion, washed with distilled boiling water for two hours, and dried in an electric furnace at 100°C to reduce the amount of alkaline impurities [18]. The hulls were heated at 800°C for 3 hours in argon to obtain the ashes from which the various products will be synthesized [19]. These ashes were characterized by AA, XRD, FTIR, and SEM with EDS.

Different pyrolysis treatments were used for the synthesis of SiC and Si_3N_4 from the ashes of the rice hulls. Synthesis of SiC was carried out at 1400°C from 3 to 8 hours in argon, whereas Si_3N_4 was obtained by treating the ashes at temperatures from 1250°C to 1400°C in a nitrogen rich atmosphere for periods of time ranging from 2 to 6 hours. Samples from either of these processes were reheated in an electric furnace at 900°C for 6 hours to eliminate any amount of carbon that may be present [18,19]. All the products obtained were characterized by XRD, FTIR, SEM, and EDS.

3. Results and discussion

Table 1 shows the high content of SiO_2 (42.16%) of the rice hulls used in this study. A series of DTA and DTG analyses were carried out to determine the ratio of carbon over silica (C/SiO_2) of the hulls. The material was heated up to 1300°C using a rate of 20°C/min, in either argon or an extra dry air atmosphere. The analysis carried out with the extra dry air atmosphere showed a final residue of 24.66% (SiO_2 ashes) and three important thermal events, Figure 1. The first one that finishes at approximately 110°C is related to moisture losses of 7.25% of the sample. The second event finishes at 348°C, with a weight loss of 39%, is associate with the degradation of organic components (cellulose, hemicelluloses and lignin). Finally, the third event that finishes at 502°C, with a weight loss of 29%, is due to oxidation of carbon residues. The trial carried out in argon showed that the first two events finished at 114 and 390°C, the third one took place at a slower place and yielded to a final residue of residue of 34.34% (SiO_2, carbon and inorganic impurities).

Table 1 . Chemical composition of the rices hulls.

Compound	Amount (%Wt)
SiO_2	42.16
K_2O	0.472
MgO	0.053
CaO	0.127
Ignition losses	57.188

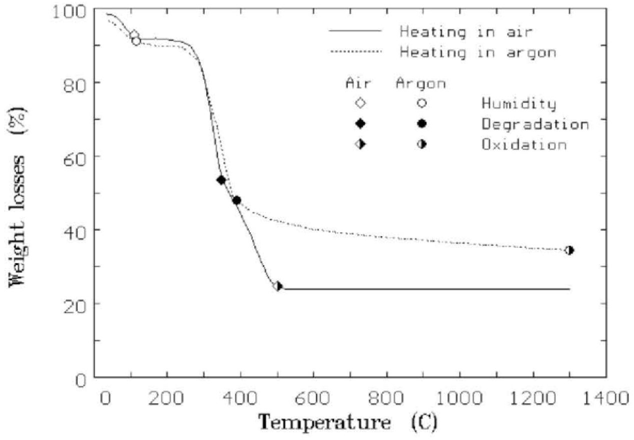

Figure 1. DTG curves of hulls treated in air and argon.

Figure 2a shows a FTIR spectrogram of the rice hulls. The characteristic absorption band at 3515 cm^{-1} is due to the O-H bonding, the one at 3347 cm^{-1} is due to water, whereas the bands at 2930 cm^{-1}, 1712 cm^{-1}, 1649 cm^{-1}, and 1310 cm^{-1} correspond to C-O, C-C, and C-H bonding, respectively. All these bands are related to organic compounds such as the cellulose, hemicelluloses and lignin present in the rice hulls. The band at 2365 cm^{-1} is characteristic of CO_2. The bands corresponding to the Si–O bonding, are observed at 1082 cm^{-1}, 787 cm^{-1}, 657 and 465 cm^{-1} [20,21]. Figure 2b shows a SEM image in backscattered electron mode of the rice hulls, the image shows a series of rectangular structures of around 75 m in size that appear as waved contoured lines.

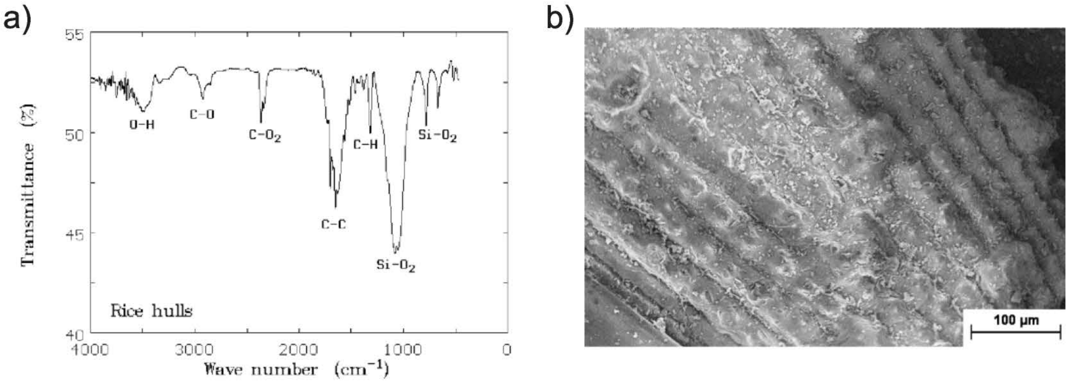

Figure 2. a) FTIR spectrum of rice hulls, b) SEM image in backscattered electron mode of a rice hull.

The ashes obtained from the thermal treatment at 800°C for 3 hours in argon were characterized by FTIR and XRD. Figure 3a shows the infrared spectra of these ashes, where it is only possible to observe the bands for the Si–O bond at 1100 cm^{-1}, 792 cm^{-1}, and 465 cm^{-1} [19]. Analysis by XRD points out the amorphous nature of the ashes, figure 3b. The broad peak centered at around 22 of 2 corresponds to vitreous silica [22]. The amorphous nature of the material implies a low activation energy that may enhance the production SiC and Si_3N_4 [8-11,23]. Figure 3c shows a SEM image in backscattered electron mode from the ashes showing the skeleton of the previous rectangular structures shown in figure 2a. The image shows a series of fibers of around 1.5 m in diameter and 92 m in length. Some other square shapes, of around 30 m in length can be appreciated.

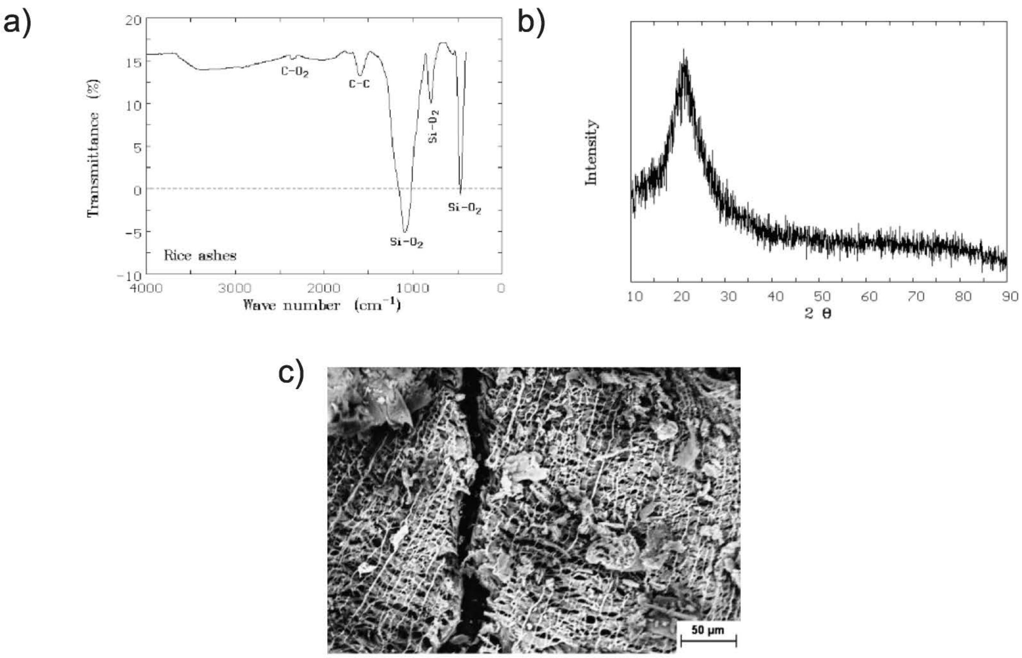

Figure 3. a) FTIR spectrum of rice ashes after pyrolysis for three hours in argon at 800°C, b) X-Ray diffraction of rice ashes, c) SEM micrograph in backscattered mode of rice hulls after pyrolysis at 800°C.

Samples obtained after thermal treatment at 1400°C in argon at times ranging from 3 to 8 hours were characterized by FTIR, XRD, and SEM. Figure 4a shows a FTIR spectrum from a sample held for 8 hours; the bands corresponding to the Si-O bonding can be appreciated, see figures 2a and 3a, together with a new band at 810 cm^{-1}, which is associated to the SiC bonding [20], although this last band may overlap with the one for Si-O that occurs at 792 cm^{-1}. The XRD spectra in figure 4b show the presence of -SiC in the material held for 5 and 8 hours, the 2θ positions for this compound are shown at the bottom of the diagram. The presence of SiO_2 was not observed and this suggests that transformation to SiC was higher than 90%.

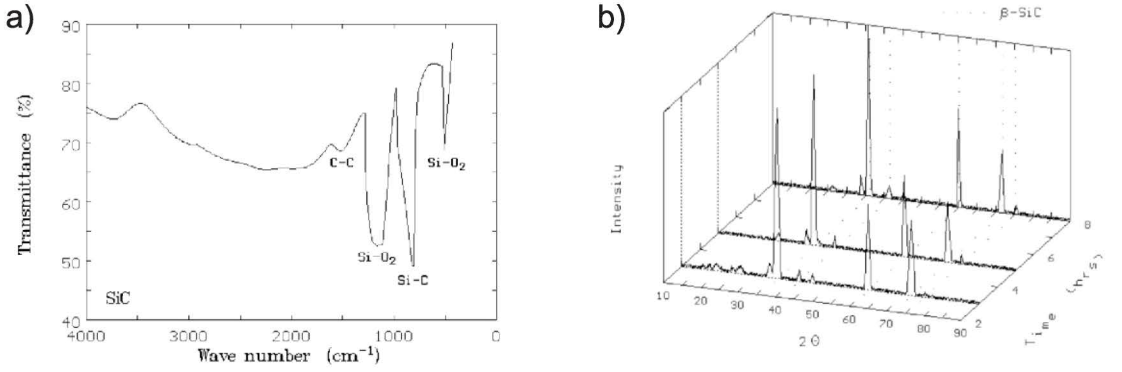

Figure 4. a) FTIR spectrum of rice ashes after pyrolysis for eight hours in nitrogen at 1400°C,
b) X-Ray diffraction of samples from ashes that were treated in argon at 1400°C for different times. The positions for β-SiC peaks are indicated.

Figure 5 shows a SEM image in secondary electrons mode of a sample held for 8 hours, the fibers were of 0.16 m in diameter and 3.52 m in length over a matrix made of particles of less than 0.5 m in diameter. The fibers were identified as SiC by EDS elemental analysis. The results of such analysis are reported in table 2. The morphology corresponds to whiskers with a proportion of length over diameter of 22.

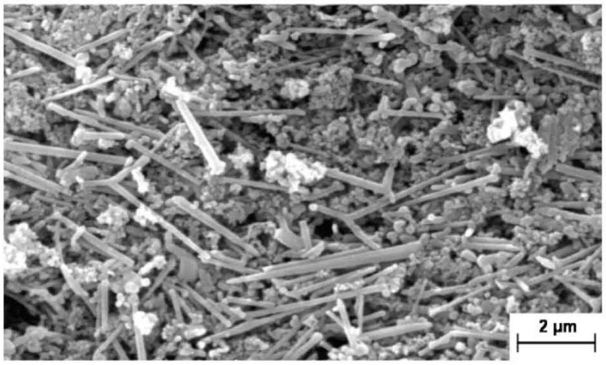

Figure 5. SEM micrograph in secondary electron mode of SiC obtained from ashes pyrolized in argon for eight hours at 1400°C.

Samples obtained after thermal treatment at 1400°C in a nitrogen rich atmosphere from 3 to 8 hours were characterized by FTIR, XRD, and SEM. Figure 6 shows a FTIR spectrum of a sample held for six hours. The multiple absorption bands corresponding to Si–N bondings occur between 850 and 1000 cm^{-1}. Frequencies of asymmetric enlargement occur in the region of 900 to 1000 cm^{-1}; frequencies of symmetric enlargement for the same group appear in the region of 400 to 600 cm^{-1} [23].

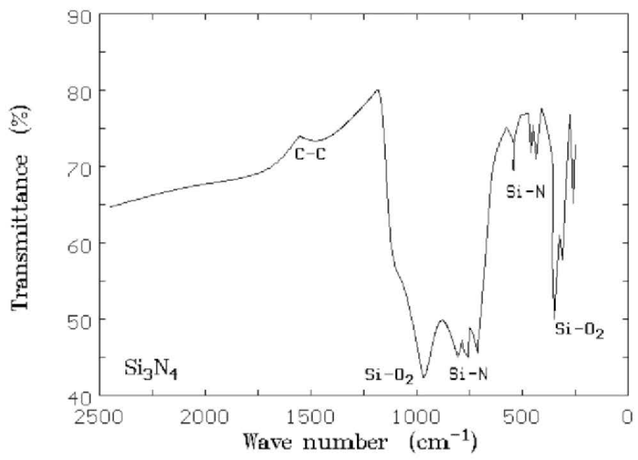

Figure 6. FTIR spectrum of rice ashes after pyrolysis at 1400°C in a nitrogen atmosphere for six hours.

The samples were analyzed by XRD to confirm the presence of -Si_3N_4. The spectra obtained from samples held for six hours at temperatures ranging from 1250 to 1400°C are shown in Figure 7. The presence of different compounds was identified (-Si_3N_4, -Si_3N_4, and -SiC), although only the peaks for -Si_3N_4 and SiC are indicated. The presence of this last compound was not expected, as the experiment was designed for total transformation to silicon nitride. However it has been reported that the presence of carbon mixed with SiO_2 promotes the formation of SiC when treating at temperatures below 1450°C [24,25].

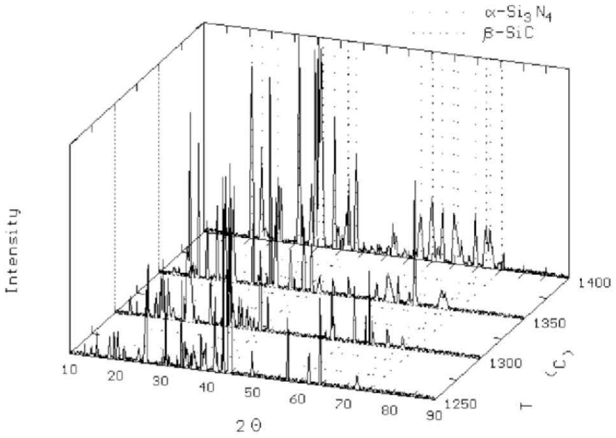

Figure 7. X-Ray diffraction of samples from ashes treated in nitrogen for six hours at various temperatures. The positions for α-Si_3N_4 peaks are indicated.

A series of treatments in which the holding time at high temperature was varied were attempted, but the presence of SiC was detected even at times as short as two hours. Close examination of Figure 7 points out that the amount of SiC increases towards the higher range of temperature, and, which is more important, the amount of SiC formed at 1250°C may be considered to be negligible. Figure 8a shows a SEM image in backscattered electrons mode of a sample held at 1250°C for 6 hours. A particle of -Si_3N_4 with rod morphology of 26 m in length and 4 m in diameter is observed. The small particles adjacent to it are made of unreacted SiO_2. Therefore, it can be considered that the boundary conditions for the synthesis of -Si_3N_4 with negligible amounts of SiC can be drawn at 1250°C for six hours. Figure 8b shows the image of a sample held at 1400°C for 6 hours. The material appears with whisker morphology of 2.3 m in length and 0.16 m in diameter. According to elemental analysis by EDS the agglomerates are made of Si, C, N, and O with traces of Fe and Ca. Results from the spectrum analysis are presented in Table 2.

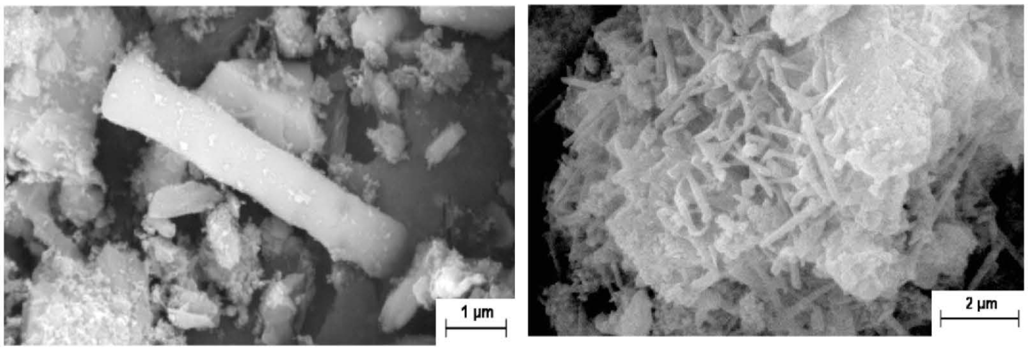

Figure 8. a) SEM micrograph in backscattered electron mode of rice hulls after pyrolysis for six hours at 1250°C in a nitrogen atmosphere, b) SEM micrograph in backscattered electron mode of an agglomerate obtained from ashes after pyrolysis for six hours at 1400°C in nitrogen.

Table 2 . Chemical composition (at.%) of treated samples.

Sample	C	N	O	Si	Ca	Fe	Al
Ashes after pyrolysis at 1400°C	38.43	0.00	22.95	38.01	0.30	0.31	0.00
Ashes after pyrolysis at 1250°C in nitrogen atmosphere	0.00	15.26	40.65	43.46	0.23	0.40	0.00
Ashes after pyrolysis at 1250°C in nitrogen atmosphere.	18.32	16.88	21.82	46.38	0.23	0.48	0.90

4. Conclusions

The results presented in this work indicate the procedure to synthesize β-SiC and -Si_3N_4. β-SiC was obtained when ashes from the hulls were reheated for at least 3 hours at 1400°C in an argon atmosphere, the morphology of the particles was that of whiskers that have a relationship of length over diameter of 22. A mixture of high purity particles made of -Si_3N_4, -Si_3N_4, and -SiC were obtained by reheating the ashes in a nitrogen rich atmosphere at 1400°C during 6 hours. The morphology of the Si_3N_4 particles obtained was mainly of whiskers and rods. The boundary for the transition of Si_3N_4 and SiC was found at 1250°C for 6 hours

5. References

[1] F. Rodríguez Reinoso and F.J. Narciso Romero, An. Quím., 87 (1991) 778.
[2] A. Oya, N. Kishimoto, S. Mashio, K. Kumakura, T. Suzuki, B. Serrano-Talavera and A. Linares-Solano, J. of Mater. Sc., 30 (1995) 6249.
[3] J. James and M. Subba Rao, Cement and Concrete Research, 16 (1986) 67.
[4] Y. Pliego, V. Lemus and P. Cabrera, Rev. IMCYC, 25 (1987) 13.
[5] V. I. E. Ajiwe, C. A. Okeke, F. C. Akigwe, Bior. Tech., 73 (2000) 37.
[6] B. Treviño Cardona, M.Sc. Thesis, FCQ-UANL, Mexico (2002).
[7] B. Treviño-Cardona and I. Gómez, CIENCIA, 5 (2002) 59.
[8] P.T.B. Schaffer, Engineering Properties of Carbides, Engineered Materials Handbook, Vol. 4: Ceramics and Glasses, ASM International, Materials Park, 1991, 804.
[8] S. Hampshire, Engineering Properties of Nitrides, Engineered Materials Handbook, Vol. 4: Ceramics and Glasses, ASM International, Materials Park, 1991, 812.
[9] W.E. Lee and W.M. Rainforth, Ceramic Microstructures, Chapman & Hall, (U.K. 1994).
[10] Yet Ming Chiang, D. Birnie III, W.D. Kingery, Physical Ceramics, Wiley (U.S.A. 1997).
[11] L. Sun, Ind. Eng. Chem. Res., 40 (2001) 5861.
[12] J.-G. Lee and I.B. Cutler, Am. Ceram Soc. Bull. 54 (1975) 195.
[13] I.B. Cutler, Production of silicon nitride from rice hulls. U.S. Patent 3,855,395, (1974).

[14] I.A., Rahman and F.L. Riley, J. Eur. Ceram. Soc. 5 (1989) 11.

[15] S.B.Hanna, N.A.L., Mansour, A.S., Taha and H.M.A. Abd-Allah, Br. Ceram. Trans. J. 84 (1985) 18.

[16] V. Rodrìguez-Lugo, E. Rubio, I. Gómez, L. Torres-Martínez, V.M. Castaño, Int. J. Environment and Pollution, 18 (2002) 387.

[17] J. A. Amorim, S. A. Eliziário, D. S. Gouveia, A. S. M. Sim δ es, J.C.O. Santos, M.M. Conceição, A.G. Souza and M. F. S. Trindade, J. Therm. An. Calorimetry,75 (2004) 393.

[18] V. Rodríguez-Lugo, M.Sc. Thesis, UNAM, México, (1997).

[19] Morrison R. T. and Boyd R. N., *Química Orgánica*, Edit. Reverté (Massachusetts, 1996).

[20] H. W. Van der Marel and H. Beutelspacher, *Atlas of Infrared Spectroscopy of Clay Minerals Their Admixtures, Elsevier Publishing,* Amsterdam, 1976.

[21] J.M. Fernández-Navarro, *El Vidrio,* 2ª Ed., Instituto de Cerámica y Vidrio, Madrid, 1991.

[22] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, Part B, Applications in Coordination, Organometallic, and Bioinorganic Chemistry, Academic Press, New York, 1997.

[23] T. K. Trout and J. M. Bellama, J. Mat. Res. 4 (1989) 399.

[24] Z. Shi-Chang and W.R. Cannon, J. Am. Ceram. Soc. 691 (1984) 67.

6. Acknowledgments

The authors express their gratitude to the staff at the Chemical Inorganic Laboratories at F.C.Q.-U.A.N.L. The financial supports from the PAICYT Projects and from the Materials Area of the National Institute of Nuclear Research are acknowledged.