JOURNAL OF MATERIALS SCIENCE **38** (2003) 4739–4744

Silicon carbide formation from pretreated rice husks

K. SUJIROTE, P. LEANGSUWAN
National Metal and Materials Technology Center, 114 Science Park, Paholyothin Km. 42, Pathumthani 12120, Thailand
E-mail: kuljiras@mtec.or.th

The differences in nature of organic matter in raw rice husks (RRH) and coked rice husks (CRH), and their effect on silicon carbide synthesis have been studied by means of infrared spectroscopy and X-ray diffractometry, so that the benefit of RH structure is fully exploited. Both RRH and CRH can be used as precursors for SiC synthesis, although different reaction kinetics and thus different control parameters are required. It is proposed that kinetics of silicon carbide synthesis from rice husks can be divided into 3 stages: organic decomposition, transformation of silica and condensed organic/graphite, and silicon carbide formation.

1. Introduction

Rice husk (RH) is an agricultural waste material abundantly available in rice-producing countries. Dry husk contains 75 to 85% organic matter (lignin, cellulose, and other organic constituents) and the inorganic remainder consists of 94–96% silica with small amounts of alkalis and other trace elements. The silica apparently occurs in a hydrated form of silica, either opal or silica gel [1], though few studies have suggested silico-organic compounds to be present [2].

Cutler [3] and Lee [4] conducted pioneering work on the formation of SiC from RHs. In the conventional process, the formation of SiC from RHs is accomplished in two steps. The RHs are coked in the absence of air at a temperature of 700–900°C and then fired at higher temperature (1500°C) in an inert or reducing atmosphere. Incentives for the coking process were to alleviate problems arising from transportation of bulky rice husks, and also to use the rice husks as fuel in rice mill plants. Later, several reports appeared in the literature on the formation of SiC from RHs [4–12].

A few studies [4, 5, 13] agreed that reactions occur during the carbothermic reduction of silica within the temperature range 25–1600°C in two ways: solid state and vapour state. One reaction involves silica and another involves silicon monoxide.

$$\mathrm{SiO_2\,(s) + C(s) = SiO\,(g) + CO\,(g)} \qquad (1)$$

$$\mathrm{SiO\,(g) + 2C(s) = SiC\,(s) + CO\,(g)} \qquad (2)$$

Therefore,

$$\mathrm{SiO_2\,(s) + 3C(s) = SiC\,(s) + 2CO\,(g)} \qquad (3)$$

These equations can be applied to the reactions in rice husks only to a certain extent, especially at the initial reaction stages, because they are based on reactions involving silica sand and carbon graphite precursors, while organic matter is present in RHs. Since the solid-state reaction is controlled by contact area of the precursors and the vapour state reaction depends on, among other things, open volume for volatiles to react, RHs represent an ideal microstructure for SiC formation. With the very high surface area and intimate contact available for carbon and silica in rice husks, it is plausible to form SiC readily and economically.

Metallic compound additives such as $FeSO_4$ [14], oxides of Fe, Co, Ni [15], $CoCl_2$ [16], nitrates of Fe, Co, Ni [17], and sodium silicate [18] were found to act as catalysts. Acid pretreatment [19] was also beneficial to the SiC formation from rice husks. Several studies have focused on SiC whisker formation [5, 7, 8, 12, 20, 21]. However, considerably less research has been devoted to study how the nature of organic matter in raw rice husk (RRH) and carbonaceous char in coked rice husk (CRH) affect the silicon carbide formation. There are indications that SiC forms more readily in RH than in burnt RHs [22], in RHs ashes [23], or in mixtures of RH silica and carbon black [24]. However a full understanding of the SiC formation mechanisms from different RH precursors has not yet been achieved.

In the present study, the RHs were pyrolysed at 1000°C under an inert atmosphere to produce charred rice husk (CRH). Thermal decomposition of the organic matter was monitored. Fourier transform infrared (FTIR) spectroscopy was applied to identify the decomposition process and chemical modification. Subsequently, both RRHs and CRHs were pyrolysed in argon at 1240–1500°C for SiC transformation. X-ray diffraction (XRD) analysis was performed to identify the phase present in the powders. The infrared (IR) absorption of the powders was measured to depict the nature of the bonding. By combining the results of these analytical methods it is possible to get a more complete picture of the processes leading to the formation of silicon carbide from rice husks.

TABLE I Chemical composition of raw rice husks

Chemical composition	wt/%
SiO_2	15.2
K_2O	0.39
CaO	0.16
Na_2O	0.04
FeO	0.01
Loss on ignition (LOI)	84.2
of which carbon	36.9

2. Experimental procedure

The RRHs used in this investigation had the chemical composition shown in Table I. Concerning environmental effects, two types of pretreatment were applied; i.e impregnation with Fe_2O_3 solution (0.6 and 0.02 wt%), and hydrothermal (120°C, pressure 2 bar). Nomenclatures used for this study were RH, Fe, and HT for rice husk, and iron-, and hydrothermal-pretreatments, respectively. When coked before pyrolysis, a C was prefixed; i.e. CRH, CFe, and CHT. Both treated and untreated RHs were ground and dried at 110°C. The coking operation was conducted in an electric tube furnace flushed with argon and then heated in a static atmosphere with 5°C min^{-1} ramp up to 1000°C. Pellets of 12 mm dia. and 30 mm length were made from ground RHs by pressing in a steel die at a pressure of approximately 15 MPa. Average apparent density of the RRHs and CRHs were 0.23, and 1.51 g/cm^3, respectively. Pyrolysis was carried out with 5°C min^{-1} ramp upto 1240, 1275, 1425, and 1500°C in an Ar atmosphere for 3 hours.

Thermogravimetric analysis (TGA) was performed using a Perkin Elmer TGA7 analyser. Approximately 20 mg samples were heated from room temperature to 900°C in flowing oxygen at a rate of 10°C/min. Standard X-ray diffraction techniques with Cu K_α radiation (JEOL JDX3530) were used to determine the crystalline phases present in the heat-treated samples.

The FTIR spectra of the products were obtained using the KBr wafer technique. Approximately 0.1 mg of a sample were ground with 45–50 mg KBr and compacted at 150 MPa. The spectra were recorded with a Perkin Elmer FT-IR 2000R Spectrometer at a resolution of 4 cm^{-1} collecting 100 scans with TGS detector at room temperature.

3. Results and discussion

3.1. Thermal decomposition of organic matters

The thermal analysis of RRH and CRH is shown in Fig. 1. RRH exhibited high weight loss from 250–425°C. Two weight loss stages appeared at 318 and 426°C. The 15 wt% of RRH ash remaining corresponded well with the amount of SiO_2 measured by chemical analysis (see Table I). On the other hand, CRH slowly decomposed in one step at 400–600°C with the highest decomposition rate at approximately 516°C. The ash contained more than 40 wt% residue. X-ray diffraction profiles of RRH, CRH and their residues exhibit no sharp peak but broad diffraction characteristic of amorphous silica ($2\theta \approx 22°$).

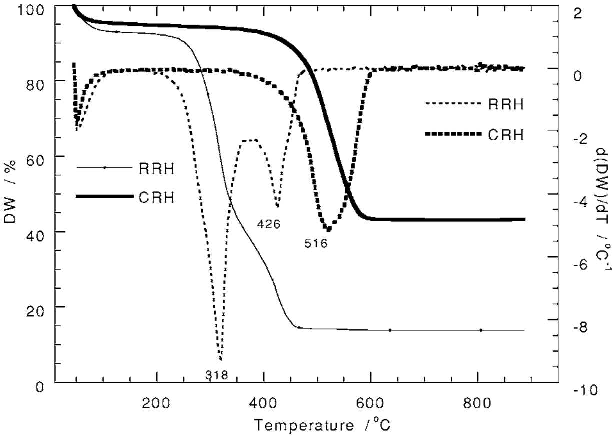

Figure 1 Thermogravimetric curves of raw rice husk (RRH) and coked rice husk (CRH). The solid lines are DW curves and the dotted are d(DW)/d*T*.

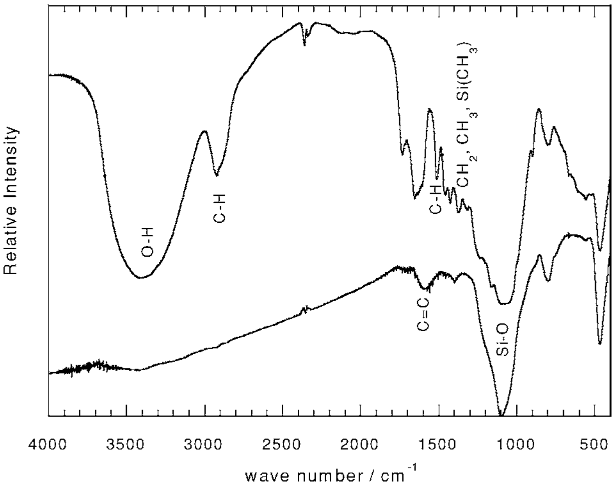

Figure 2 FTIR spectra of RRH and CRH.

Ideally, SiC formation (Equation 3) requires 1.67 weight ratio of SiO_2/C to produce approximately 40 wt% SiC. Comparing the SiO_2/C ratio with the ratio available in RRH and CRH, it can be seen that excess carbon is available in both RHs. The RRH represents SiO_2/C ratio of 0.41 with a large excess of carbon, and should produce approximately 17 wt% SiC. While for CRH $0.41 < SiO_2/C < 1.67$, which implies that a lower amount of excess carbon is available for SiC formation.

Fig. 2 shows the infrared absorption spectra of RRH and CRH. The FTIR spectrum of RRH contains several absorption bands, which have been assigned to individual structural units as listed in Table II. The carbothermic treatment at 1000°C leads to dehydration and progressive aromatization. The indication of dehydration is revealed by the negligible intensity of the O—H stretching band (3600–3100 cm^{-1}) in CRH compared with that in RRH. Organic decomposition can be observed from the absence of a 2900 cm^{-1} band representing C—H absorption, and peaks of CH_2 and CH_3 at 1500–1200 cm^{-1} dramatically diminished. In addition, absorbance bands in the 1600 cm^{-1} (C=C) and 1700 cm^{-1} (C=O) implies that there are some aromatic structures present in the CRH. The band from 1050–1100 cm^{-1} corresponds to the Si—O bond vibration

TABLE II Absorption bands in the FTIR spectra and their assignment

Region (cm^{-1})	Assigned to	References
3600–3100	O—H stretching	26, 27
3000–2850	C—H stretching	26, 28
1600	Aromatic C═C vibrations activated by neighboring oxygen groups	29
1500–1415	C—H deformation	26, 27
1500–1200	CH_2, CH_3, $Si(CH_3)$, $C(CH_3)$	30
1500–1000	Aromatic C═C skeletal vibration	27
1360–1310	C—C and C—O skeletal vibration	27
1100–1000	Si—O stretching	31–33
970	SiC (reflection)	34
898–825	Characteristic Si—C bonds appears beside Si—O vibrations	29
825–800	Antisymmetric Si—C stretching	31, 35
780	Si—C	36
460, 796, 1093	Characteristic of Si—O bonds	29, 37

mode appeared sharper as the organic matter was pyrolysed.

Combining the TGA and FTIR results, it can be envisaged that the first exotherm is due to the dehydration, decomposition, and rearrangement of the products. The second exotherm is due to the cross bridging and aromatic cyclization of charred residue. As dehydration and decomposition occurred, the inherent amorphous silica appeared more clearly.

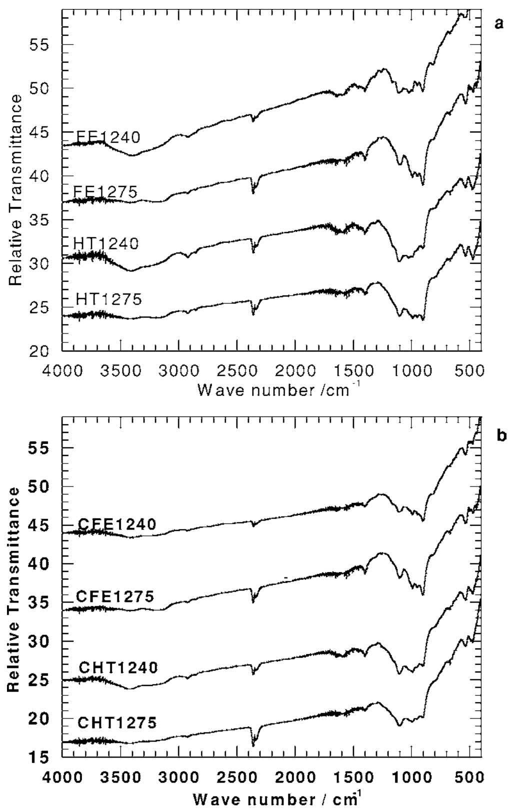

Figure 3 FTIR spectra of (a) uncoked and (b) coked samples.

3.2. Transformation of silica and condensed organic/graphite

FTIR spectra of samples heated to 1240°C showed that some unsaturated C—C bonds (1360–1310 cm^{-1}) and carbonyl groups (1500–1415 cm^{-1}) were formed. When pyrolysed at a higher temperature (1275°C) these compounds progressively transformed to aromatic and condensed aromatic compounds, corresponding to the 1600 cm^{-1} band. This results in a rapidly growing three-dimensional network polymer, which continuously grows by trapping small reactive pyrolysis products [27].

As the temperature is increased from 1240 to 1275°C, a change in absorption at 1100 cm^{-1}(corresponding to the vibration of Si—O bond) with respect to that at 900 cm^{-1} (Si—C—O) is observed (Fig. 3). There tends to be stronger absorption at 900 cm^{-1} and hence enhancement of the transformation for the samples heat-treated to higher temperature, or Fe pretreated. The absorption ratios of the bands Si—O/Si—C—O may be indicative of the progressive transformation from silica to SiC [37]. However, the identification of specific absorption bands over the range of interest was made difficult because of band over-lapping. The transformation process was further investigated by XRD technique.

Fig. 4 shows X-ray diffraction patterns of the powders RH, Fe, CFe, and CHT which had undergone carbothermic reduction at 1240 and 1275°C. At 1240°C, four peaks attributing to organic char at $2\theta = 19.96°$ and 18.78°, silica at 21.68°, and graphite at 26.7° were observed. The condensed aromatic peaks corresponded well with the FTIR spectra in that the char consisted of benzene rings connected with silane and small amount of phenyl or vinyl groups. Combining the matched phases from the JCPDS files for the XRD profiles and the types of corresponding chemical bonds from the FTIR spectra, a few possible phases present are vinyl-tris-triphenylsiloxysilane ($C_{56}H_{48}O_3Si_4$), 4-hexylrosorcinol ($C_{12}H_{18}O_2$), and 3,3-Dimethylhexaphenyltrisiloxane ($C_{38}H_{36}O_2Si_3$). Weak peaks for β-SiC in the (111) direction and for α-SiC in the (103) direction were noticeable, which demonstrated the onset of the nucleation of SiC. At a higher temperature (1275°C), silica was not detectable by XRD, whereas organic matter still remained, and a larger amount of SiC was formed.

Hydrothermal treatment leads to an increase in the amount of silica remaining in RHs. Fig. 4c illustrated that a high amount of silica existed up to 1275°C. This may be due to leaching out of carbonyl and other organic groups during the pretreatment.

From Fig. 4b, RH treated with iron exhibited a similar behaviour to Fe untreated RH except that SiO_2 was not detectable and SiC was formed at a lower temperature (1240°C). Comparing the X-ray diffraction patterns for the Fe-treated and normal RH (Figs 4a and b), it is apparent that Fe promotes the formation of SiC. While for the uncoked (Fig. 4b) and the coked (Fig. 4d) materials, the conversion to SiC is more complete than in the former.

3.3. Silicon carbide formation

The profile of IR spectra for samples heated to 1425°C are nearly identical (Fig. 5a). A very strong, broad and asymmetric absorption peak from 700–970 cm^{-1}, covering the range of Si—C and Si—C—O vibration, was

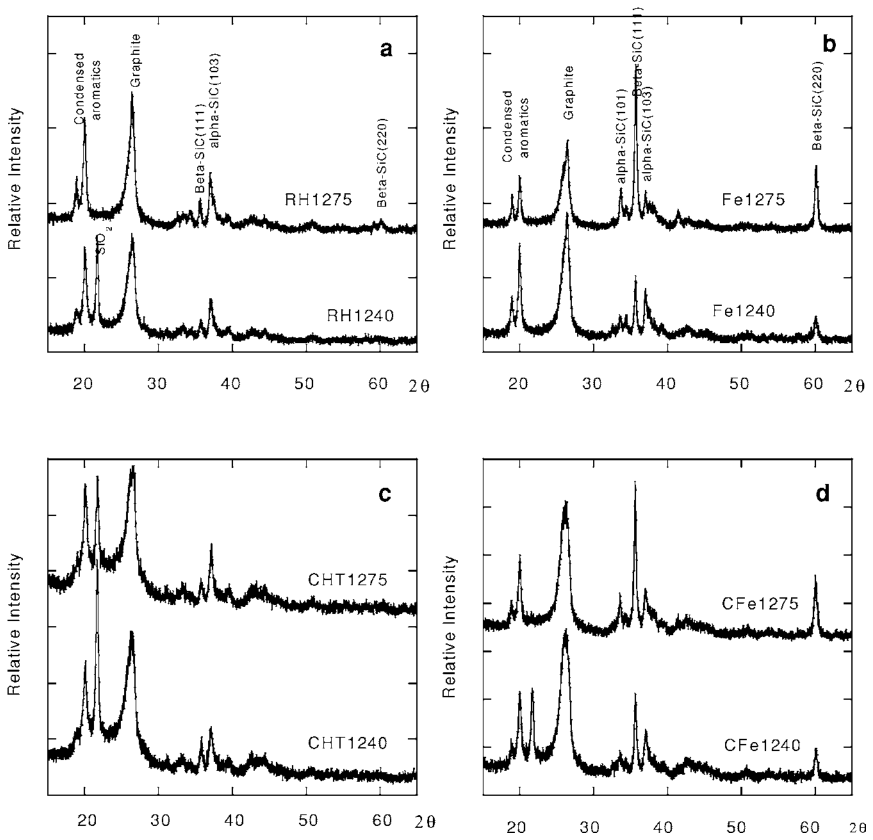

Figure 4 XRD profiles of (a) RH, (b) Fe, (c) CHT, and (d) CFe, respectively.

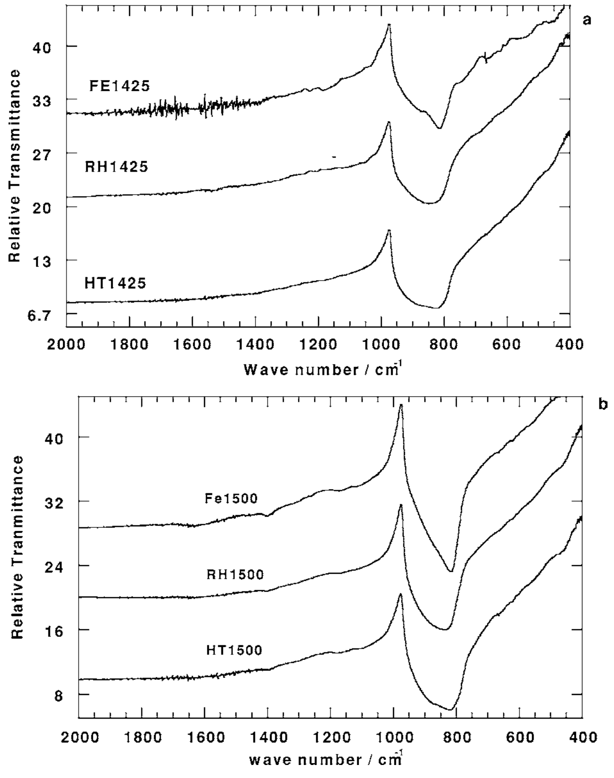

Figure 5 FTIR spectra of RH, Fe and HT heated to 1500°C.

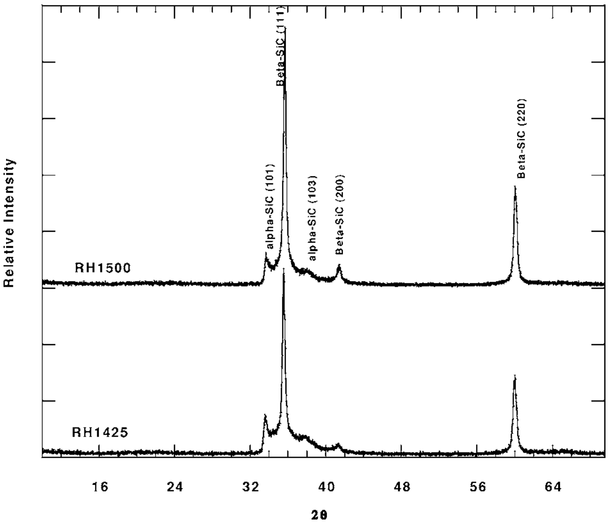

Figure 6 XRD profiles RH fired at 1500 and 1425°C.

observed. In addition, the intensity of the aromatic C=C vibration at ∼1600 cm^{-1} tends to decrease when compared with that from the samples heated at lower temperature. In the 1500°C spectra (Fig. 5b), the broad peak narrowed, evident in the Fe sample, and is centred at about 825 cm^{-1}, indicating that the carbothermic reduction is almost completed. The apparent increase in the tranmittance at approximately 970 cm^{-1} may be related to effects associated with the size of the SiC particles [34].

In Fig. 6, it was evident as expected that the conversion of α-SiC to β-SiC is promoted; it is consistent with the FTIR results which comfirms the more structurally arranged SiC following higher temperature treatment.

Examination by SEM (Fig. 7) showed that the products are consisted of submicron SiC whiskers and particles. Typically, RHs form particulates and Fe accelerates the formation of whiskers. The average crystallite

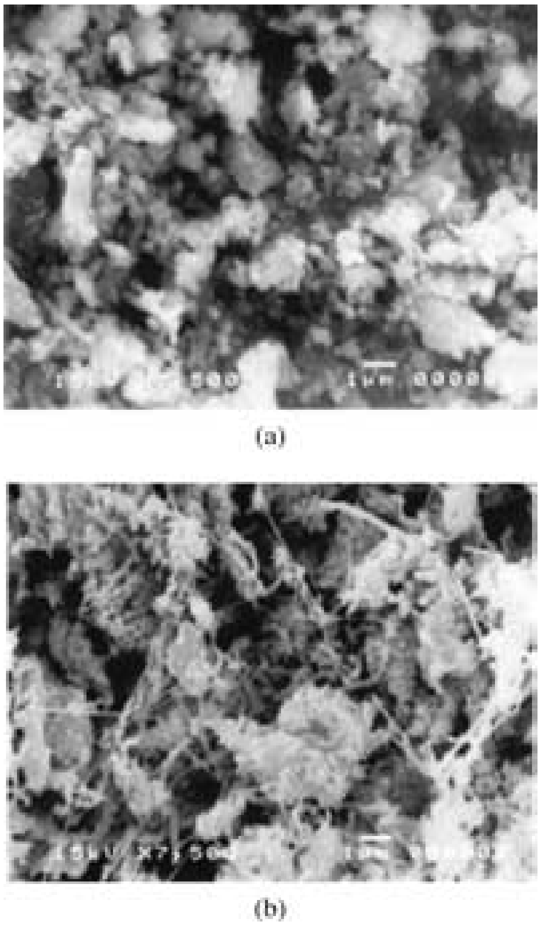

Figure 7 SEM micrographs of (a) RH and (b) Fe pyrolysed at 1500°C.

size of particulates was approximately 0.1–1 μm. The fine primary particles were located together to form agglomerates of different forms and sizes. BET surface area was approximately doubled from 4 m^2/g in RRH to 8 m^2/g in RH. The surface area (a_s) was determined as 8.7 m^2/g by nitrogen adsorption. Using this value, an average particle size of 0.3 μm was calculated according to $d = 6/\rho a_s$, where ρ is the density of SiC.

4. Conclusion

The kinetics of silicon carbide synthesis from rice husks can be divided into 3 stages: organic decomposition, transformation of silica and condensed organic/graphite, and silicon carbide formation. Both RRH and CRH can be used as precursors for SiC synthesis, although different reaction kinetics and thus different control parameters are required. The highly open structure and intimately mixed silica with organic matter are beneficial for the reaction can be completed at 1425°C. On the other hand, although C/Si ratio of CRH is adequate for the reaction, the high aromaticity and less open structure dramatically retards the reaction so that a much higher temperature is needed to complete the reaction. Pretreatment with iron increases β-SiC and whisker formation. Hydrothermal pretreatment retards the reaction by leaching off most of the carbonyl groups, although the low C/SiO_2 ratio leads to lower amounts of graphite in the products.

Acknowledgements

The authors wish to thank Dr. Pakamard Seawong, Ms. Patarawan Kahawong, Mr. Chitsakon Pakjamsai and Mr. Thanawit Pothsree for technical support.

References

1. D. F. HOUSTON, in "Rice Chemistry and Technology" (Am. Assoc. Cereal. Chemists., St. Paul, MN, 1972) p. 301.
2. S. L. LIU, *Chem. Abstr.* **58** (1963) 8234g.
3. I. B. CUTLER, U.S. patent no. 3,754,076 (1973).
4. J. G. LEE and I. B. CUTLER, *Amer. Cer. Soc. Bull.* **54** (1975) 195.
5. B. C. BECHTOLD, R. L. BEATTY and J. L. COOK, in "Progress in Science and Engineering of Composites ICCM-IV," Tokyo, edited by T. Hayashi, K.Kawata and S. Umekawa (1982) p. 113.
6. S. N. LAKIZA and YU. P. DYBAN, *Sov. Powder Metall. Met. Ceram.* **21** (1982) 117.
7. N. K. SHARMA, W. S. WILLIAMS and A. ZANGVIL, *J. Amer. Cer. Soc.* **67** (1984) 715.
8. R. V. KRISHNARAO, M. M. GODKHINDI, M. CHAKRABORTY and P. G. MUKUNDA, *J. Mater. Sci.* **29** (1994) 2741.
9. P. K. MISHRA, B. B. NAYAK and B. MOHANTY, *J. Amer. Cer. Soc.* **78**(9) (1995) 2381.
10. B. B. NAYAK, B. C. MOHANTY and S. K. SINGH, *J. Amer. Cer. Soc.* **79**(5) (1996) 1197.
11. S. F. MOUSTAFA, M. B. MORSI and A. ALM EL-DIN, *Canadian Mettal. Quart.* **36**(5) (1997) 355.
12. K. M. KNOWLES and M. V. RAVICHANDRAN, *J. Amer. Cer. Soc.* **80**(5) (1997) 1165.
13. D. H. FILSINGER and S. A. JANSSON, *ibid.* **73**(6) (1990) 1726.
14. S. B. HANNA, L. M. FARAG and N. A. L. MANSOUR, *Therm. Acta* **81** (1984) 77.
15. M. PETEL and A. KAREERA, *J. Mater. Sci. Lett.* **8** (1989) 955.
16. R. V. KRISHNARAO, *J. Mater. Sci.* **30** (1995) 3645.
17. F. J. NARCISO-ROMERO and F. RODRIGUEZ-REINOSO, *ibid.* **31** (1996) 779.
18. K. JANGHORBAN and H. R. TAZESH, *Ceram. Intern.* **25** (1999) 7.
19. R. V. KRISHNARAO and Y. R. MAHAJAN, *J. Eu. Cer. Soc.* **15** (1995) 1229.
20. S. R. NUTT, *J. Amer. Ceram. Soc.* **71**(3) (1988) 149.
21. R. V. KRISHNARAO, M. M. GODKHINDI, M. CHAKRABORTY and P. G. MUKUNDA *ibid.* **74** (1991) 2869.
22. R. V. KRISHNARAO, M. M. GODKHINDI and M. CHAKRABORTY, *J. Mater. Sci.* **27** (1992) 1227.
23. R. V. KRISHNARAO and M. M. GODKHINDI, *Ceram. Int.* **18** (1992) 35.
24. R. V. KRISHNARAO, *J. Mater. Sci. Lett.* **12** (1993) 1268.
25. W. G. SPITZER, D. A. KLEINMAN and C. J. FROSCH, *Phys. Rev.* **113**(1) (1959) 133.
26. L. J. BELLAMY, in "The Infra-Red Spectra of Complex Molecules," Vol. 1 (Chapman, London, 1975).
27. I. PASTOROVA, R. E. BOTTO, P. W. ARISZ and J. J. BOON, *Carbohydrate Research* **262**(1) (1994) 27.
28. C. J. POUCHERT, in "The Aldrich Library of Infrared Spectra," 3rd ed. (Aldrich Chemical Company, WI, 1981).
29. H. PREISS, L. M. BERGER and M. BRAUN, *Carbon* **33**(12) (1995) 1739.
30. D. K. BASA and F. W. SMITH, *Thin Solid Films* **192** (1990) 121.
31. A. L. SMITH and D. R. ANDERSON, *Appl. Spectrosc.* **38** (1984) 822.
32. K. SATO, F. KUROSAWA and O. KAMMORI, *Bull. Chem. Soc. Jpn.* **42** (1969) 3593.
33. J. L. NIETO, *Analyst* **103** (1978) 128.
34. C. F. BOHREN and D. R. HUFFMAN, in "Absorption and Scattering of Light by Small Particles" (John Wiley, New York, 1983) Chapt. 12.

35. M. FALK and S. KARUNANITHY, *Mater. Sci. Eng.* A **114** (1989) 209.
36. G. LUCOVSKY, J. YANG, S. S. CHAO, J. E. TYLER and W. CZUBATYJ, *Phys. Rev.* B **28** (1983) 3224.
37. D. M. WOLFE, B. J. HINDS, F. WANG, G. LUCOVSKY, B. L. WARD, M. XU, R. J. NEMANICH and D. M. MAHER, *J. Vac. Sci. Technol.* A **17**(4) (1999) 2170.

Received 22 November 2002
and accepted 29 July 2003