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Sol–gel synthesis and crystallization of aluminum borosilicate

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Abstract

The Al_2O_3–B_2O_3–SiO_2 system is explored; in the composition $Al_{16}B_6Si_2O_{37}$, for the effect of the preparation conditions on the properties of the final product. The sol–gel method was tried to prepare this composition both in an aqueous and non aqueous media. The crystalline phases developed were found to be mullite, $Al_4B_2O_9$ and B-mullite ($Al_{18}B_4O_{33}$) in addition to some amorphous compositions of the aluminum borosilicate system rather than a pure crystalline $Al_{16}B_6Si_2O_{37}$ phase. XRD and FT–IR showed that the gel prepared in non-aqueous medium could be thermally treated giving some crystalline species at lower temperatures than the gel formed in aqueous medium. In contrast to this result, DTA of the former product show an exothermic change at higher temperature than that of the later. This change could be attributed probably to an oxidation rather than to crystallization.

Keywords: A. Sol–gel process; Crystallisation; Aluminum borosilicate

1. Introduction

Aluminum borosilicates represent a group of interesting compositions and are extensively studied by many authors [1,2]. The existence of ternary miscibility in the Al_2O_3–B_2O_3–SiO_2 system is also claimed [3]. One of these systems ($Al_8B_2Si_2O_9$) was synthesized at fluid pressure of 1–4-k bar and a temperature of 800–830°C [4].

Mullite, ($Al_6Si_2O_{13}$), and aluminum borate, ($Al_6B_4O_{12}$, $Al_{18}B_4O_{33}$), are the known phases studied recently by many authors [1,2]. Mullite exhibits some attractive properties like high refractoriness, low thermal expansion and conductivity, good chemical stability, and excellent mechanical properties at high temperatures. The $9Al_2O_3.B_2O_3$ phase enjoys whiskers microstructure that has good mechanical strength and is widely used as reinforcement for metal matrix composites.

Boralsilite is a natural anhydrous Al-B-silicate mineral of the general formula ($Al_{16}B_6Si_2O_{37}$). It is discovered by Huijsmans [5] and described in details by Grew et al. who also claimed the possible coexistence of boralsilite with silliminite and andalusite [6]. This mineral is estimated to have formed between 600 and 750°C and 3–5 K bar at conditions where $P_{H_2O} < P_{total}$. It is a white to colorless solid of 3.07-g/cm^3 density and a vitreous luster. Boralsilite is a material of high contents of alumina and silica, and low content of borate. Boralsilite is usually found in direct contact with minerals like quartz, K-feldspar, plagioclase, grandidierite, and tourmaline.

Throwing some light on the possible routes of preparation of boralsilite amorphous materials and investigating their crystallization trends provide a valuable knowledge about the properties of these materials. The present work aims to study the possibility of preparation of aluminum borosilicate composition in the starting nominal ratio corresponding to boralsilite by the sol–gel method. The effect of water on the course of the reaction and the nature of the final product, the crystallization trends of the amorphous products, and the effect of thermal treatment are also of main interest.

Preparation of boralsilite by the conventional methods (namely; the melt quenching and co-precipitation methods) is difficult because high working temperatures and pressures are required. An alternative route to prepared boralsilite can be the sol–gel one. In this way, a good control of the interacting liquid precursors, energy saving, less pollution, high homogeneity, control of the final product's morphology can be achieved. The alkoxide precursors of boron, silicon, and aluminum are suggested candidates for the reaction mixture in organic media. Starting from a mixture of aqueous solutions may lead to some difficulties concerning the fast precipitation of aluminum hydroxide and boric acid and the difficulty of

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obtaining homogeneous distribution of the reacting species.

2. Experimental procedure

2.1. Preparation

The preparation and characterization of the samples in different conditions can be described as follows:

(1) Aluminum ethoxide, weighed into a glove box, was dissolved in a dry mixture of toluene, chloroform, and benzene. Dissolution was carried out in a 500-ml round glass-stopped flask by adding the solvent mixture through a 250-ml feeding cylinder (aided with a side-feed tube for air compensation [7]). The solvent mixture (with the ratio of 1:1:2) was added with constant magnetic stirring under argon atmosphere. The prepared solution was analyzed using the flame photometry technique to be 8.5% wt./vol. aluminum.

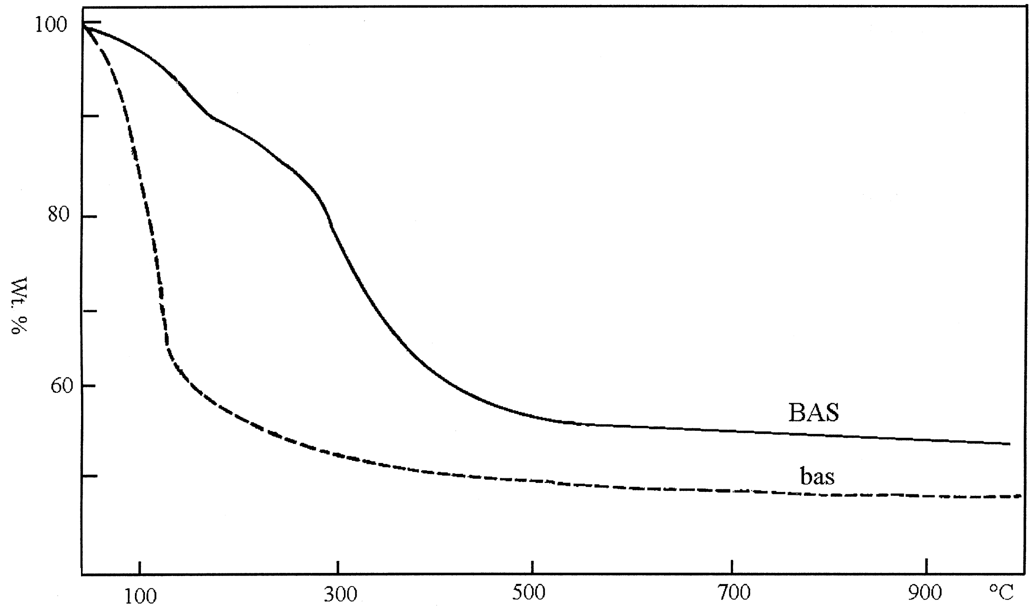

Fig. 1. TG curves of dried gels.

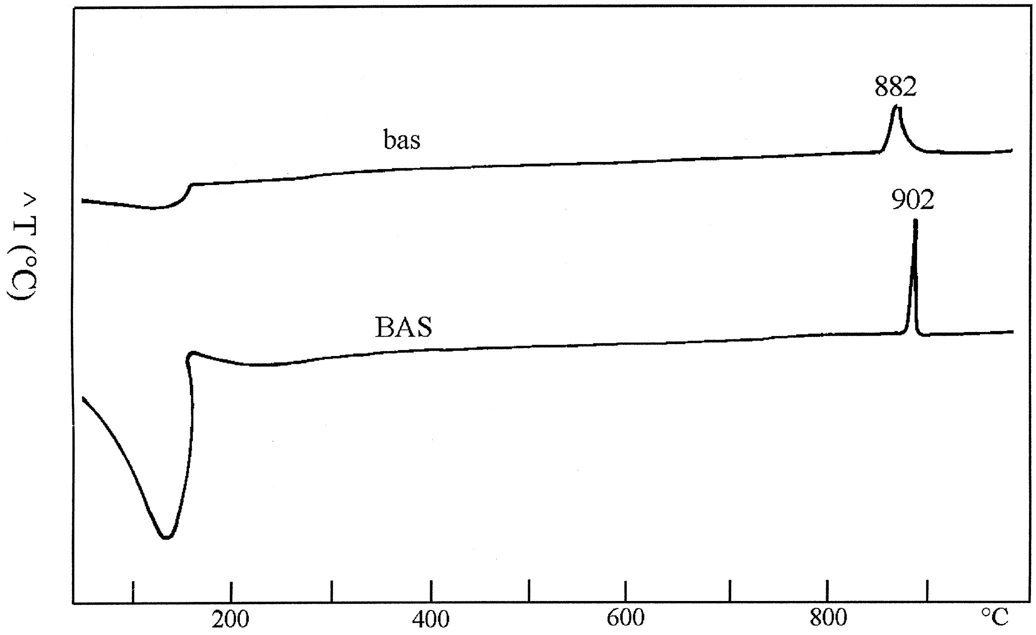

Fig. 2. DTA curves of samples dried at 550°C.

(2) Similarly, tetraethoxy silane (Aldrich 98.5 + %) to obtain a 35% solution. Boron triethoxide (Aldrich 98 + %) was diluted to 22.5% by ethanol in the same manner.

(3) Into a four-necked 500-ml round bottle, a calculated volume of the silane solution was added, with constant stirring, to a portion of the borate solution to obtain a molar ratio of 1/3 for Si/B. Aluminum ethoxide solution was then added to the mixture in the ratio of 8/3 for Al/B. The three alkoxide mixture were then stirred under dry nitrogen flux for 6 h. The resulting solution mixture was clear and transparent as long as the reaction flask was tightly closed, except for traces of white cloud.

(4) The solution was then divided into two equal portions where to the first portion; (namely *BAS*), a 10% ethanol solution of ethylene glycol was added (1% glycol/Al). The other portion of the reaction mixture; (namely *bas*), was left in an open beaker with stirring. The *BAS* portion was immediately changed into a transparent gel. The *bas* portion remained liquid. It was continuously stirred on a water bath, where the water vapor was allowed to be in contact with the surface of the solution, for about 4 h at about 55°C. The resulting cloudy solution gradually formed a white suspension and then a white precipitate.

(5) Both the *BAS* and *bas* portions were then put into a dryer at 80°C overnight and the temperature was then raised to 120°C for 3 days. The *BAS* gel was dried into a white powder.

(6) The two products (the white *BAS* powder and the *bas* precipitate) were ground and further dried at 120°C for 2 days.

2.2. Characterization

The two powders from step (6) above were thermally characterized by TG and DTA runs. The measurements were performed in a rate of 10°C/min using a Perkin Elmer Instrument Model DTA 7 series (Norwalk Connecticut, USA) in a nitrogen gas flow of, 50 cm^{-3}/min.

Infrared spectra of the samples in the form of KBr pellets were charted using Bomem-FT–IR (Michelson-Canada) between 400 and 4000 cm^{-1}.

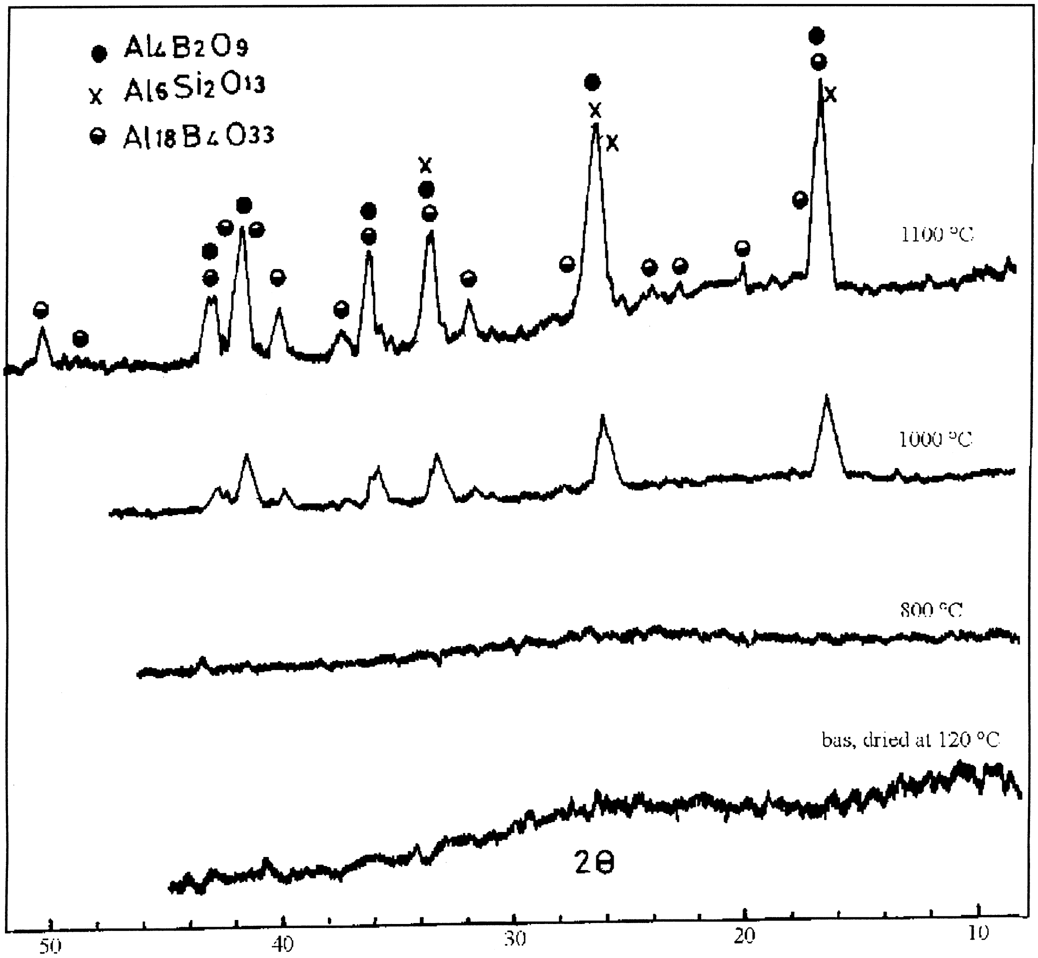

Fig. 3. XRD patterns of *bas* sample treated at different temperatures for 2 h.

Different samples of both powders from step (6) were heat-treated at different temperatures each for 2 h with a heating rate of 20°C/min. Crystallization of the heat-treated samples and qualitative study of the formed phases were followed by a Philips 1390 X-ray powder diffractometer.

3. Results and discussion

3.1. Thermal analysis

Fig. 1 shows the thermo gravimetric curves of both the products as prepared and dried at 80°C overnight. There seem two weight-loss steps on heating the *BAS* sample. The first step starts at about 80°C and it can be attributed to the evaporation of the moisture adsorbed by the samples. This moisture may have been adsorbed during the cooling down of the samples to room temperature at ambient atmosphere. The second weight loss starts at about 280°C and continues to about 450°C. This loss may correspond to the evolution of organic ligands of the starting reaction precursors. The total weight loss of the *BAS* sample is about 40% summing for both the solvents and decomposition losses.

On the other hand, the *bas* sample shows a nearly single-step weight loss. Most of the weight loss (about 40%) occurs before the temperature reaches 140°C while the rest of the evaporation and/or decomposition weight losses (about 6.54%) continue afterwards. It may be concluded that the evaporation of solvents, evaporation of excess water, and the evolution of the gases of decomposition took place very successively to the extent that there was some overlap between the weight losses corresponding to the three processes. This means that the decomposition of the *BAS* gel started from a nearly dry (or almost solvent-free) gel sample while that of the *bas* precipitate started decomposition from a nearly wet and solvent-contaminated sample.

For both products, weight losses seem to halt at temperatures above 550°C. The difference in weight loss between the two samples (about 6.5%) is explained by the loss of water retained in the *bas* sample.

The DTA curves of the two samples (preheated at 550°C for 5 h) are shown in Fig. 2. The endothermic peaks below 200°C for both samples may be due to the

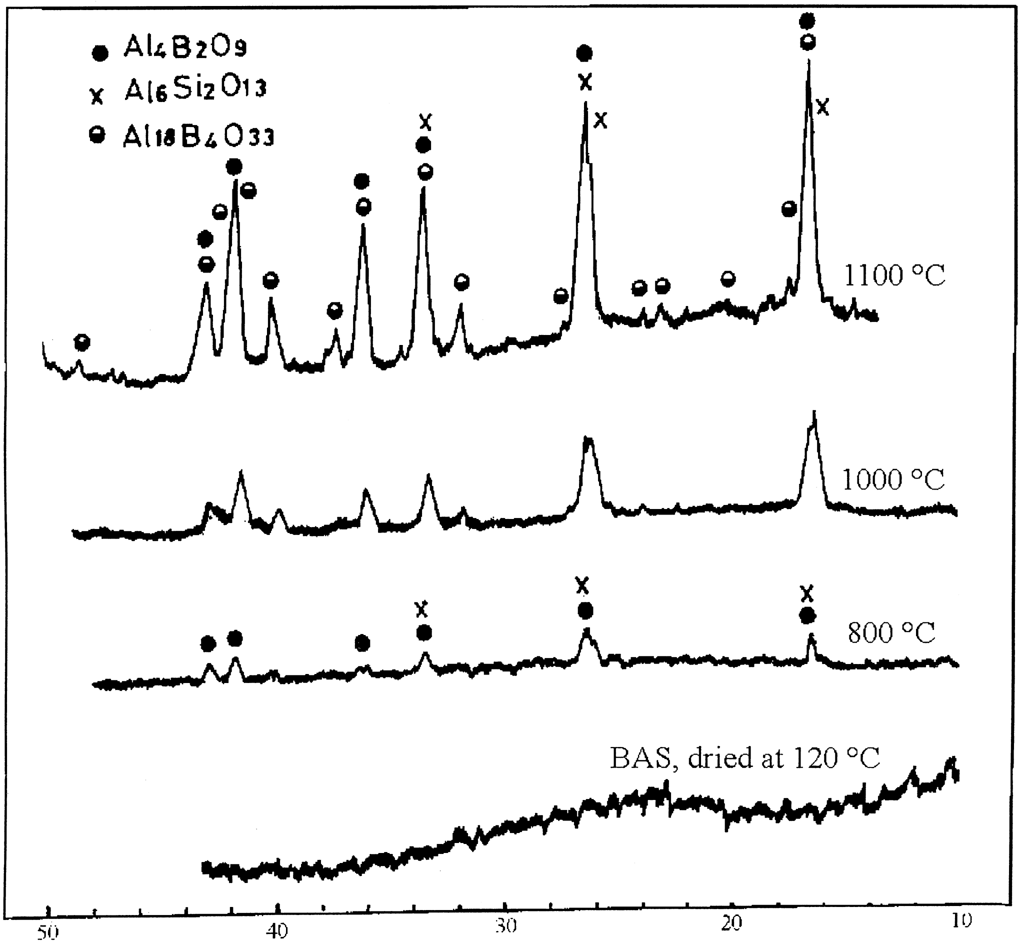

Fig. 4. XRD patterns of *BAS* sample treated at different temperatures for 2 h.

elimination of adsorbed water. For each sample, an exothermic change took place at high temperatures (about 882 and 902°C for *bas* and *BAS* respectively). The exothermic peak for the *bas* sample is a bit broader if compared to the sharp one of the *BAS* sample. The exothermic peak of sample *BAS* is sharper than that of sample *bas* that also has an onset-offset range wider than that of sample *BAS*. These peaks may correspond to an oxidation change in each case at the respective temperature. It is hard to consider these exotherms as indicating crystallization of the samples. This will be a clear contradiction to the results obtained by XRD as will be shown below unless these two peaks represent crystallization of a little percentage of each sample that could not be detected by XRD [8].

3.2. X-ray diffraction patterns

It is clear from Fig. 3 that the sample *bas* is amorphous even at temperatures up to 800°C. The crystallinity is improved gradually when the sample is thermally treated at high temperatures up to 1100°C. The XRD pattern of this sample at 1000°C shows predominating crystalline species of $Al_4B_2O_9$ and $Al_6Si_2O_{13}$ (mullite) in addition to the growth of some traces of $Al_{18}B_4O_{33}$ (B-mullite) crystals [9].

The comparison between Figs. 3 and 4 display that the temperature at which the *BAS* sample starts crystallization is lower than that at which sample *bas* does. In addition, and in contrast to the case of sample *bas*, the early stage of crystallization in Fig. 4 at 800°C shows a

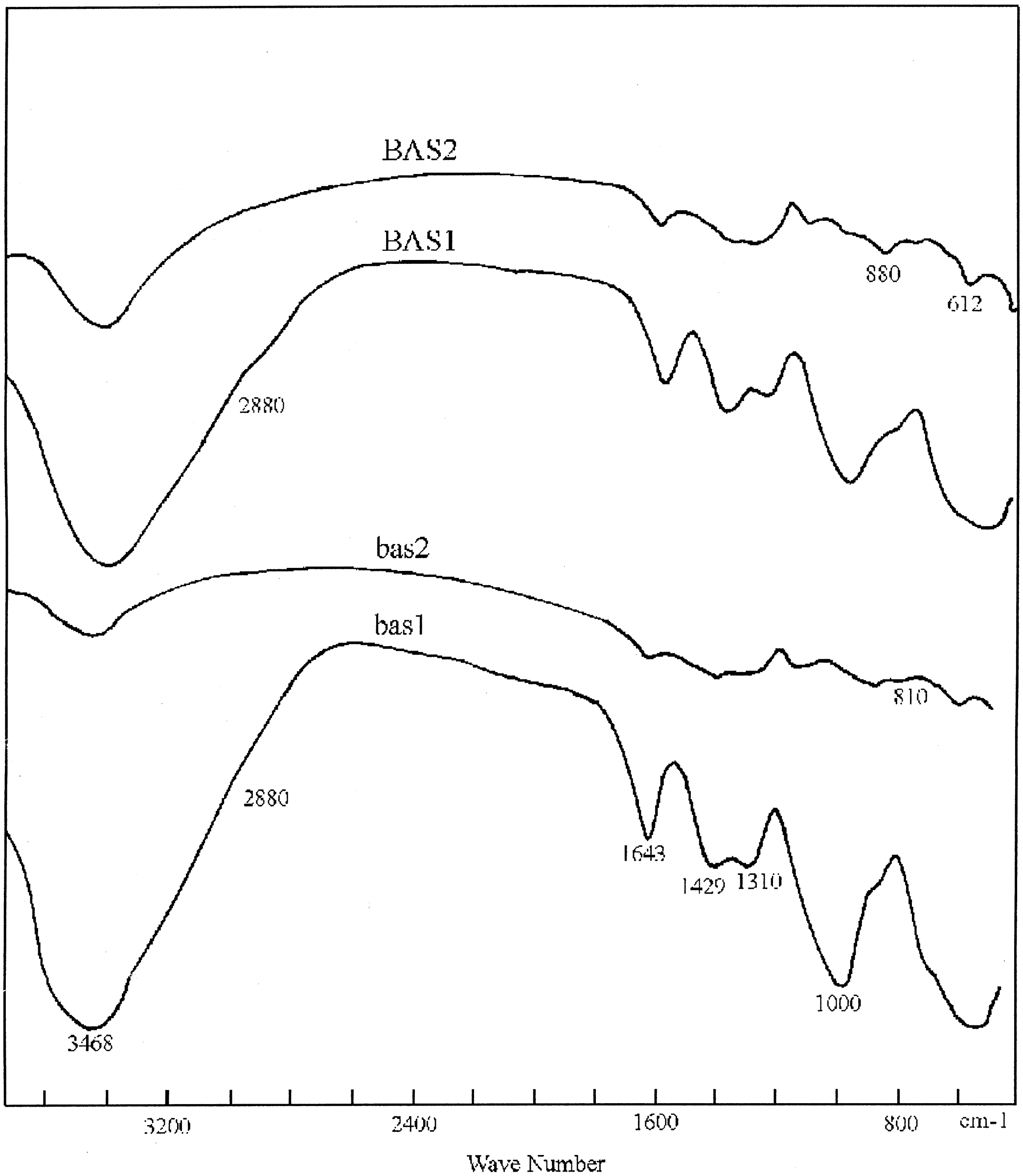

Fig. 5. FT–IR spectra of the dried gels and thermally treated samples.

predominating mullite crystals and a little of $Al_4B_2O_9$ crystals. At higher temperatures, $Al_4B_2O_9$ and B-mullite crystallize as well up to 1100°C. This explains the exothermic peak of sample *BAS* in Fig. 2.

The overall result here is that mullite and $Al_4B_2O_9$ in the *BAS* sample; prepared in non-aqueous medium, crystallize earlier than in the *bas* sample, prepared in the presence of the water sample *bas*. It is also clear that these phases are stable within the temperature range of our study. On the other hand, $Al_{18}B_4O_{33}$ (B-mullite) and $Al_4B_2O_9$ are the most stable phases in the Al_2O_3–B_2O_3 system [9]. Both phases are still stable in the ternary system Al_2O_3–B_2O_3–SiO_2 [4]. The early crystallization of mullite in the *BAS* sample may be due to the higher solubility of the silica species and its tendency to be strongly adsorbed on the surface of amorphous aluminum oxides [10]. The formation of mullite seems to be favored in samples prepared with low water content and/or prepared in acid medium [11]. This explains why mullite appeared at the first stages of crystallization of the *BAS* sample than in the *bas* one.

3.3. IR results

In Fig. 5 is shown the FT–IR absorption bands of both *BAS* and *bas* samples. Both products were checked as gels dried at 120°C (*BAS* 1 and *bas* 1) and as thermally treated at 1100°C for 5 h (*BAS* 2 and *bas* 2). This figure shows that besides some amount of associated organic residues; (mainly solvents 2880 cm^{-1}), molecular water (δ H_2O around 1645 cm^{-1}; ν at 3500 cm^{-1}) is still present in samples *BAS* 1 and *bas* 1 [12]. The water contamination in sample *bas* 1 is evident, as it is already prepared in aqueous medium. Some moisture may have been adsorbed by the sample *BAS* 1 on cooling. On the other hand, both *BAS* 2 and *bas* 2 samples show organic free spectra. Although largely reduced in intensity, th0e broad band around 3455 cm^{-1} corresponding to the OH group for the high-temperature thermally treated samples is attributed to little moisture adsorbed by the cold samples as indicated by their TG curves.

A distinct band located at 1446–1429 cm^{-1} assigns the asymmetric stretching of trigonal BO_3 unit. This band is more intense in the spectrum of *BAS* samples. For all samples, a band at 1310–1300 cm^{-1} is noticed which reflects the B–O–B linkage in which both boron atoms are triangularly linked. A strong band at 1020–1000 cm^{-1} with a shoulder near 1170 cm^{-1} is indicating the Si–O–Si asymmetric stretching vibration [13]. The shoulder appeared at 900–880 cm^{-1} in the spectra of each dry gel (*BAS* 1 and *bas* 1) is due to condensation of Si–OH groups [14].

The IR spectra of the thermally treated samples show a new band at 610 cm^{-1} corresponding to the formation of Si–O–Al bond in which the Al^{3+} ions are octahedrally coordinated [14]. This octahedral coordination denotes the formation of mullite crystals at high temperatures. However, an overlap between this band and the band assigning B–O–Si bridges should be taken into consideration [15]. This is in accordance with the XRD patterns of these samples. The small band at 810 cm^{-1} is associated with the stretching vibrations of AlO_4 tetrahedral structure [16].

4. Conclusions

In this work the sol–gel method was tried to prepare the $Al_{16}B_6Si_2O_{37}$ composition which is not easy to prepare following the traditional melt-quenching route. Based on XRD results, it was found that the product prepared in non-aqueous medium crystallizes, at relatively lower temperatures than the one prepared in aqueous medium. The former product develops crystalline species at about 800°C while the later starts crystallization at about 900°C. The exothermic change showed by DTA curves could be considered as oxidation peaks rather than crystallization changes. The Boralsilite crystalline phase could not be formed in these conditions while mullite, ($Al_6Si_2O_{13}$), aluminum borate, ($Al_6B_4O_{12}$), and B-mullite, ($Al_{18}B_4O_{33}$), were formed. On crystallization of the sample prepared in non-aqueous medium, mullite and aluminum borate appear first while B-mullite appears at higher temperatures. On the other hand, both of the three phases appear altogether in case of the sample prepared in aqueous medium.

References

[1] M. Zhou, J.M.F. Ferreira, A.T. Fonseca, J.L. Baptista, Hydrothermal ageing effects on the co-precipitated mullite-alumina composite precursor, J. Eur. Ceram. Soc. 17 (1997) 1539–1544.

[2] J.X. Li, T. Narita, J. Ogawa, M. Wadasako, In situ synthesis of porous ceramics with a framework structure of aluminum borate whisker, J. Mater. Sci. 33 (1998) 2601–2605.

[3] E.H. Nickel, M.C. Nichols, Mineral Reference Manual, Van Nostrand Reinhold, New York, 1997, p. 25.

[4] G. Werding, W. Schreyer, Synthesis and stability of werdingite, a new phase in the system MgO–Al_2O_3–B_2O_3–SiO_2 (MABS), and another new phase in the ABS-system, Eur. J. Mineralogy 4 (1992) 193–207.

[5] J.P.P. Huijsmans, A grandidierite-bearing pegmatite from the Almgjotheii, Rogaland, SW Norway, MS thesis (petrology), Institute of Earth Sciences, State University of Utrecht, The Netherlands, 1981, p. 38.

[6] E.S. Grew, J.J. McGee, M.G. Yates, D.R. Peacor, R.C. Rouse, J.-P.P. Huijsmans, C.K. Shearer, M. Wiedenbeck, D.E. Thost, S.-C. Su, Boralsilite ($Al_{16}B_6Si_2O_{37}$): A new mineral related to sillimanite from pegmatites in granulite-facies rocks, Am. Min. 83 (1998) 638–651.

[7] A.F. Ali, P. Mustarelli, A. Magistris, Optimal synthesis of organo-phosphate precursors for sol–gel preparations, Mater. Res. Bull. 33 (5) (1998) 697–710.

[8] C.S. Hutchison, Laboratory Handbook of Petrographic Techniques, John Wiley and Sons, 1973, p. 438.

[9] D. Mazza, M. Vallino, G. Busca, Mullite-type structures in the systems Al_2O_3–Me_2O (Me = Na, K) and Al_2O_3–B_2O_3, J. Am. Ceram. Soc. 75 (1992) 1929–1934.

[10] M.D. Sacks, H.W. Lee, J.A. Pask, A review of powder preparation methods and densification procedures of fabricating high density mullite, in: S. Somiya, R.F. Davis, J.A. Pask (Eds.), Ceramic Transactions 6, Mullite and Mullite Matrix Composites, American Ceramic Society, Westerville, OH, 1990, pp. 167–207.

[11] I.M. Salvador, J.M. Fernandez, Al_2O3–SiO_2 glassy materials prepared by the alkoxide route, in: P. Duran, J. F. Fernandez (Eds.), Spain, 1993, pp. 115–1120.

[12] H. Schmidt, H. Scholze, ?. Kaiser, Contribution to kinetics of glass formation from solutions, J. Non-Cryst. Solids 48 (1982) 65–77.

[13] M. Nogami, Glass preparation of ZrO_2–SiO_2 system by the sol–gel process from metal alkoxides, J. Non-Cryst. Solids 69 (1985) 415.

[14] V.C. Farmer, The Infrared Spectra of Minerals, The Mineralogical society, London, 1974.

[15] A.S. Tenney, Wong, Vibrational spectra of vapor-deposited binary borosilicate glasses, J. Chem. Phys. (1972) 56.

[16] C. Huang, E.C. Behrman, J. Non-Cryst. Solids 128 (1991) 310.