Hydrothermally Assisted Sol-Gel Process on Binary Mixtures of Aluminum and Titanium Alkoxides: A Novel Route for the Fabrication of Single Phase Tialite

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ABSTRACT

Combination of sol-gel and hydrothermal routes in the metal alkoxide binary system of $Al(OR)_3$-$Ti(OR)_4$ (R= $-CH(CH_3)_2$ or $-CH_2CH_2OCH_3$) was investigated to prepare single phase aluminum titanate (tialite). The effects of various parameters, such as hydrothermal processing temperature, solvent polarity and the type of alkoxide precursor, in phase development of the product powders have been investigated. Phase development of the product powders was examined by Fourier Transform Infrared Spectroscopy (FTIR), X-ray powder diffraction (XRD) and Thermogravimetric analysis (TGA/DSC). The XRD results showed that when the polarity of solvent increased by using a mixture of toluene and isopropanol instead of pure toluene solvent, phase development of the product powder retarded and needed higher temperature (more than 1400°C) to produce single phase tialite. A similar effect was observed when aluminum 2-methoxyethoxide and titanium 2-methoxyethoxide were used instead of the aluminum *iso*-propoxide and titanium *iso*-propoxide. These observations are attributed to the more controlled hydrolysis conditions in the hydrothermally assisted sol-gel process.

1-Introduction

Tialite (aluminum titanate, Al_2TiO_5) is a synthetic ceramic with low thermal expansion coefficient (about $1–2\times10^{-6}$ K^{-1}) [1-3], chemical inertness [4, 5], good thermal shock resistance (≈500 Wm^{-1}) [6], low thermal conductivity (0.9-1.5 $Wm^{-1}K^{-1}$) [7-10], low modulus of elasticity (30 Gpa) [11-12], low wettability in molten non-ferrous metals [13-14], high melting point (over 1850ºC) [15], and high electrical resistance properties [16]. Therefore, it has a potential interest for many structural applications such as thermal insulator component in internal combustion engine [8-10], aluminum casting dies [11] and shielding material for use in nuclear fusion reactors [12-13], and metallurgy and thermal barriers [14-17]. Tialite has also been used as a filter for diesel engine exhaust treatment [3-4] and other industrial-environmental applications in the form of highly porous and micro-cracked monolithic bodies [11]. On the other hand, as a coating, it can provide wear-resistant coated surfaces [1], high temperature protective coatings [4] and it can also be used as a solid oxide lubricant [18]. These properties entirely arise from tialite structure which is isomorphous with pseudobrookite (Fe_2TiO_5)

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mineral [6, 17]. Other A_2BO_5 binary oxides like Ti_2MgO_5 and Ti_3O_5 have similar physical and structural properties [19].

Two allotropes, α and β, which refer to the low and high-temperature phases, have been observed for tialite. The low-temperature β-phase tialite is stable from 25-750°C and 1280-1820°C and the high-temperature α-phase is formed above 1820°C and stable up to its melting point at 1860°C [1-2]. It has been accepted that between 750 to 1280°C, tialite decomposed to its constituent components and only rutile and corundum could be identified [1-2, 6]. This phenomenon was attributed to the different ionic radii of Al^{III} (50 pm) and Ti^{IV} (68 pm) which destabilized the distorted tialite crystal lattice by insertion of the small size aluminum cation in the bigger size structural site [6]. Two mechanisms have been proposed for the decomposition of tialite. Initially, it was proposed that this is a nucleation and grain growth controlled process, and effectively dependent on the microstructure of the tialite precursor and thermal treatment process [6, 15]. But recently, Skala et al. investigated high-temperature crystal structure of tialite and proposed that the decomposition mechanism was controlled by diffusion of Al at high-temperature [17].

Most of the researches on tialite are focused on microstructure [9, 14], improvement of mechanical properties [20-22], lowering fabrication temperature [15] and contracting thermal instability [5-7, 12-13, 23]. To the best of our knowledge, there are only a few reports on comparison of the various chemical routes for the preparation of tialite [24-26]. Similar to many other mixed oxide ceramics, bulk tialite has been prepared conventionally, by mixing and sintering stoichiometric amounts of its components, alumina and titania, which can be provided from powders [3-7, 12-13, 17, 21-22] or gels [8, 15, 23-29]. Application of tialite is not limited only to the bulk form; tialite thin films have been fabricated by chemical vapor deposition (CVD) [30]. However, considering the limitations of CVD in preparation of tialite thin films and ceramic procedure in the preparation of bulk tialite, the sol-gel process remains as the ideal technique for the preparation of tialite thin films or bulk, using spin or dip-coating techniques [1-2, 18]. On the other hand, the hydrothermal method is a powerful ceramic processing technique, which has been used for the preparation of various fine metal oxides at lower processing temperature in comparison with the traditional methods. Recently, in a new approach, we have combined the sol-gel and hydrothermal methods for the preparation of bohemite [31-33], rutile and anatase TiO_2 [33], tenorite CuO [33], Nb_2O_5 [33], $MgAl_2O_4$ [34] and $KNbO_3$ [35]. In continuation of our interest in the preparation of binary metal oxides by combining these methods, in this study, we used the hydrothermally assisted sol-gel process on binary aluminum and titanium alkoxide mixtures, for the preparation of single phase tialite. The effect of different parameters, such as solvent polarity, hydrothermal processing temperature and the type of alkoxide precursor, in phase development of the material has been investigated.

2-Experimental

2-1-Material

All manipulations were carried out under nitrogen, using standard inert atmosphere apparatus (Schlenk techniques). All chemicals were purchased from Merck and used as received. Solvents were refluxed and dried over appropriate drying agents under an atmosphere of nitrogen and collected by distillation. Aluminum and titanium 2-methoxyethoxide were prepared by the alcohol exchange method from aluminum and titanium *iso*-propoxid.

2-2-Hydrolysis

For the hydrothermal assisted hydrolysis, aluminum and titanium *iso*-propoxide or 2-methoxyethoxide were mixed in the Al/Ti molar ratio of 2 and diluted in toluene or mixture of toluene and *iso*-propanol to 0.25 M of titanium-aluminum alkoxide. The mixture was then loaded in a glass container which was placed in a 300 ml stainless steel autoclave. The gap between the autoclave chamber and the glass container was filled with 50 ml of distilled water and then the autoclave was heated at either 100 or 200°C. The transfer of titanium-aluminum alkoxides into the autoclave was done in a moisture-free atmosphere to prevent the hydrolysis of precursor prior to being introduced into the hydrothermal chamber. After 5 h, the autoclave was cooled and the resulting powder was filtered and dried overnight at 100°C and then calcined at 700, 1200 and 1400°C. Experimental conditions for the hydrothermally-assisted sol-gel processing of metal alkoxide mixtures are given in Table 1.

Table 1. Experimental condition for the preparation of tialite.

Sample	Precursor	Concentration of $Al_2Ti(OR)_{10}$ (M)	Solvent	Hydrothermal temperature (°C)
AT1	$2Al(O^iPr)_3+Ti(O^iPr)_4$	0.25	Toluene + ^iPrOH	100
AT2	$2Al(O^iPr)_3+Ti(O^iPr)_4$	0.25	Toluene + ^iPrOH	200
AT3	$2Al(O^iPr)_3+Ti(O^iPr)_4$	0.25	Toluene	200
AT4	$2Al(OEtOMe)_3+Ti(OEtOMe)_4$	0.25	Toluene	200

2-3-Analytical methods and instrumentation

The infrared spectra were recorded on a Bomem MB-Series FT-IR spectrophotometer in KBr pellets at a resolution of 4 cm^{-1}. X-ray diffraction (XRD) patterns of the calcined powders were collected on a Phillips PW-1800 diffractometer with Cu-Kα radiation. Thermal analysis was carried out in a Rheometric Scientific STA-1500 at a heating rate of 10°C/min in air.

3-Results and Discussion

3-1-FTIR spectroscopy

Fig. 1 shows the IR spectra of various samples as prepared and after calcination at 700°C. Boehmite is the only semi-crystalline phase in all samples before calcination. Boehmite had two different stretching vibrations at 3280 and 3075 cm^{-1}, which were assigned to the bridged and terminal hydroxyl groups of BNPs, respectively. These stretching vibrations were accompanied by two bending vibrations for the bridged and terminal hydroxyl groups at 1150 and 1075 cm^{-1}, respectively. Also, it had some distinguishable Al-O related vibrations at 740, 610, and 480 cm^{-1} in the IR spectrum.

Apparently, aluminum and titanium alkoxide molecules in the precursors hydrolyzed distinctively and there is no Al-O-Ti bond in the precursor or hydrolysis product.

The IR spectrum of the as prepared sample, AT1, shows two overlapped bands at 3100 and 3350 cm^{-1} which shows that AT1 is at the first stage of boehmite crystallization. This is associated with the low hydrothermal hydrolysis processing temperature of the sample, 100°C, which is low for the complete crystallization of boehmite. The IR spectra of the other as prepared samples, AT2, AT3 and AT4, also showed two sharp bands in the range of 3000-3080 and 3300 cm^{-1}. These completely resolved bands are a good evidence for the formation of well crystallized boehmite by hydrothermal hydrolysis at 200°C [31-33]. This phenomenon was also observed for other characteristic bands of boehmite in these samples.

3-2-Thermogravimetric analysis

Fig. 2 shows thermograms (TG/DSC) of various samples. Weight losses of about 15% in the TG curve of AT1, below 200°C, and about 1% in TG curves of AT2, AT3 and AT4, below 100°C, accompanied by endothermic peaks in the DSC curves are due to the elimination of physically adsorbed water. Interestingly, AT4 is the only sample that shows about 5% weight loss in the temperature range of 200 to 350°C in the TG curve. This weight loss which is accompanied by an exothermic peak in DSC curve is attributed to the combustion of the organic residue. The following weight losses for these samples are in the temperature range of 350 to 500°C and are all accompanied by endothermic peaks in their DSC curves. The weight losses for these samples are about 7% for AT1, 10% for AT2 and AT3 and about 8% for AT4, and are associated with the dehydroxylation of boehmite and transformation to γ–alumina [31]. Total weight losses of AT2, AT3, and AT4 are about 11, 12 and 14%, respectively, which are much lower than 25 to 60% weight losses reported for the hydrolytic and non-hydrolytic sol-gel processes [8, 16, 25, 27, 29, 36]. Such weight losses are attributed to the complete hydrolysis of alkoxides mixture as a result of the hydrothermal process at 200°C and are in accordance with the absence or presence of very little organic residue in the samples. Lower weight losses of AT2, AT3 and AT4 in comparison with AT1 (22%) are associated with the lower degree of crystallinity, due to the lower hydrothermal processing temperature of the latter sample, as demonstrated by broad bands in the IR spectra of the aforementioned sample. The presence of only 5% organic residue in AT4 can be attributed to the higher boiling point of 2-methoxyethanol (125°C) in comparison with 2-propanol (82.5°C) that leaves some alcohol in this sample after hydrothermal hydrolysis.

3-3-Powder X-ray Diffraction

Fig. 3 shows the PXRD patterns of all samples after calcination at 700, 1200 and 1400°C. As can be seen, after calcination at 700°C, all samples convert to the metastable, anatase and γ-alumina phases. By increasing the calcination temperature to 1200°C rutile, α–alumina and anatase phases in AT1 and tialite, rutile, anatase and α–alumina phases in AT3 and AT4 developed in contrast to AT2 which did not exhibit any changes.

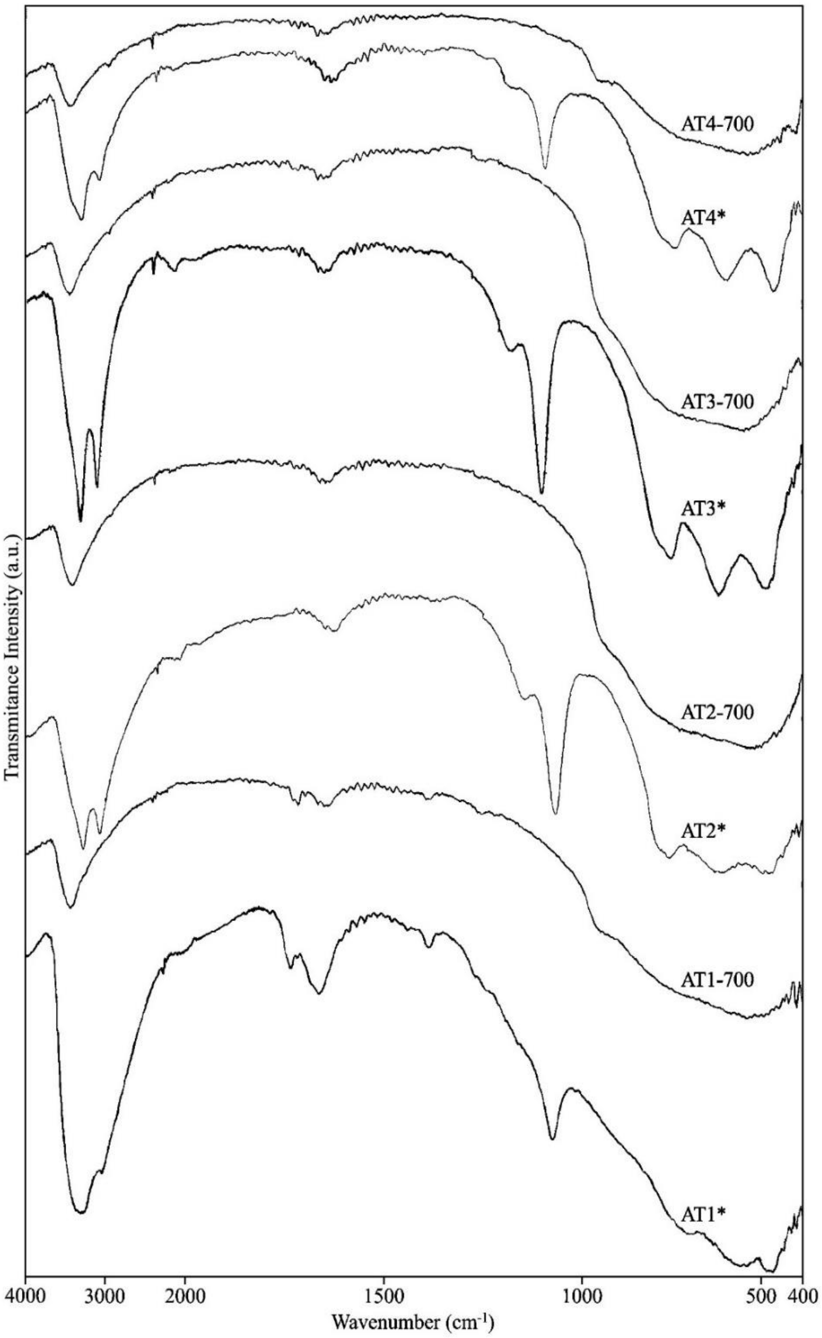

Fig. 1. FTIR spectra of AT1, AT2, AT3 and AT4 samples, as prepared (showed by *) and after calcination at 700°C.

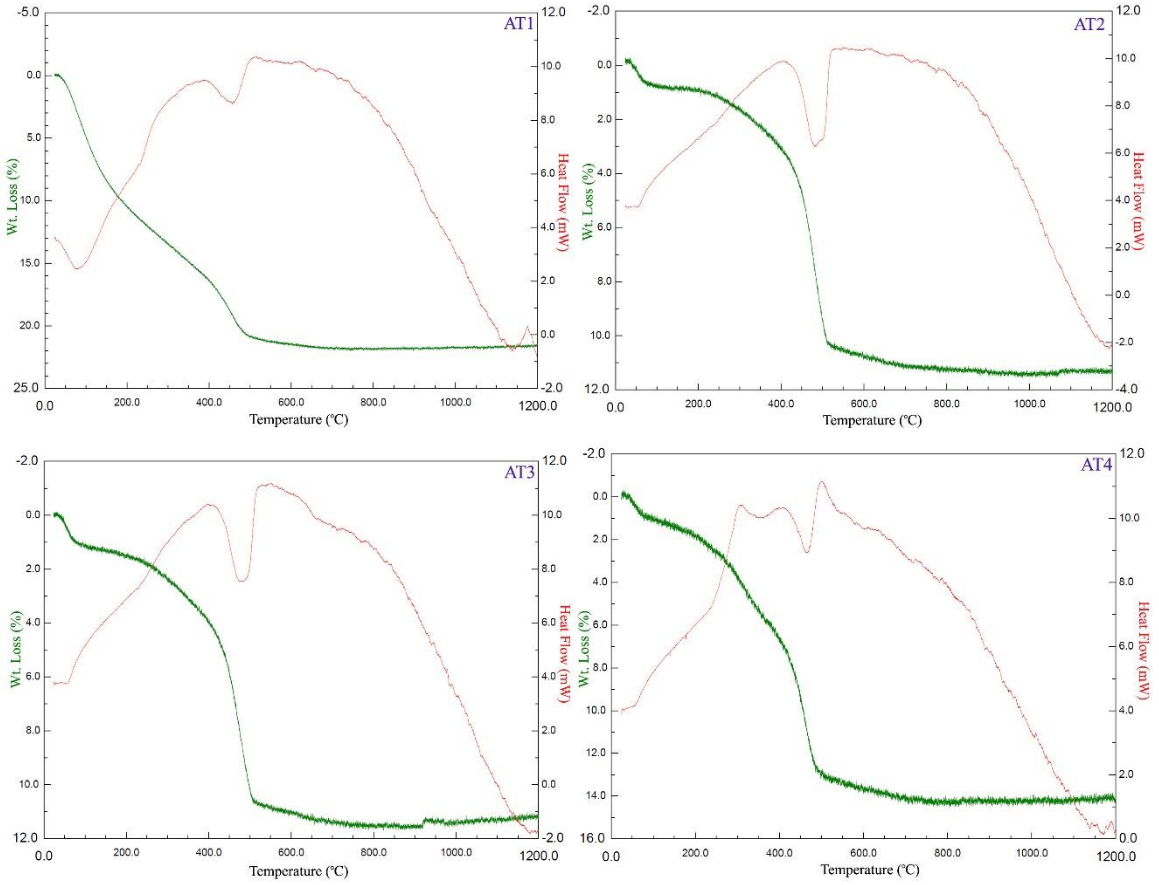

Fig. 2. TG/DSC thermograms of AT1, AT2, AT3 and AT4 samples.

Interestingly, by increasing the calcination temperature to 1400°C, AT1 converted to the single-phase Al_2TiO_5, AT2 converted to tialite and rutile phases and the amount of tialite phase in AT3 and AT4 increased to some extent and some rutile and α–alumina phases remained in the latter ones. PXRD results showed that when the solvent polarity increased in AT1 and AT2, by using a mixture of toluene and *iso*-propanol instead of pure toluene in AT3 and AT4, phase development retarded and after calcination at 1200°C, tialite phase was not seen in AT1 and AT2 (Table 2 and Fig. 3). Similar results were observed when aluminum and titanium 2-methoxyethoxide were used instead of aluminum and titanium *iso*-propoxide. This was evidenced by a shorter Al_2TiO_5 line intensity in the PXRD pattern of the AT4 sample after calcination at 1200°C in comparison with the AT3 sample. On the other hand, the positive effect of the solvent polarity increase was observed after the calcination of the samples at 1400°C. According to the Fig. 3 and Table 2, AT1 produced pure single-phase Al_2TiO_5 after calcination at 1400°C, and in AT2 with polar solvent only a small amount of rutile phase as impurity along with tialite phase was formed. increasing the solvent polarity the phase development in the AT1 and AT2 retarded, the process was completed more quickly in comparison with AT3. Moreover, there is only rutile phase as impurity in AT4 similar to AT2 after calcination at 1400°C.

On the contrary, in AT3 which was processed only in toluene as the solvent, alumina phase along with rutile and tialite phases was observed. Although this shows that by These observations show that the solvent polarity and the use of chelating ether-alcohols have significant effects on tialite phase development. This can be attributed to the interaction of diffusing water molecules with polar molecules of *iso*-propanol or with etheric-oxygen atoms of aluminum and titanium 2-methoxyethoxide in the hydrothermal processing conditions. Apparently, these interactions slow down the hydrolysis during the hydrothermal process and, therefore, the hydrolysis condition can be easily tuned and controlled.

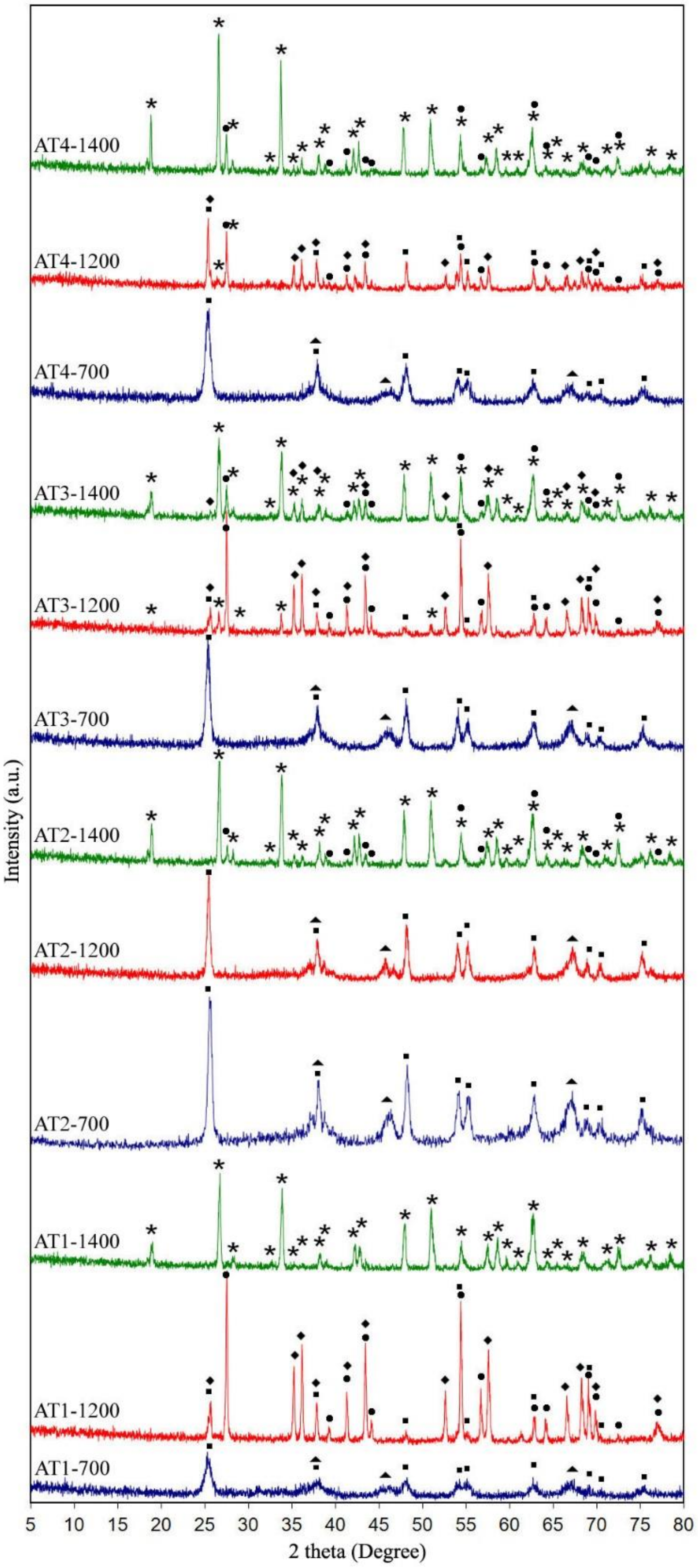

Fig. 3. PXRD patterns of AT1, AT2, AT3 and AT4 samples, after calcination at 700, 1200 and 1400°C. *-Al_2TiO_5 (05-0466), ●-TiO_2 (Rutile, 21-1276), ■- TiO_2 (Anatase, 01-0562), ▲-Al_2O_3 (01-1308) and ♦-Al_2O_3 (corundum, 42-1468).

Table 2. Phase development of various samples during heat treatment

Sample	Heat treatment	Phase development
AT1	As prepared	beginning of Boehmite crystallization + amorphous TiO_2[a]
	700°C	Anatase + γ-Alumina[b]
	1200°C	Rutile + Anatase + α-Alumina[b]
	1400°C	Al_2TiO_5[b]
AT2	As prepared	Boehmite + amorphous TiO_2[a]
	700°C	Anatase + γ-Alumina[b]
	1200°C	Anatase + γ-Alumina[b]
	1400°C	Rutile + Al_2TiO_5[b]
AT3	As prepared	Boehmite + amorphous TiO_2[a]
	700°C	Anatase + γ-Alumina[b]
	1200°C	Rutile + Anatase + α-Alumina + Al_2TiO_5[b]
	1400°C	Rutile + α-Alumina + Al_2TiO_5[b]
AT4	As prepared	Boehmite + amorphous TiO_2[a]
	700°C	Anatase + γ-Alumina[b]
	1200°C	Rutile + Anatase + α-Alumina + Al_2TiO_5[b]
	1400°C	Rutile + Al_2TiO_5[b]

a: according to IR data, b: according to PXRD data.

Another crucial factor which affects the development of tialite in the hydrothermal process is hydrothermal temperature. At lower temperatures, because of the lower water vapor pressure, hydrolysis step is slowed down. This phenomenon reinforces the effect of the solvent polarity and produces single-phase tialite without any phase impurity, especially in the sample AT1, after calcination at 1400°C. This observation can be attributed to the slower hydrothermal hydrolysis process because of the use of both more polar solvent and lower hydrothermal temperature. This was confirmed by the lower crystallinity of boehmite in AT1 and also resulted in narrower distribution of alumina and titania particles and hence the formation of single phase tialite.

4-Conclusion

It was shown that during the course of hydrothermal hydrolysis of a mixture of aluminum and titanium alkoxides, phase separation occurs but at lower hydrothermal processing temperature and the use of the polar solvents a more uniform gel is produced which can result in the production of single-phase tialite. This was attributed to tialite which decomposes to its components over 750°C and is recrystallized over 1000°C. Furthermore, this work demonstrated that the hydrothermally-assisted sol-gel processing can be a novel route for the fabrication of Al_2TiO_5 because of its unique conditions and the hydrolysis step can be easily controlled and slows down the hydrolysis step in the sol-gel process.

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