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BRIEF COMMUNICATION

FTIR as a Tool to Study High-Temperature Phase Formation in Sol–Gel Aluminium Titanate

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A FTIR spectrum is used to study the formation characteristics of aluminium titanate precursor gel under the influence of temperature. From an analysis of the spectra of the gel heated at different temperatures in the 30–1400°C range, it is found that both octahedral and tetrahedral Al–O coordinations are present up to 800°C. At temperatures above 800°C, the tetrahedral Al–O coordination decreases and becomes negligible at 1050°C. α-alumina and rutile phases are formed at 1000°C and the aluminium titanate phase is formed at 1300°C. The Al–O coordination in aluminium titanate is found to be octahedral. © 1997 Academic Press

INTRODUCTION

Aluminium titanate has been identified as an important high-temperature ceramic in view of its low thermal expansion coefficient, low thermal conduction, excellent thermal shock resistance, and high melting point (1, 2). It is usually prepared by the reaction sintering of stoichiometric mixtures of alumina and titania above 1400°C (3). Sol–gel techniques with different preparative conditions are also employed to synthesize this ceramic because of the possibility of formation of this high-temperature phase at temperatures lower than 1400°C (4). In this procedure the aluminium titanate phase is generated by the heat treatment of precursors derived either by the cohydrolysis of alkoxides of aluminium and titanium or by the hydrolysis of titanium alkoxide in the presence of aluminium nitrate or boehmite (5). To identify the transformations in the sol precursor during the evolution of the final product, different techniques become necessary. The XRD method has limitation in the early stages of precursor decomposition due to its amorphous nature and the nanosize particles. In view of the fact that particle size and state of aggregation are shown to have a strong effect on the IR spectra, a FTIR study is performed to understand the formation characteristics of aluminium titanate using this technique (6).

EXPERIMENTAL

Aluminium nitrate $(Al_2NO_3)_3 \cdot 9H_2O$ (Glaxo India Ltd.), as alumina source and titanium isopropoxide (Aldrich Chemicals, UK) as titania source were used as starting materials. Boehmite (AlOOH) was prepared following the procedure reported earlier (7) by controlled hydrolysis of aluminium nitrate. The titanium isopropoxide (23.64 g) was stabilized with glacial acetic acid (35 ml) and mixed with 268.94 g boehmite sol (100 ml sol contained 3.68 g Al_2O_3) in an ice bath, keeping the temperature less than 10°C. The clear solution was allowed to gel at 30°C for 24 hr. The gel thus obtained was heat treated at the temperatures 250, 400, 800, 1100, 1300, and 1400°C.

FTIR spectra of aluminium titanate precursor gel (Fig. 1) and the heat treated ones at different temperatures were obtained (Fig. 2) on a Nicolet FTIR spectrometer with the samples as KBr pellets. A Bio-Rad FTS 40 FTIR spectrometer with the sample in polyethylene was used to get the far-IR spectra (Fig. 3). The observed spectral frequencies are given in Table 1. The XRD pattern (Fig. 4) of the precursor gel heated over the temperature range up to 1350°C was recorded in a Rigaku, Japan, spectrometer with a Cu$K\alpha$ radiation source.

RESULTS AND DISCUSSION

Water and OH Vibrations

To identify the changes taking place within the gel under the influence of temperature, it is important to take into consideration the spectral ranges (i) 3000–3500 cm^{-1} where the OH stretching vibrations of water and OH groups appear and (ii) 200–850 cm^{-1} where the Al–O and Ti–O stretching and bending vibrations occur.

In the FTIR spectrum of the gel, a very broad band appears above 3000 cm^{-1} with peaks at 3142 and 3452 cm^{-1}. The band at 3452 cm^{-1} is assigned to the

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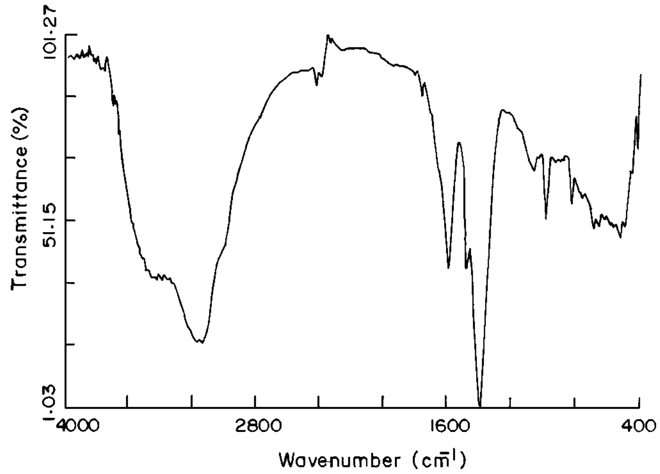

FIG. 1. FTIR spectra (400–4000 cm^{-1}) of aluminium titinate precursor gel (65°C).

stretching modes of adsorbed water. The medium intense band at 1581 cm^{-1} is assigned to its bending mode. The OH stretching mode of the hydroxyl group is mainly responsible for the intense band at 3142 cm^{-1}. The corresponding bending mode appeared as a medium intense band at 1061 cm^{-1}. The intensity of these bands decreases gradually with increase in temperature and disappears around 800°C. The spectra thus give evidence for the dehydration and dehydroxylation of the sample during heat treatment.

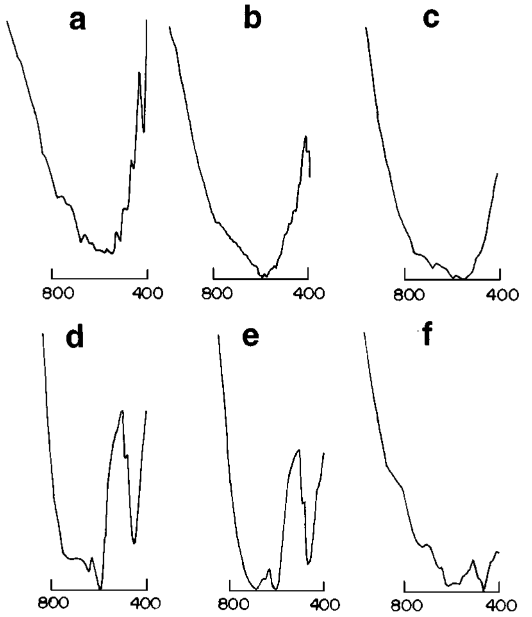

FIG. 2. FTIR spectra (400–1000 cm^{-1}) of aluminium titanate precuror gel heated at the temperature (a) 250, (b) 400, (c) 800, (d) 1100, (e) 1300, and (f) 1400°C.

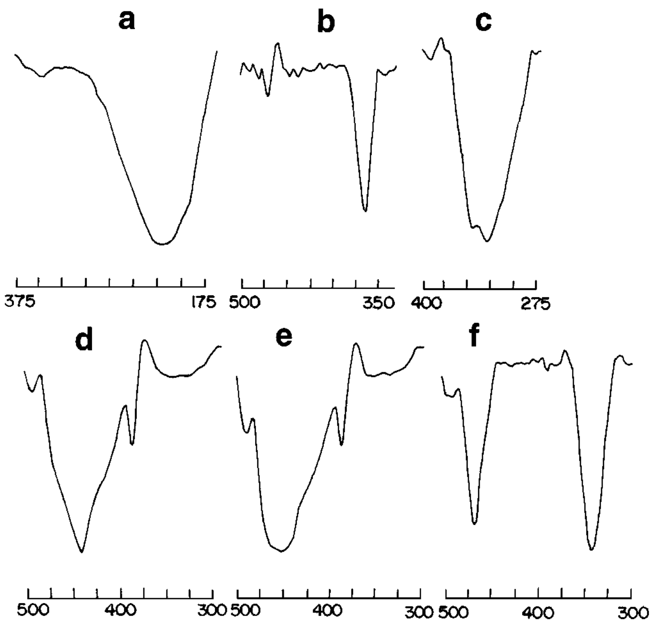

FIG. 3. Far-IR spectra of aluminium titanate precursor gel at the temperatures (a) 65, (b) 400, (c) 800, (d) 1100, (e) 1300, and (f) 1400°C.

Al–O Stretching and Bending Vibrations

The structural evolution taking place within the gel during heat treatment can be understood by studying metal–oxygen coordination. An octahedral Al–O coordination gives Al–O stretching modes in the region 500–750 cm^{-1} and bending modes in the region 330–450 cm^{-1} (8–10). However, a tetrahedral coordination is expected to give the Al–O stretching modes in the narrow region 750–850 cm^{-1} and bending modes between 250 and 300 cm^{-1} (8–10). In the system under consideration, although the vibrational frequencies of Al–O overlap with those of Ti–O, certain conclusions can be made from the spectra as the IR active Ti–O stretching modes appear below 730 cm^{-1} (6, 11). Hence, frequencies appearing above 750 cm^{-1} can only be due to Al–O stretching modes with tetrahedral coordination.

The IR bands of the gel (Fig. 1) at 513 and 681 cm^{-1} are assigned to Al–O (octahedral) and Ti–O stretching vibrations and the weak band at 829 cm^{-1} to Al–O (tetrahedral) stretching vibrations. At 250°C a very broad band extending from 480 to 820 cm^{-1} indicate the presence of tetrahedral Al–O coordination. This status continues up to 800°C (Fig. 2). In the temperature range 800 to 1050°C, the changes in the 400–900 cm^{-1} region of the FTIR spectrum is only marginal. However, at 1100°C this region splits into two groups, one with a sharp peak at 441 cm^{-1} along with a shoulder at 491 cm^{-1} and the other with peaks at 583, 639, and 730 cm^{-1} (Fig. 2). In the bending mode region, three bands at 332 (broad), 382, and 441 (s) cm^{-1} have been observed. The absence of bands in the 750–850 cm^{-1} and

TABLE 1
Observed Frequencies (cm^{-1}) of Aluminium Titanate Precursor Gel Heat Treated at Different Temperatures

65°C	250°C	400°C	800°C	1100°C	1300°C	1400°C	Assignment
3430 sh	3431 sbr	3431 wbr					ν-H_2O
3142 vs		3220 m	3227 w				ν-OH
1581 m	1574 m	1585 w					δ-H_2O
1476 sh	1462 sh						δ-CH_2
1384 vs^a	1384 s	1392					
1061 m	1075 w	1068 sh	1082 sh				δ-OH
984 m							
829 w	820	840	840			843 sh	δAl–O(t)
681 mbr	to vsbr	to vsbr	to vsbr	730	681	723	νAl–O(o)
	480	480	480	639 vs br	646 sh	653 vs br	&
513 sbr				583	597		νTi–O
				491	490		
				441	452	466	δAl–O(o)
345	364		387 w	384	385	384 vw	&
	318		341 s	332 br	330	341	δTi–O
			261 s			259 vw	δAl–O(t)
214							

Note. ν, stretching; δ, bending; sh, shoulder; (t), tetrahedral; (o), octahedral; br, broad; s, strong; vs, very strong.

[a] CH_2 vibration of residual acetic acid and isopropoxide used for the preparation of the gel.

250–320 cm^{-1} regions and the observation of an intense band at 441 cm^{-1} clearly indicate the absence of tetrahedral Al–O coordination. The splitting of the stretching mode region into two groups (12) and the α-alumina are in accordance with the results of FTIR spectrum. Further heating to 1300°C gives indication of the formation of the aluminium titanate phase (Fig. 4). At 1350°C, the formation seems to be complete. The XRD pattern of the gel heated to above 1400°C does not indicate any decomposition characteristics probably since it is insignificantly small for detection by XRD.

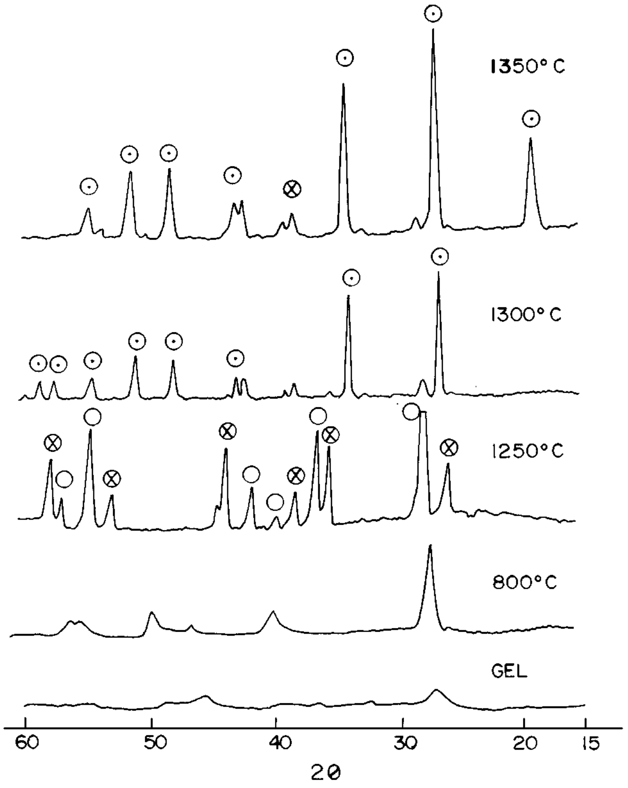

FIG. 4. XRD patterns of aluminium titanate precursor gel calcined at different temperatures. ⊗, α-alumina; ⊙, aluminium titanate; O, rutile.

CONCLUSIONS

1. Both octahedral and tetrahedral Al–O coordinations are present in aluminium titanate gel up to 800°C. Above 800°C, the tetrahedral Al–O coordination decreases and becomes negligible at 1050°C. At 1100°C the Al–O coordination becomes completely octahedral consequent to the formation of α-alumina and rutile.
2. The aluminium titanate phase is formed at 1300°C with complete octahedral Al–O coordination.

FTIR is thus a useful tool to follow the structural changes taking place in the precursor gel.

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