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Thermal decomposition of (Sr, Ti) organic precursors during the Pechini process

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The evolution of (Sr, Ti) resin intermediates from the solutions during the Pechini process, and their pyrolysis to $SrTiO_3$ were investigated using differential thermal analysis, thermogravimetric analysis, infrared spectroscopy, and X-ray diffraction techniques. In order to understand the Pechini process better, the organic solutions containing either only titanium ions or no metal ions were also prepared and thermally polymerized so that their decomposition processes could be examined in the same manner. In the case of the initial (Sr, Ti) organic solutions, all organic acid groups were bonded mainly either with ethylene glycol forming esters, or with Sr/Ti ions forming unidentate complexes. With heat treatment, the nature of the bonding between carboxylate groups and Sr/Ti ions changed: unidentate → bridging → ionic. Carbonate species were detected at 530° C using infrared spectra. Their concentration was reduced as $SrTiO_3$ formed. On the basis of powder X-ray diffraction data, it is doubtful that $SrCO_3$ and TiO_2 were formed as distinct intermediate phases. Possibly, a carboxylate complex ($Sr_2Ti_2O_5CO_3$) was formed prior to the formation of $SrTiO_3$.

1. Introduction

Conventional ceramic powder preparation processes usually involve a mixed-oxide process which first requires mixing the oxides and/or carbonates using ball-milling and then calcining the resulting mixture at an appropriate temperature. Such processes have well-recognized disadvantages such as inhomogeneous mixing, impurities which are introduced during milling, and incomplete carbonate burn-out during calcination.

There have been many studies whose goal is developing new processing methods which avoid the problems which arise using the conventional ceramic techniques. The Pechini method (also called "liquid-mix" or "resin intermediate" method) is one of the powder preparation techniques that have been developed to address such problems. This method was first developed by Pechini [1] in 1967, and many ceramic compounds have been synthesized successfully using this process [2–4]. The original patent for the process [1] indicates that certain alpha-hydroxycarboxylic acids (for example, citric, lactic and glycolic acids) form polybasic acid chelates with titanium, zirconium, and niobium ions. These chelated products can undergo polyesterification when they are heated with a polyhydroxy alcohol. The study also claimed that the decomposition of the resin intermediate (for example, a barium titanium resin) does not proceed through the formation of $BaCO_3$–TiO_2 mixture, but rather through a basic carbonate which then decomposes to $BaTiO_3$.

Hennings and Mayr [5] investigated a similar process which involved thermal decomposition of (Ba, Ti) citrate. They detected the presence of $BaCO_3$ from their X-ray diffraction patterns, and concluded that $BaCO_3$ and TiO_2 were present as intermediate compounds during the pyrolysis of (BaTi) citrate. They mentioned that the polyester resin prepared during the Pechini method also showed similar behaviour. However, no experimental data were given for the decomposition of the Pechini polyester resin.

Studies involving thermal decomposition of barium titanyl oxalate have shown contradictory results. Gallagher and Thomson [6] proposed that highly reactive $BaCO_3$ and TiO_2 were formed prior to the formation of $BaTiO_3$. In contrast, Gopalakrishnamurthy *et al.* [7] denied the appearance of $BaCO_3$ and TiO_2 as intermediate phases, and suggested that a carbonate complex ($Ba_2Ti_2O_5CO_3$) formed as a final intermediate phase.

The objective of the present study was to clarify the nature of the structural species that are generated upon the evolution of the (Sr, Ti) resin intermediate from the solution during the Pechini process, and its pyrolysis to $SrTiO_3$.

2. Experimental procedure

(Sr, Ti) organic solutions were prepared using tetraisopropyl orthotitanate (TPT) (Kodak, Rochester, New York), reagent grade strontium carbonate (Baker Chemical, Philipsburg, New Jersey), ethylene glycol (Fisher Scientific, Fair Lawn, New Jersey), and citric acid anhydrous (Fisher Scientific, Fair Lawn, New Jersey). The modified Pechini process that was described earlier by Chan *et al.* [2] was employed to prepare the solutions. In order to prepare appropriate solutions, the following procedure was applied. 150 ml of TPT was added with stirring to 1.5 l ethylene glycol, and then 300 g citric acid was added to this solution. The resulting solution was stirred with

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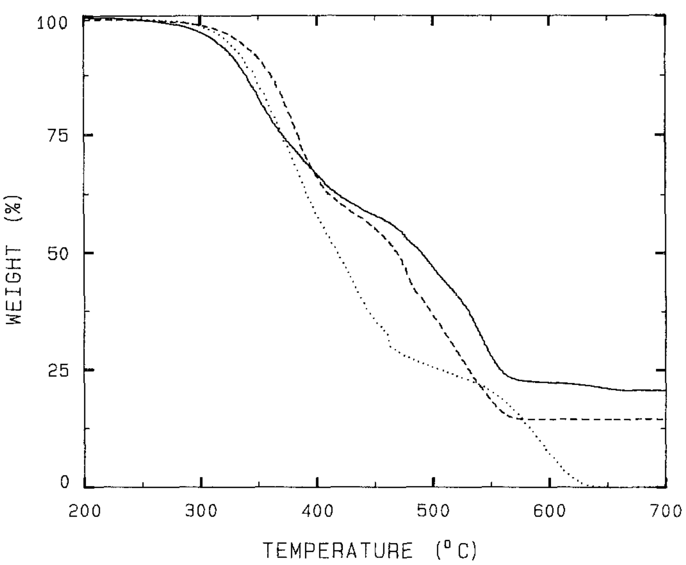

Figure 1 TGA of resin intermediates: (——) (Sr, Ti) organic precursor, (– – –) Ti-organic precursor, and (····) pure organic resin.

heating until complete dissolution occurred, and then heated further until the strong odour of isopropyl alcohol disappeared. The titanium contents of the solutions were determined gravimetrically using thermally polymerized weighed batches of the solutions that were calcined to TiO_2. (Sr, Ti) organic solutions were prepared by dissolving strontium carbonate powder in the titanium containing solutions with heating and stirring so that their molar Sr/Ti ratios were unity. These solutions were evaporated in an oven at 250° C for 12 h to form the resin intermediates for $SrTiO_3$, which were ground to coarse particles using an agate mortar and pestle. Organic solutions containing only titanium were prepared in the same manner except that strontium carbonate was excluded from the solutions. These solutions were also thermally polymerized to form resins under the same conditions described previously. Pure organic solutions which did not contain any metallic ions were also prepared, but the ratio of organic components was the same as in the other solutions. Thermal polymerization of these solutions were performed in the oven at 250° C for 24 h, because the resins were too viscous to grind when they were evaporated for 12 h similar to the other two solutions. Hereafter, the resulting resin intermediates will be referred to as the (Sr, Ti) organic precursor, and the pure organic resin.

The three different starting solutions were investigated using a Fourier transform infrared (FTIR) spectrometer (Nicolet 60SXR, Nicolet Analytical Institute, Burlington, Massachusetts) using KBr pellets. Thermal decompositions of the (Sr, Ti) organic precursor, the Ti-organic precursor, and the pure organic resin were examined using thermogravimetric analysis (TGA) (Cahn TG716, Cahn Institute, Cerritos, California), differential thermal analysis (DTA) (Immersion type, Harrop Industry, Columbus, Ohio), FTIR spectroscopy and X-ray diffraction (XRD) analysis (Norelco., Phillips Electronic Institute, Mount Vernon, New York). TGA and DTA of the resin intermediates were performed at a heating rate of $5° C min^{-1}$ in flowing air. In order to investigate the chemistry of the thermal decomposition of those resins, the residues of decomposition at various temperatures were withdrawn from the TGA apparatus and examined using both FTIR spectroscopy and X-ray diffraction analysis (Cu*K*α target). The samples for the infrared spectral analysis were prepared by mixing them with KBr powder and then pelletizing as thin discs.

3. Results

The TGA and DTA curves for the (Sr, Ti) organic precursor, the Ti-organic precursor, and the pure organic resin are illustrated in Figs 1 and 2, respectively. Although the three different resins showed many similarities in thermal behaviour, the (Sr, Ti) precursor had more complicated decomposition steps. Decompositions of the (Sr, Ti) organic precursor, the Ti-organic precursor, and the pure organic resin were completed at 670, 575 and 640° C, respectively for a heating rate of $5° C min^{-1}$ in flowing air.

The infrared spectra of the (Sr, Ti) organic solution and its intermediate resins are illustrated in Fig. 3. Two strong absorption bands related to carboxylate group stretching modes were observed at 1735 and $1645 cm^{-1}$ for the (Sr, Ti) solution. Because the band at $1735 cm^{-1}$ was also observed for the Ti-organic solution (see Fig. 4a) and for the pure organic solution (see Fig. 5a), this band can be assigned to the C = O stretching mode for the ester which was formed by esterification of citric acid with ethylene glycol. The band at $1645 cm^{-1}$ for the (Sr, Ti) solution which was observed at $1650 cm^{-1}$ for the titanium solution and was not observed for the pure organic solution can be assigned to antisymmetric COO^- stretching mode for a unidentate complex [8, 9]. Because no band was observed at $1728 cm^{-1}$ for protonated COOH groups, all organic acid groups in the (Sr, Ti) organic solution were considered to be bonded either with ethylene glycol forming esters, or with Sr/Ti ions forming unidentate complexes. The other infrared bands that were observed at 1700 to $750 cm^{-1}$ were nearly identical for the three different solutions and were attributed to the organic network or the COH groups [10]. Some additional bands were observed in the 700 to $550 cm^{-1}$ region for the (Sr, Ti) solution. Modes associated with Ti–O stretching vibrations may be found in this region.

The (Sr, Ti) organic precursor that was prepared by

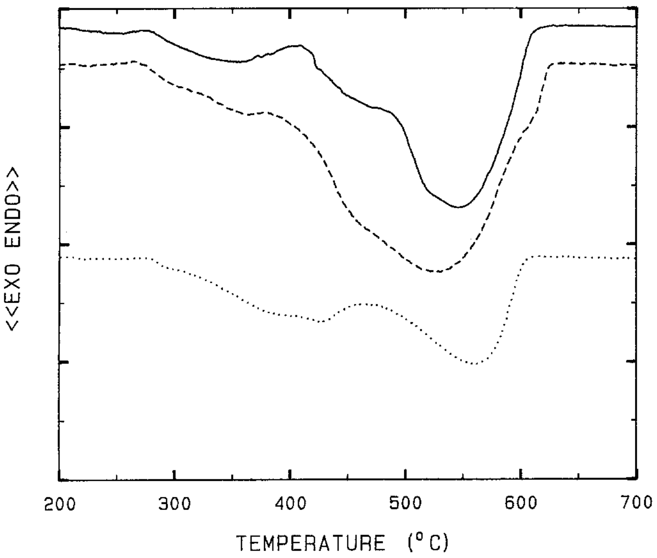

Figure 2 DTA of resin intermediates: (——) (Sr, Ti) organic precursor, (– – –) Ti-organic precursor, and (· · · ·) pure organic resin.

evaporating the solution at 250° C for 12 h possessed an additional band at 1580 cm^{-1} along with the band for the ester at 1735 cm^{-1} and the band for the unidentate complex at 1630 cm^{-1}. This band can be assigned to the antisymmetric COO$^-$ stretching mode for a bridging complex [8, 9]. Further heat treatment led to an intensity increase for the band at 1580 cm^{-1} and an intensity decrease of the band at 1630 cm^{-1} (see Fig. 3c). The decomposition product formed at 400° C showed significant changes in its infrared spectra (see Fig. 3d). Intensity of the band for esters at 1735 cm^{-1} was reduced dramatically, and the stretching modes for unidentate and bridging complexes disappeared. New bands were observed at 1560 and 1410 cm^{-1} which are typical of antisymmetrical and symmetrical stretching vibrations for carboxylate ions [5, 9]. These changes in the infrared spectra suggested that most of the polyester chains were broken and that the metal ions and carboxylate groups formed ionic bonds involving bidentate complexes at this stage of pyrolysis. The bands related to the hydrocarbon skeleton and the COH groups were also reduced significantly. Only a trace of the band for the ester remained at 450° C (see Fig. 3e), and a new weak band was observed at 1700 cm^{-1} which as also observed both for the residue of Ti-organic precursor withdrawn at 500° C (see

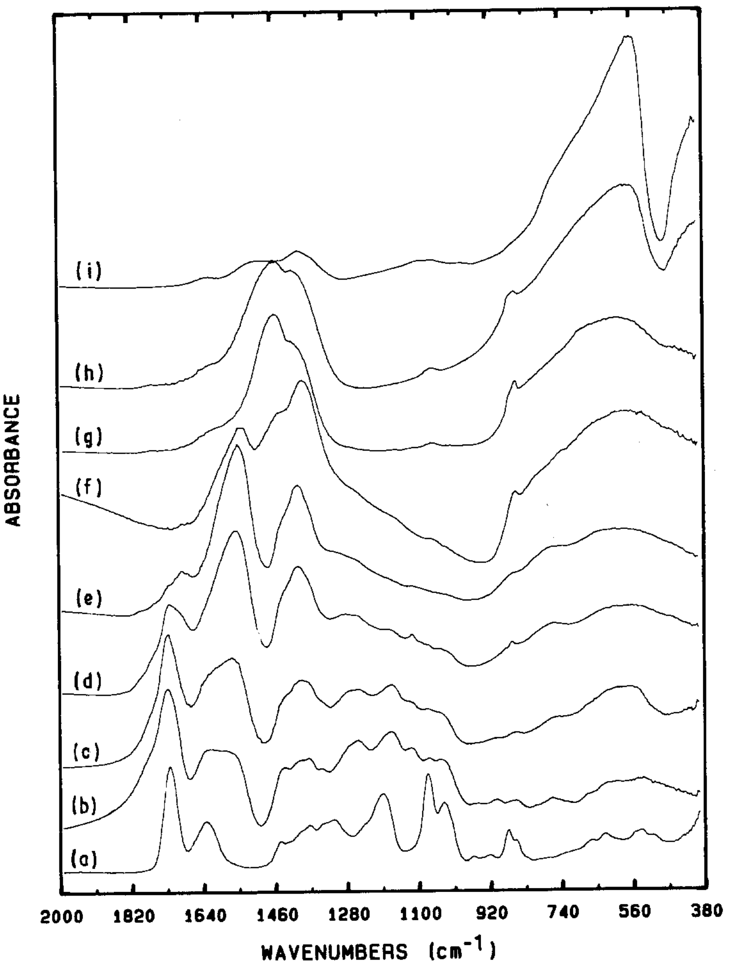

Figure 3 Infrared spectra of (Sr, Ti) organic solution and resin intermediates: (a) solution, (b) resin intermediate evaporated at 250° C for 12 h, (c) to (i) decomposition product at (c) 350° C, (d) 400° C, (e) 450° C, (f) 530° C, (g) 575° C, and (h) 630° C (i) 700° C.

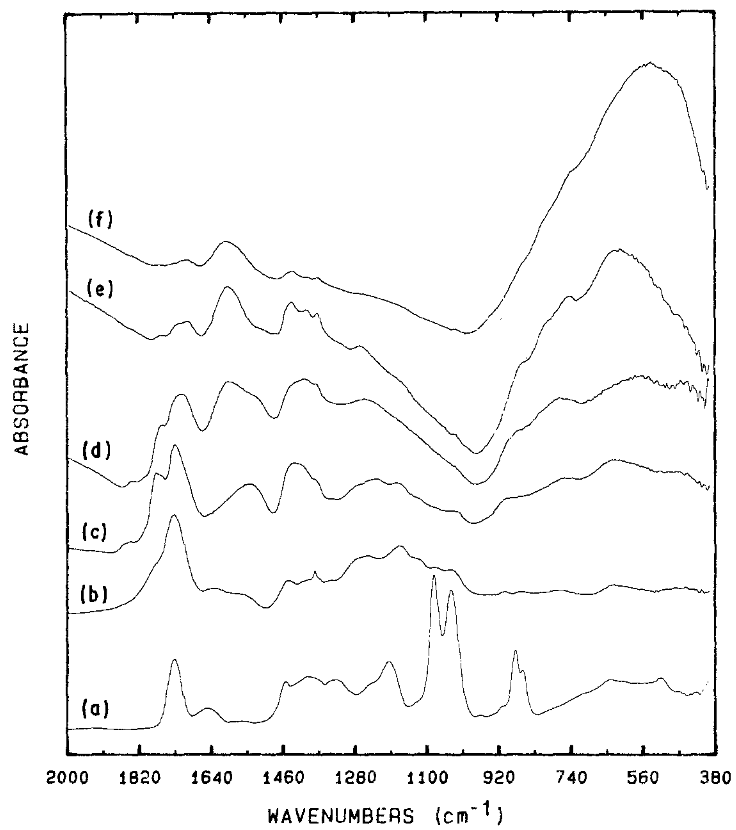

Figure 4 Infrared spectra of Ti-organic solution and resin intermediates: (a) solution, (b) resin intermediate evaporated at 250° C for 12 h, (c) to (f) decomposition product at (c) 400° C, (d) 450° C, (e) 500° C, and (f) 530° C.

Fig. 4e) and for the residue of the pure organic resin withdrawn at 550° C (see Fig. 5e). This new band, therefore, appears to be related to a decomposition product of citric acid (possibly, itaconic acid) which possesses a strong band at 1700 cm^{-1} [11]. All bands associated with the hydrocarbon skeleton and COH groups were not observed at this temperature. The intensity of the band at 1560 cm^{-1} was reduced and new bands were observed at 1452 and 862 cm^{-1}, while the band at 1700 cm^{-1} has almost disappeared at 530° C (see Fig. 3f). The two new bands at 1452 and 862 cm^{-1} can be assigned to carbonate ions [4, 5, 12]. The bands attributed to carbonate ions at 1460, 1068 and 860 cm^{-1} were very clear upon heat treatment at 575° C, while stretching vibrations of ionic complex in the 1560 to 1550 cm^{-1} and 1410 to 1400 cm^{-1} regions disappeared completely (see Fig. 3g). A band corresponding to the Ti–O stretching mode for $SrTiO_3$ was observed at ~ 580 cm^{-1} upon heat treatment at 630° C, while the infrared bands for the carbonate ions were reduced slightly (see Fig. 3h). The XRD patterns for the decomposed product at this temperature showed $SrTiO_3$ peaks clearly (see Fig. 6c). The infrared band for $SrTiO_3$ was intense after heat treatment at 700° C (see Fig. 3i). No X-ray diffraction peaks were observed at this temperature in the XRD pattern except those for $SrTiO_3$ (see Fig. 6d).

The infrared spectra for the Ti-organic precursor illustrated in Fig. 4 possessed characteristics intermediate to those of the (Sr, Ti) organic precursor and the pure organic resins. Because the mole fraction of metal ions present in the titanium-resin was half of that in the (Sr, Ti) resin, significantly more pure organic species were present in the titanium-resin, and hence, its infrared spectra had bands observed for both the (Sr, Ti) resin and the pure organic resin. The bands corresponding to the unidentate and the bridging complexes were observed at 1635 and 1565 cm^{-1} respectively (see Fig. 4b). Upon heat treatment at 400 and 450° C (see Figs 4c and d), the stretching modes for the ionic bidentate complex were observed along with two new bands that can be assigned to the C = O stretching modes for the acid anhydride which were observed at 1845 and 1780 cm^{-1} [11]. These latter bands were not present for the (Sr, Ti) resin, but were present for the pure resin upon treatment at 460, 500 and 550° C (see Figs 5c to e). A strong band was observed at ~ 1600 cm^{-1} upon heat treatment at 450° C which remained throughout the pyrolysis process. The same band, which was not observed for the (Sr, Ti) resin, was observed for the pure organic resin upon treatment at temperatures higher than 460° C (see Fig. 5). Therefore, this band is probably related to a decomposed product from the pure organic resin. A band observed at ~ 540 cm^{-1} for the decomposed product formed at 530° C can be assigned to a Ti–O stretching mode for TiO_2 (anatase). The presence of anatase can be detected using the related XRD pattern (see Fig. 7a). No infrared bands for carbonate ions were observed in the spectra of any of the heat-treated titanium resins. One characteristic in the infrared spectra of the heat-treated pure organic resins was the presence of the band for an ester group at ~ 1735 cm^{-1} in the decomposition process (see Fig. 5). No attempt was made to identify specifically the nature of various bands found for the heat-treated pure organic resins, because that was beyond the intent of this study.

4. Discussion

One of the major concerns in this study was whether $SrCO_3$ and TiO_2 were distinct intermediate phases

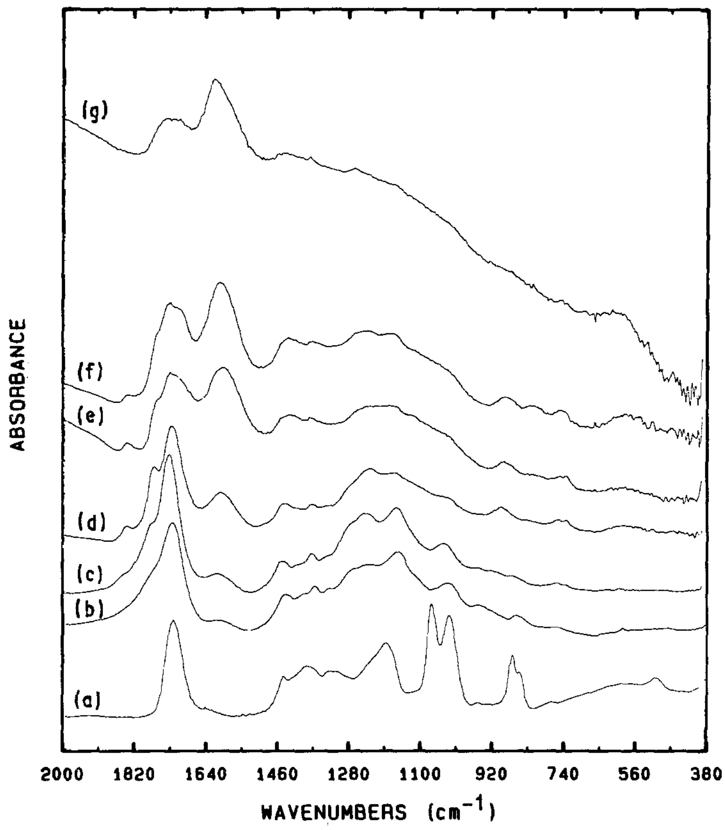

Figure 5 Infrared spectra of pure organic solution and resin intermediates: (a) solution, (b) resin intermediate evaporated at 250° C for 24 h, (c) to (f) decomposition product at (c) 460° C, (d) 500° C, (e) 550° C, (f) 600° C and (g) 700° C.

formed prior to the formation of $SrTiO_3$ during the decomposition of the (Sr, Ti) organic precursor. It is clear from the observed infrared spectra that a carbonate species was formed as an intermediate phase, but this species could be either crystalline $SrCO_3$ or a basic carbonate as claimed in the original patent [1]. The XRD pattern indicated a barely identifiable peak for $SrCO_3$ in the decomposition product formed at 575° C. However, this peak was too weak to determine $SrCO_3$ as a distinct intermediate phase due to the following reasons.

(i) If $SrCO_3$ was formed as an intermediate compound, TiO_2 (anatase) would be expected to be present at the same time. Because the major XRD locations for $SrCO_3$ (1 1 1) and TiO_2 (anatase) (1 0 1) planes are very close ($\Delta 2\theta$ is 0.11°), peak overlap is expected. Therefore, a reasonably intense peak as shown in the XRD pattern for the Ti-organic precursor formed at 575° C (see Fig. 7b) would be expected, if $SrCO_3$ and TiO_2 were formed as intermediate compounds.

(ii) The infrared band for the Ti–O stretching mode of anatase was not detected in the infrared spectra for the heated (Sr, Ti) organic resins. Therefore, it seems doubtful that $SrCO_3$ and TiO_2 were formed as distinct intermediate phases prior to the formation of $SrTiO_3$.

In order to clarify the nature of the carbonate species generated during the pyrolysis of the (Sr, Ti) organic precursor, the TGA results were examined carefully. It was impossible to investigate the route of pyrolysis from the starting resin, but we could examine the final

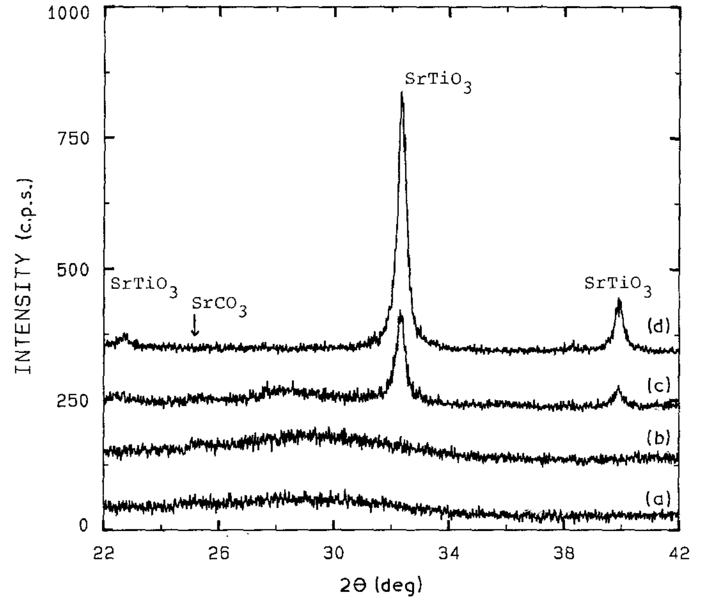

Figure 6 XRD patterns of (Sr, Ti) resin intermediates: (a) to (d) decomposition product at 530° C, (b) 575° C, (c) 630° C, and (d) 700° C.

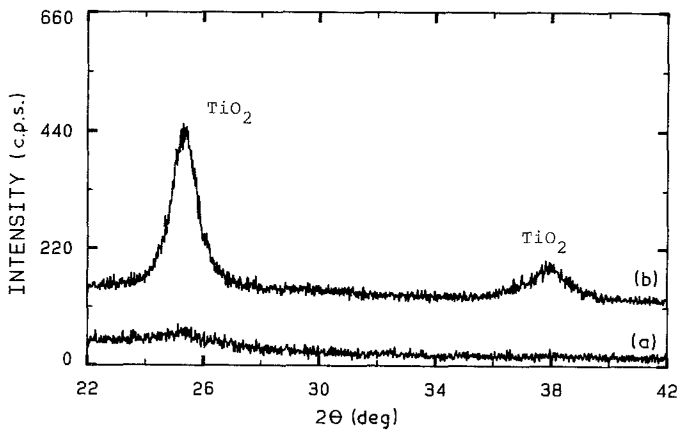

Figure 7 XRD patterns of titanium-resin intermediates: decomposition product at (a) 530° C and (b) 575° C.

decomposition step which started at 565° C and ended at about 680° C, as shown in Fig. 1. The weight of the decomposition product was 7.540 mg at 680° C, and 8.610 mg at 565° C. Because no further weight loss was detected higher than 680° C, 7.540 mg was the weight of $SrTiO_3$ that was produced. When the intermediate species were assumed to be $SrCO_3$ and TiO_2, the expected weight at 565° C is 9.348 mg which is significantly heavier than the observed value. Next, the possibility of a carbonate complex ($Sr_2Ti_2O_5CO_3$), which is analogous to $Ba_2Ti_2O_5CO_3$ that was suggested as an intermediate carbonate complex in the pyrolysis of barium titanyl oxalate by Gopalakrishnamurthy *et al.* [7], was examined. The calculated weight for this carbonate complex is 8.444 mg, which is very close to the observed value (8.610 mg). There was a unidentified broad peak near $2\theta = 28.5°$ in the XRD pattern for the sample formed at 630° C (see Fig. 6c). Because this peak was not observed for the titanium-intermediate precursors, it might be assignable to an intermediate $Sr_2Ti_2O_5CO_3$ phase. Eror *et al.* [13] found that carbonates were formed on the surface of $BaTiO_3$ prepared by the Pechini method below 700° C due to the presence of the high-temperature hexagonal $BaTiO_3$ phase. However, they also observed that the formation of surface carbonate was not possible for $SrTiO_3$ [14]. They obtained carbonate-free $SrTiO_3$ above 497° C which is lower than the temperature at which carbonate was detected in this study. Probably, this difference occurred because the pyrolysis process employed in this study was quite fast (5° C min^{-1}) with no holding time. Therefore, $SrCO_3$ detected below 700° C in this study would not be surface carbonate, rather a $SrCO_3$-containing phase which was formed locally due to nonstoichiometry or inhomogeneity.

The thermal decomposition process for (Sr, Ti) organic precursor can be explained on the basis of the infrared spectra and TGA results.

1. Room temperature to 250° C. With the heat treatment in this temperature range, the bonding nature betweeen carboxylate groups and Sr/Ti ions from unidentate to bridging complexes. Both unidentate and bridging complexes coexisted at 250° C.

2. 250 to 450° C. All ethylene glycol/citric acid polyester chains were broken in this temperature range, and many of the organic species involving the hydrocarbon skeleton were eliminated. Approximately half the total weight loss of the starting resin during pyrolysis occurred in this temperature range. All organic acid complexes converted to bidentate ionic complexes.

3. 450 to 530° C. Organics were further decomposed and the bidendate complexes started to decompose. Carbonate species were formed near 530° C. A very broad peak was observed near $2\theta = 30°$ in the XRD pattern.

4. 530 to 565° C. All bidentate complexes were decomposed, and the bands for the carbonate species were predominant in the infrared spectra. The carbonate complex at the end of this temperature range was presumably $Sr_2Ti_2O_5CO_3$. A very weak X-ray peak that is assignable to $SrCO_3$ was detected, and a broad X-ray peak was found near $2\theta = 29°$ in the XRD pattern (see Fig. 6b). A significant weight loss was observed in the TGA curve.

5. 565 to 680° C. The intermediate carbonate complex (presumably $Sr_2Ti_2O_5CO_3$) decomposed to $SrTiO_3$. X-ray peaks for $SrTiO_3$ together with an unidentified broad X-ray peak (at $\sim 2\theta = 28.5°$) which was possibly assignable to $Sr_2Ti_2O_5CO_3$ were observed in the XRD pattern. Very little weight loss was detected at this temperature range.

5. Conclusions

The organic acid groups in the (Sr, Ti) organic solutions prepared during the Pechini process were bonded either with ethylene glycol forming esters or with Sr/Ti ions forming unidentate complexes. Upon heat treatment, the bonding nature between the carboxylate groups and the Sr/Ti ions changed: unidentate → bridging → ionic. Carbonate species were detected at 530° C and their concentration reduced as $SrTiO_3$ formed. It is doubtful that crystalline $SrCO_3$ and TiO_2 were formed as distinct intermediate phases. Possibly, a carbonate complex (presumably $Sr_2Ti_2O_5CO_3$) formed prior to the formation of $SrTiO_3$.

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