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SOL–GEL PROCESSED $BaTiO_3$: STRUCTURAL EVOLUTION FROM THE GEL TO THE CRYSTALLINE POWDER

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An amorphous solid, precursor to $BaTiO_3$, has been prepared by the sol–gel route and its structural organization studied by LAXS as a function of temperature. In the low-temperature solid, the barium atoms keep the same environment as in barium acetate. The titanium alkoxide reacts with acetic acid to give an hexanuclear molecule.

1. Introduction

A survey of scientific literature published in the last few years would reveal a great number of studies on sol–gel processed oxides. Among those, $BaTiO_3$ appears very frequently in consideration of its technological importance.

These contributions are essentially related to the sol–gel processing itself (effects of the reaction parameters) [1], the control of particle shape [2,3] or the control of physical properties [4,5]. But, except for studies by electron microscopy, little has been done about the structural aspects of the sol–gel route.

The present work is devoted in the study of the local order in the gel and its evolution during the heat treatment which leads to crystalline $BaTiO_3$.

2. Synthesis

Barium acetate is dissolved in glacial acetic acid with stirring and heating. After cooling, methanol is added to give a clear colourless solution. Then, tetraethoxytitanium(IV) is added in stoichiometric amount (molar ratio $Ba/Ti = 1$). The hydrolysis is performed by adding excess water (molar ratio $H_2O/Ba = 65$). The gelification is obtained, by heating this solution, after 30 min.

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The gel is dried at 50 °C for 20 h and then heated up to 1000 °C, by steps of 50 °C for 4 h. At each step, a sample is taken for the structural study.

3. Evolution of the local order as a function of temperature

This evolution is followed by the large angle X-ray scattering (LAXS method) [6–8]. After corrections and normalization of the scattered intensities, a Fourier transform leads to a radial distribution of the interatomic distances in the solid (RDF curve).

It is necessary to make a preliminary remark before examining the LAXS results. The scattering power of barium is much greater than that of titanium. So, the main features in the RDF curve come from interactions between barium atoms and the other atoms.

Fig. 1a shows the RDF evolution up to 600 °C. Three domains of temperature can be considered:

- below 250 °C (fig. 1b), there is no important change in the local order i.e. in the barium vicinity. This domain corresponds to a loss of solvents (methanol–acetic acid).
- between 250 °C and 400 °C (fig. 1c), there is still a loss of solvents and the organic ligands begin to decompose. In the RDF curves, the

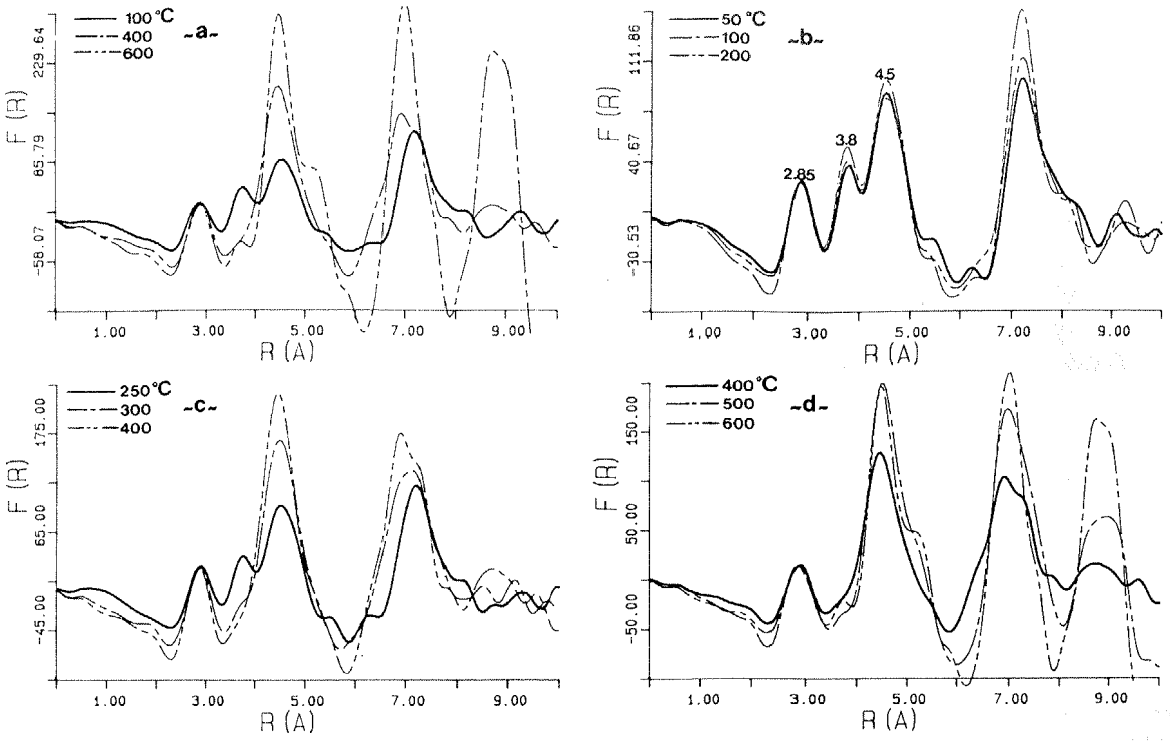

Fig. 1. Experimental RDF curves of "$BaTiO_3$" gel as a function of temperature.

intensity of the two main peaks, at 4.5 Å and 7.2 Å increases and the peak at 3.8 Å disappears.

- between 400 °C and 650 °C (fig. 1d), the transformation of the amorphous solid is very fast; this corresponds to the formation of new phases leading to a great modification of the RDF curve, especially at 9 Å.

$BaTiO_3$ begins to crystallize at 650 °C, but a pure phase is only obtained at 850 °C.

4. First domain (T < 250 °C): structural study of the gel

The experimental RDF curve being difficult to interpret, the modelling of the local order can only be done on the basis provided by a thorough analysis of the known crystal chemistry, allowing the construction of a pertinent surrounding for both barium and titanium atoms.

4.1. Barium environment

Several experiments have been performed to precisely examine this environment.

(a) The crystal structure of $Ba(CH_3COO)_2$ has been determined [9]. It can be described as a tridimensional network of interconnected $Ba_4(CH_3COO)_8$ basic units. This Ba_4L_8 formal association is generated by a 4 axis (fig. 2). The four barium atoms are *strongly linked* by four μ_2-O (O3 atoms) and four μ_3-O (O2 atoms) belonging to acetate groups. They shape a flattened tetrahedron with four short barium–barium distances (4.338 Å). The metal environment is achieved by nine oxygen atoms making a very distorted monocapped square antiprism.

(b) A theoretical RDF has been calculated with this structure as a model and compared to the experimental one (fig. 3). The peak at 2.85 Å, corresponding to the coordination distances around Ba, and the peak at 4.5 Å, corresponding

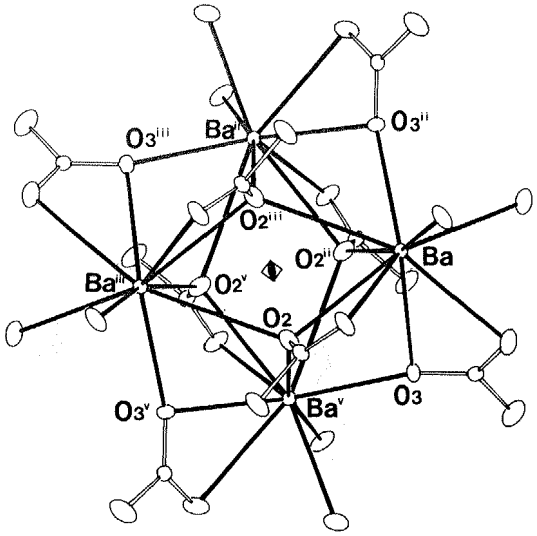

Fig. 2. $Ba_4(CH_3COO)_8$ unit in the barium acetate structure.

to Ba–Ba interactions in the Ba_4L_8 unit, are fully explained. However, this is not the case for the peak at 3.8 Å.

(c) A LAXS measurement has been performed on a solution (1 mol l^{-1}) of barium acetate in acetic acid. The RDF curve shows the main features at 2.8 Å and 4.5 Å with correct relative intensities.

(d) A gel of barium acetate ("Ba" gel) has been prepared by the following way. Barium acetate is dissolved in glacial acetic acid. After cooling, ethanol is added to this solution. This mixture is allowed to stand at room temperature in the air. The gelification occurs after 30 min. The RDF

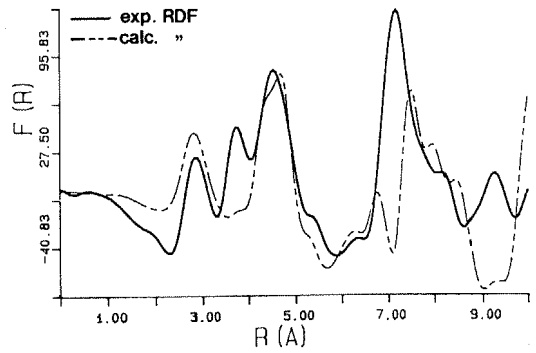

Fig. 3. Comparison between "$BaTiO_3$" gel (exp. RDF) and the structure of barium acetate (calc. RDF).

curve, obtained by the LAXS method, shows again strong peaks at 2.8 Å and 4.5 Å.

(e) The "$BaTiO_3$" gel was heated at 100 °C, for three weeks, in a closed bomb. Very good single crystals of $Ba(CH_3COO)_2$ were grown from the gel in these conditions.

(f) The IR spectrum of the "$BaTiO_3$" gel shows the characteristic absorption bands of barium acetate.

All these clues suggest that the *$Ba_4(CH_3COO)_8$ units, observed in the barium acetate structure, are still present in the low-temperature "$BaTiO_3$" gel.*

4.2. Titanium environment

Titanium atoms might be present in the gel as a hexanuclear molecule: $Ti_6(\mu_3\text{-}O)_2(\mu_2\text{-}O)_2(\mu_2\text{-}OC_2H_5)_2(\mu\text{-}CH_3COO)_8(OC_2H_5)_6$. Indeed, this complex crystallizes very easily by slow evaporation of an alcoholic solution of $Ti(OC_2H_5)_4$ in acetic acid. The preparation is as described in section 2, except that barium acetate is not added. It is noteworthy that a gelification occurs when the evaporation rate is faster ("Ti" gel).

The crystal structure of the hexanuclear complex was investigated [10]. The molecules can be considered as an association of two triangular units $Ti_3(\mu_3\text{-}O)$ connected by six bridges, two oxygen atoms and four acetate groups (fig. 4). Such $M_3(\mu_3\text{-}O)$ units are well known for a variety of metallic atoms (Ti–V–Cr–Fe–Zr–Ru). The bridging scheme imposes a great dispersion in the Ti–Ti distances: Ti1–Ti3 = 3.102 Å, Ti1–Ti2 = 3.430 Å, Ti2–Ti3 = 3.600 Å. The titanium atoms are situated in distorted oxygen octahedra exhibiting a large dispersion of Ti–O bond lengths from 1.752 Å to 2.174 Å.

A theoretical RDF has been calculated from this structure and a LAXS measurement performed on the "Ti" gel. The striking similarity of the two curves (fig. 5) shows that *the hexanuclear molecules exist in the "Ti" gel.*

4.3. Local order in the "$BaTiO_3$" gel

The RDF curve of the "$BaTiO_3$" gel shows an unexplained peak at 3.8 Å. This distance cannot correspond to Ba–Ba interactions, the Ba–O–Ba

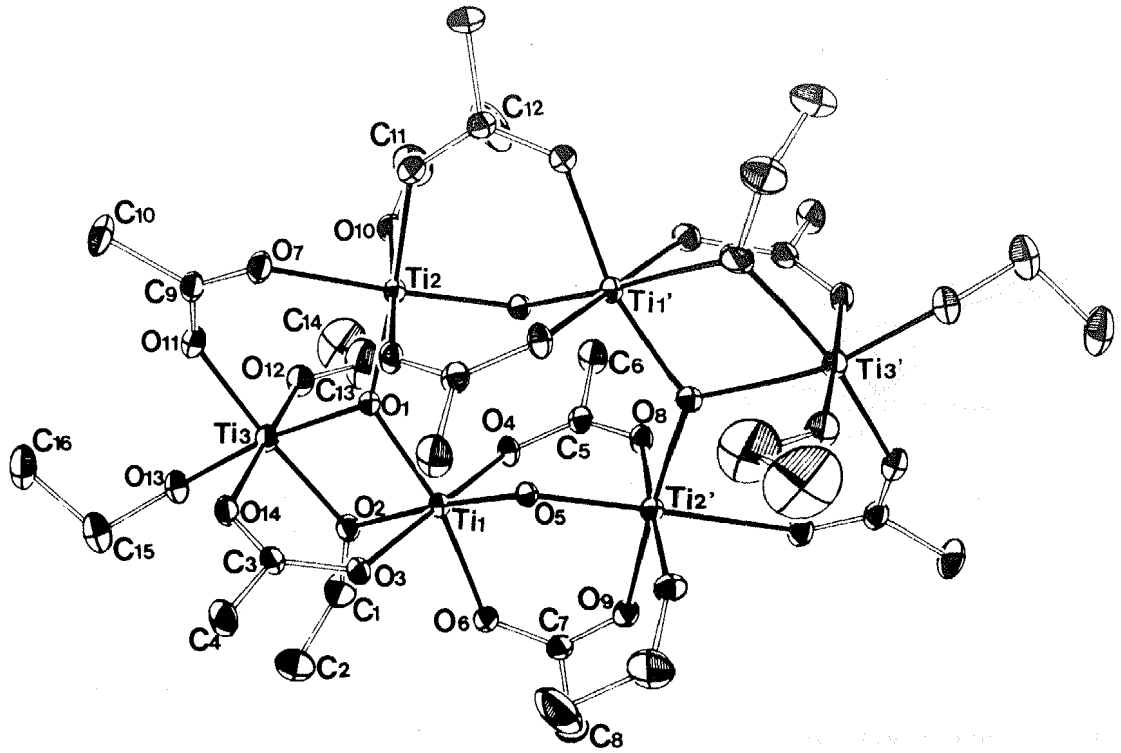

Fig. 4. Structure of the hexanuclear titanium complex.

angle would be too narrow. On the contrary, Ba–Ti interactions through an oxygen bridge, like those observed in $BaTi_4O_9$, give this distance.

Thus, it is possible to imagine a structural model in which Ba_4L_8 entities would connect titanium tri- or hexanuclear molecules through acetate bridges, such a connection giving Ba–Ti interactions at 3.8 Å.

In order to test this hypothesis experimentally, a mixture, in stoichiometric amounts, of the "Ba" gel and of the "Ti" gel has been prepared and

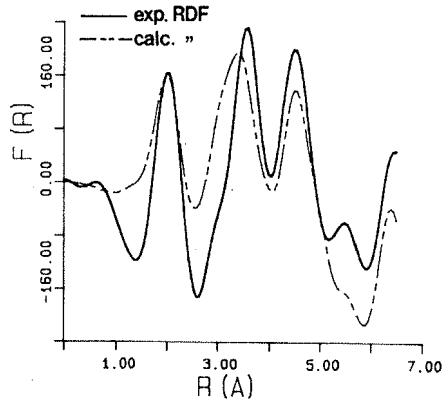

Fig. 5. Comparison between the experimental RDF and the calculated one for "Ti" gel.

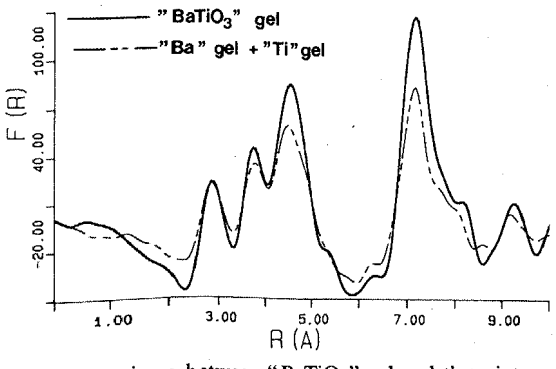

Fig. 6. Comparison between "$BaTiO_3$" gel and the mixture of "Ba" gel + "Ti" gel.

heated at 100 °C for 24 h. An amorphous powder has been obtained and studied by LAXS. The RDF curve of this powder is almost identical to the curve corresponding to the "$BaTiO_3$" gel (fig. 6).

This leads to the conclusion that *an association between $Ba_4(CH_3COO)_8$ units and Ti_3 or Ti_6 complex molecules might actually exist in the low-temperature "$BaTiO_3$" gel.*

5. Second domain (250 °C < T < 400 °C)

This domain corresponds to the pyrolysis of organic ligands. This is followed by DTA analysis (fig. 7) showing an intense exothermic peak between 230 °C and 400 °C with maximums at 277 °C and 320 °C. These two peaks may correspond to the pyrolysis of the different ligands in the solid (OC_2H_5 and CH_3COO).

The disappearance of the peak at 3.8 Å in the gel heated at 300 °C (fig. 1c) is explained by the breaking off of the Ba–O–Ti bonds during the pyrolysis of the bridging ligands.

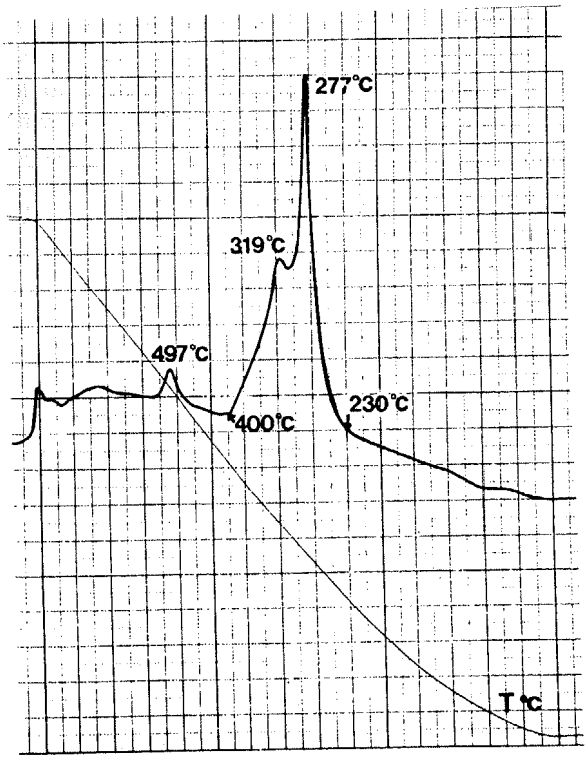

Fig. 7. DTA analysis of "$BaTiO_3$" gel.

6. Third domain (400 °C < T < 650 °C): structural study of the amorphous solid

The RDF curve of the amorphous solid obtained at 600 °C corresponds to a new compound or a mixture of new phases from which $BaTiO_3$ crystallizes.

The IR spectra show clearly the $BaCO_3$ absorption bands above 400 °C. But it is not possible to exclude the presence in the solid of oxides, like BaO or titanates, which would give only broad bulks in the low frequency domain.

So, theoretical RDF curves have been calculated for BaO, $BaTi_4O_9$, Ba_2TiO_4 and $BaTi_2O_5$. Comparison with the experimental curve shows a large disagreement and allows these products to be eliminated as $BaTiO_3$ precursors.

As the heat treatment at 700 °C of the "Ti" gel gives TiO_2 anatase, a theoretical RDF curve, based on a stoichiometric mixture of $BaCO_3$ and TiO_2, has been calculated. The good agreement with the experimental RDF curve (fig. 8) shows that $BaTiO_3$ actually crystallizes from this mixture.

7. Conclusion

The association of several X-ray techniques, powder diffraction–single crystal structural study

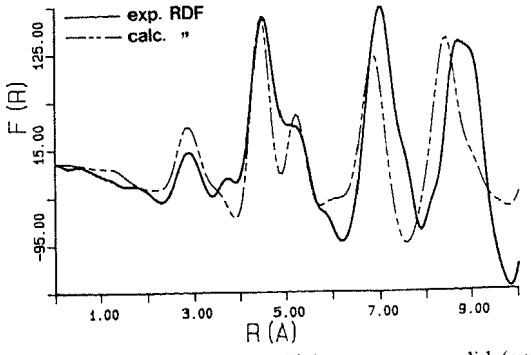

Fig. 8. Comparison between the high-temperature solid (exp. RDF) and the mixture of $BaCO_3$ and TiO_2 (calc. RDF).

–large angle X-ray scattering allows the structural evolution of the amorphous solid to be followed.

The gel, precursor to $BaTiO_3$, is prepared by hydrolysis of a mixture of $Ba(CH_3COO)_2$ and $Ti(OC_2H_5)_4$ with acetic acid as catalyst.

The barium acetate is characterized by $Ba_4(CH_3COO)_8$ units. The titanium alkoxide reacts with acetic acid to give a hexanuclear molecule. The local order in the "$BaTiO_3$" gel can probably be described as an association between those two species.

The pyrolysis of the organic ligands, between 230 °C and 400 °C, leads to the formation of $BaCO_3$ and TiO_2 from which $BaTiO_3$ is formed at 650 °C and crystallizes with the typical perovskite network.

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