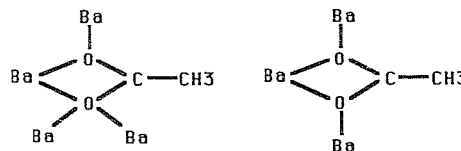


coordinated Ti^{+4} ions. The structure can be described as being made up of chains of Ti^{+4} octahedra surrounding Ba^{+2} filled pentagonal tunnels, $[Ba_2Ti_8O_{20}]^{-4}$ alternating with chains of $[Nd_4TiO_7]^{+2}$ held together by the $[Ba_x(Nd,Sm)_{2/3-2/3x}]^{+2}$ ions. Alternately, it can be described as corner shared groups of perovskite-like molecules of $[Nd_4Ti_9O_{27}]^{-6}$ containing three kinds of tunnels, pentagonal Ba^{+2} , diamond shaped $[Ba_x(Nd,Sm)_{2/3-2/3x}]^{+2}$, and vacant triangular sites.

High resolution electron microscope lattice images taken down the *c*-axis show a "herring-bone weave" pattern, with angles near 60° . All postulated structures based on the 1:1:5 composition shown calculated lattice images with 90° angles. However, calculated images based on the present structure agree with the observed.

group I4). Barium atoms are surrounded by nine oxygen atoms achieving a very distorted polyhedron. The acetate ligands are involved in two kinds of coordination scheme as shown on the figure :



07.9-10 STRUCTURAL PRECURSORS IN THE SOL-GEL PROCESSING OF $BaTiO_3$.

I. Gautier-Luneau, A. Mosset and J. Galy, Laboratoire de Chimie de Coordination du CNRS, 205 route de Narbonne, 31077 TOULOUSE Cédex, France.

Sol-gel processed $BaTiO_3$ is prepared from barium acetate and tetraethoxy titanium(IV) in glacial acetic acid and ethanol. The so-obtained gel is dried and heat-treated until $BaTiO_3$ recrystallises at $650^\circ C$.

Three domains of temperature can be considered on the basis of a LAXS study of the amorphous solid (LAXS: Large Angle X-ray Scattering):

- 1) Below $250^\circ C$, there is no important change in the local order. This domain corresponds to a loss of solvents.
- 2) Between $250^\circ C$ and $400^\circ C$, there is still a loss of solvents and the organic ligands begin to decompose.
- 3) Between $400^\circ C$ and $600^\circ C$, the transformation of the amorphous solid is very fast, corresponding to the formation of new products. The modelling of the high temperature ($600^\circ C$) solid shows that $BaTiO_3$ crystallises from a mixture of "native" barium carbonate and titanium dioxide.

The aim of the present study is to define the structural precursors in the room-temperature gel. Titanium might be present as an hexanuclear species $Ti_6(\mu_3-O)_2(\mu_2-O)_2(\mu_2-OC_2H_5)_2(\mu-CH_3COO)_8(OC_2H_5)_6$, built up of two trinuclear oxo-centered units. This complex crystallises in the triclinic system (space group P1). The metal-oxygen-metal bridging scheme is highly asymmetrical. This asymmetry results in a great dispersion in the Ti-Ti distances and in the Ti-(μ_3-O) bonding (I. Gautier-Luneau et al., Z. Krist., in print).

Barium might be present as the $Ba(CH_3COO)_2$ acetate or a solvate like $Ba(CH_3COO)_2 \cdot x CH_3COOH \cdot y H_2O$. The crystal structure of the first compound has been determined. It crystallises in the tetragonal system (space

07.9-11 $U_{14}Au_{51}$, A NEW PHASE IN THE SYSTEM U - Au.

F. Hulliger and A. Dommann, Laboratorium für Festkörperphysik, ETH-Hönggerberg, CH-8093 Zürich, Switzerland.

The published phase diagram of the system U-Au only shows two intermetallic compounds: U_2Au_3 and UAu_3 . We synthesized the new phase $U_{14}Au_{51}$ and found its structure to be of the $GdAg_{3.6}$ type. Some speculations about this structure type will be offered.