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Synthesis of $(Bi,La)_4Ti_3O_{12}$ by a new aqueous solution-gel route

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Abstract

A new aqueous solution-gel route for the synthesis of ferroelectric lanthanum substituted bismuth titanate was developed, based on aqueous Bi^{3+}- and La^{3+}-citrate solutions and an aqueous peroxocitrato-Ti(IV) solution. A homogeneous, amorphous precursor gel was prepared by evaporation of the BLT precursor solution. The homogeneity was maintained throughout the entire thermo-oxidative decomposition of the gel, as shown by TEM measurements on freestanding thin films. This molecular scale mixing and high degree of homogeneity led to the direct crystallization of the Aurivillius phase from the amorphous phase. As a consequence the crystallization temperature was as low as 525 °C, which was shown by a high temperature X-ray diffraction study of the stoichiometric precursor. The addition of an excess of Bi^{3+} decreased the crystallization temperature, but also introduced a Bi_2O_3 secondary phase.

Keywords: Aqueous; Electron microscopy; Layered perovskites; Sol-gel processes; X-ray methods

1. Introduction

Recently there has been great interest in ferroelectric materials due to their possible application in the production of non-volatile random access memories (ferroelectric RAM). This application is based on the existence of two opposite polarization states which can be used to store binary information in a non-volatile way as they are stable in the absence of an external electric field. In practice the materials have to satisfy several requirements, e.g. a low coercive field, a low processing temperature and a large remanent polarization (P_r) which is constant in time ("retention") and with repeated switching between the "0" and "1" states ("fatigue"). In the past PZT ($Pb(Zr,Ti)O_3$) and SBT ($SrBi_2Ta_2O_9$) have received the most attention. Only very recently it was discovered that BLT ($(Bi,La)_4Ti_3O_{12}$) may be an even better alternative.[1,2] BLT thin films and ceramics have been prepared by several routes such as MOSD,[3] CSD,[4] pulsed laser deposition[1,2,5] and solid-state routes.[6,7] It is widely recognized that chemical synthesis routes provide a better homogeneity and a lower formation temperature of the desired oxide phase, due to molecular scale mixing in the precursor phase. They also allow the fabrication of uniform large area thin films. A very commonly applied route is the sol-gel synthesis. This route usually starts from metal alkoxides or salts, dissolved in alcoholic solvents, implying a high cost and a great ecological risk. Therefore, in our laboratory aqueous solution-gel routes are being explored for the synthesis of (multi-)metal oxides such as SBT ($SrBi_2Ta_2O_9$),[8] SBN ($SrBi_2Nb_2O_9$),[9] PZN [$Pb(Zn_{1/3}Nb_{2/3})O_3$],[10] ZnO[11] etc. These routes have all the advantages of their alcoholic counterparts, but they have the surplus of a smaller risk for both the environment and experimenter. Furthermore it is not necessary to take special precautions in order to protect the starting products from air or humidity.

BiT ($Bi_4Ti_3O_{12}$) as well as BLT have been synthesized in our laboratory by an aqueous metal–chelate gel route, which was based on aqueous solutions of acetate salts and a peroxocitrato–Ti(IV) complex.[12,13] These solutions, however, turned out to be unsuitable for the spin-coating deposition of thin films due to their low concentration (total metal ions ca. 0.05M) and corresponding low viscosity. Other disadvantages are their limited stability towards precipitation and the presence of acetic acid (ca. 5 vol.%). The latter is only necessary to prepare the aqueous Bi(III)– and La(III)–acetate solutions, but of no importance for the gelation of

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the precursor solutions and therefore considered as redundant.

In this paper a newly synthesized, stable, aqueous BLT precursor is presented, suitable for the deposition of thin films as will be reported in the future.

2. Experimental details

The starting materials for the preparation of the precursor solutions are bismuth citrate ($Bi(C_6H_5O_7)_3$, 99.99%, Aldrich), lanthanum oxide (La_2O_3, 99.99%, Alfa Aesar), Ti(IV)isopropoxide ($Ti(iOPr)_4$, 98+%, Acros), ammonia (NH_3, 32% in H_2O, extra pure, Merck), ethanolamine (C_2H_7NO, redistilled, 99.5+%, Aldrich), citric acid ($C_6H_8O_7$, 99%, Aldrich) and hydrogen peroxide (H_2O_2, 35 wt.% in H_2O, p.a., stabilized, Acros).

Thermal analysis experiments were performed with differential thermal analysis (DTA, TA Instruments 1600), and thermogravimetric analysis (TGA, TA Instruments TGA 951-2000). Transmission Electron Micrographs (Philips CM12) were taken from free-standing thin films, prepared on gold TEM grids and heated in the TG furnace. The phase formation during the heat treatment was studied in situ by high temperature XRD (Siemens D-5000, including Göbel mirror, Pt heating stage (HTK 10, Anton Paar) and PSD (mBraun), CuK_α).

3. Results and discussion

3.1. Precursor preparation

Bismuth citrate is known to be only slightly soluble in water, but dissolves upon addition of ammonia.[14] This solution is unstable and precipitation occurs very quickly, but the addition of ethanolamine (EA) leads to a substantial increase of its stability. By adding ethanolamine in a 1.5:1 molar ratio against Bi^{3+} together with ammonia, a 1 M solution of bismuth citrate in water (pH = 7) could be obtained, which remains stable for at least several months. This solution is used as the Bi^{3+}-precursor.

To our knowledge lanthanum citrate is not commercially available, but it can be prepared from sodium citrate and lanthanum nitrate.[15] However, the sodium will remain in the product obtained after thermal treatment and it will influence the oxide's properties. Therefore a new synthesis route for an aqueous lanthanum citrate precursor has been designed. Lanthanum oxide was the preferred starting product as opposed to the acetate or nitrate because it does not lead to the input of any redundant material, which has to be removed during the decomposition of the gel. The procedure for the preparation of the La^{3+}-precursor was as follows. Lanthanum oxide is dispersed in a small amount of water and citric acid is added in a 3:1 molar ratio against La^{3+}. The mixture is refluxed at 95 °C for 1–1.5 h, during which time a solid but largely amorphous lanthanum citrate is formed, as was shown by XRD and FTIR (Fig. 1). Differences in its IR spectrum from the citrate prepared from lanthanum nitrate and sodium citrate are ascribed to the excess of citric acid used in the reaction (e.g. peak at 1750 cm^{-1}) and to a difference in hydration.[15] Ammonia and ethanolamine in a molar ratio of 2.5:1 La^{3+} are then added to the obtained dispersion of the solid citrate in water, resulting in a clear 0.5 M solution (pH = 8) after refluxing at 60 °C.

The precursor for Ti^{4+} was a water-soluble peroxo-citrato–Ti(IV) complex, synthesized analogous to the procedure described before.[10,12,13] However, here it has been prepared with a higher concentration (about 1 M in stead of 0.1 M) and a lower H_2O_2:Ti molar ratio (1.1:1 in stead of 2:1), the latter being necessary in order to reach the higher concentration without precipitation.

The exact concentrations of the monometallic precursor solutions are determined by ICP-AES (Perkin Elmer, Optima 3000) so that by mixing them a BLT-precursor solution with the desired stoichiometry can be prepared. The obtained BLT-precursor is stable against precipitation for at least several months. By evaporation of this solution in an air-flushed furnace at 60 °C, a clear and amorphous gel is formed (Fig. 2).

3.2. Thermo-oxidative decomposition and gel homogeneity

The thermo-oxidative decomposition of the stoichiometric BLT-gel was studied by thermogravimetric analysis and differential thermal analysis (Fig. 3). The entire organic matrix is removed by 520 °C upon heating at

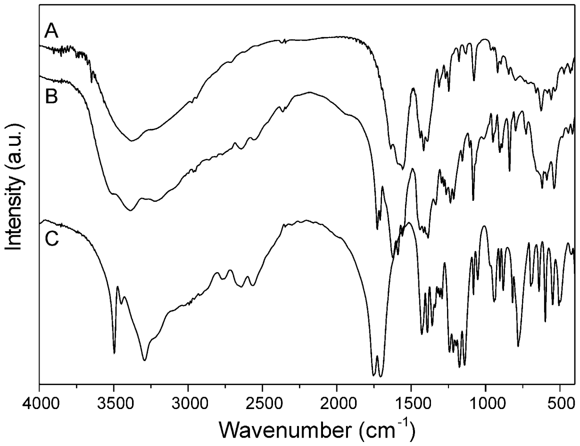

Fig. 1. FTIR spectra: (A) lanthanum citrate from sodium citrate and lanthanum nitrate, (B) lanthanum citrate from La_2O_3 and citric acid, (C) citric acid.

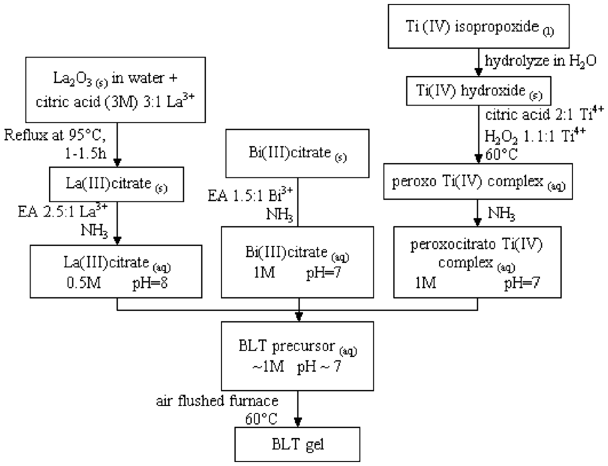

Fig. 2. Flowchart of the synthesis route for the aqueous BLT precursor.

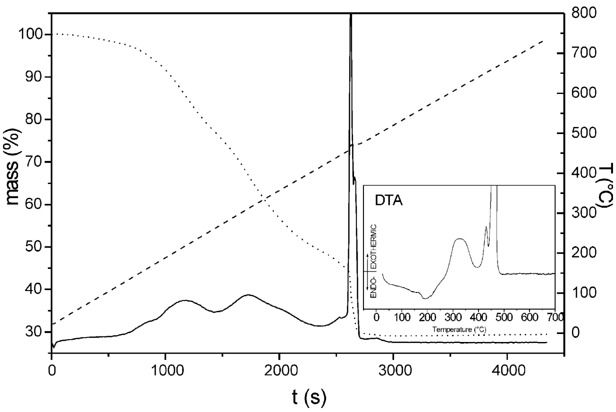

Fig. 3. TGA and DTA (10 °C/min, 100 ml/min dry air) of the BLT precursor gel.

10 °C/min in 100 ml/min synthetic dry air. Up to 460 °C the decomposition occurs very gradually, but at 460 °C an exothermic step takes place, during which approximately 15% of the original gel mass is lost within 80 s. A possible explanation for the persistence of organic material up to such high temperatures is the formation of nitrogen containing organic compounds, such as (poly-)amides, during the thermal treatment of the gel.[12]

In order to check that the gel's homogeneity is conserved during the entire thermal treatment, freestanding thin films were prepared for TEM analysis, as described earlier.[10] The TEM grid carrying the precursor film is heated in a TG-furnace (10 °C/min, 100 ml/min dry air) up to the desired temperature and then quenched. In this way it is possible to investigate the homogeneity during every step of the decomposition. Here we focused on the temperature interval around the final decomposition step. TEM images (bright field (BF), dark field (DF) and diffraction patterns) of freestanding thin films heated up to 410 and 500 °C followed by quenching were recorded. At 410 °C the film is still amorphous and homogeneous. At 500 °C the BF image only shows the puffed up morphology arising from the evolution of gaseous reaction products and the diffraction pattern shows several diffuse rings, typical of amorphous samples. Nevertheless, in DF some very small crystallites, less than 5 nm in size, do light up. A film heated up to 500 °C and kept isothermal for 20 min, shows an increased number of these crystallites. After heating to 550 °C (2 min isothermal) the images shown in Fig. 4 were recorded. The presence of Aurivillius phase crystal aggregates was proven by determination of the d-spacings.

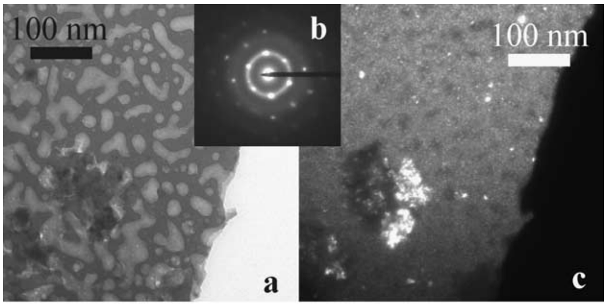

Fig. 4. TEM on freestanding thin film heated to 550 °C: (a) BF image, (b) diffraction pattern, (c) DF image.

From these experiments it is concluded that the gel formed by evaporation of the BLT precursor solution is homogeneous and stays homogeneous throughout the entire thermo-oxidative decomposition. Only after the entire organic matrix is decomposed, around 500 °C at a heating rate of 10 °C/min in synthetic dry air, does the crystallization start.

3.3. Phase formation of BLT powder

The phase formation starting from the BLT precursor was studied by means of high temperature X-ray diffraction (HT-XRD), allowing the in situ observation of the phase formation during heating of the gel. The precursor (10 mg) was heated at 10 °C/min in static air to the desired temperature and after a 30 s delay time an XRD spectrum was recorded, which takes approximately 9 min. The results are shown in Fig. 5, where the Pt peaks are due to the sample stage. The gel remains amorphous up to 500 °C. Starting from 525 °C diffraction peaks at the same positions as for the layered perovskite $Bi_4Ti_3O_{12}$ (JCPDS 35-0795) are seen, which shows the substitution of Bi with La was succesful. These diffraction peaks sharpen due to grain growth at higher temperatures and no intermediate or secondary phases are detected at any temperature. Phase segregation by crystallization of the different monometallic oxides at different temperatures is efficiently avoided. It is concluded from this experiment that the newly developed synthesis route presented here is indeed a

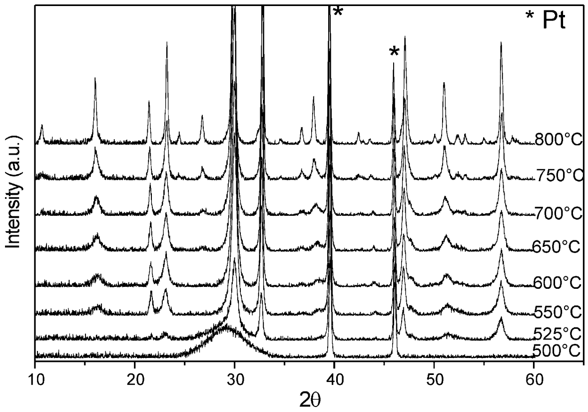

Fig. 5. HT-XRD of a $Bi_{3.5}La_{0.5}Ti_3O_{12}$ precursor gel (10 °C/min in static air).

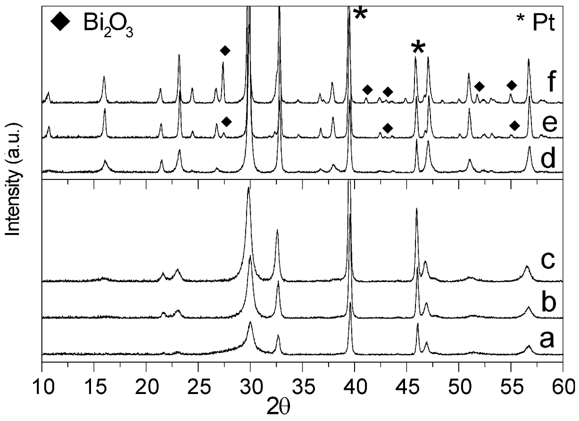

Fig. 6. (a) Stoichiometric, (b) 10% Bi-excess and (c) 25% Bi-excess precursor at 525 °C and (d) stoichiometric, (e) 10% Bi-excess, (f) 25% Bi-excess precursor at 750 °C.

successful way of producing phase pure multimetal oxide powders at low temperatures.

Additional HT-XRD experiments have been performed to check the possibility of lowering the crystallization temperature by the addition of an excess of Bi^{3+} to the precursor even though it was already very low. It was found from measurements on gels containing 10 and 25% Bi^{3+}-excess (Fig. 6a–c) that indeed the peak intensity increases with increasing amount of Bi^{3+} at the same temperature. For the precursor containing 25% Bi^{3+}-excess, a diffractogram similar to the one at 525 °C of the stoichiometric precursor is observed at 500 °C already. However, at higher temperatures the Bi-excess also leads to the formation of a bismuth oxide secondary phase (Fig. 6d–f), which is identified as metastable, cubic Bi_2O_3 (JCPDS 45-1344). Bismuth oxide has a melting temperature of 825 °C,[14] so that further heating of the powder above this temperature resulted in the disappearance of the Bi_2O_3 from the spectrum.

4. Conclusion

A new, stable, aqueous precursor solution for the synthesis of lanthanum substituted bismuth titanate has been developed.

Starting from stable aqueous solutions of bismuth citrate, lanthanum citrate and a water soluble peroxocitrato-Ti(IV) complex a homogeneous precursor gel could be prepared. Transmission electron microscopic investigations have shown that this gel remains homogeneous down to nanometer level throughout the entire thermal treatment.

In situ study of the phase formation by means of high temperature XRD, has shown that the Aurivillius phase is formed at 525 °C without the occurrence of any intermediate or secondary phases. The crystallization temperature could be lowered by the addition of an excess of Bi^{3+} to the precursor solution, but this also led to the formation of a secondary Bi_2O_3 phase.

Future work will focus on the spin-coating deposition of ferroelectric thin films for nonvolatile digital memory applications.

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