Journal of the European Ceramic Society 21 (2001) 2047–2049
www.elsevier.com/locate/jeurceramsoc

Synthesis of $SrBi_2Ta_2O_9$ (SBT) by means of a soluble Ta(V) precursor

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Received 4 September 2000; received in revised form 16 November 2000; accepted 15 December 2000

Abstract

Aqueous sol-gel processing of pentavalent metals like Ta and Nb is very complicated since the only water soluble compound is the oxalate, which is not very suited for gel formation. Nevertheless, starting from Ta oxalate, it is possible to prepare a water soluble Ta(V) precursor that remains stable in the pH range needed for gel formation. During synthesis the oxalate is oxidized with H_2O_2 and subsequently complexed with citric acid and as a result the peroxo–citrato tantalum(V) complex is formed. This Ta(V) precursor is afterwards used for the synthesis of the ferroelectric $SrBi_2Ta_2O_9$ (SBT). The formation of the SBT crystalline phases was investigated by means of high temperature X-ray diffraction (HT–XRD). © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Perovskites; Sol-gel processes; $SrBi_2Ta_2O_9$ (SBT); Tantalates

1. Introduction

Strontium bismuth tantalate ($SrBi_2Ta_2O_9$) (SBT) is one of the most promising materials with a view to nonvolatile ferroelectric random access memory (NVFRAM) applications due to its minimal polarization fatigue and the possibility of using low polarization switching voltages. SBT has the general formula $ABi_2B_2O_9$, where A is the divalent metal ion Sr and B is the ion Ta with valence +5. The lattice structure of SBT is orthorhombic and consists of perovskite-like layers, having the net composition $(SrTa_2O_7)^{2-}$, alternating with $(Bi_2O_2)^{+2}$ layers.[1–3]

The ferroelectric properties of ceramic materials like SBT are strongly dependent on the homogeneity of the material. In this respect the ‘wet’ or chemical precursor routes are extremely appropriate to their synthesis. These methods allow chemical homogeneity and stoichiometric control through molecular level mixing of the starting compounds in a solution.[4,5]

In most cases SBT is prepared by alkoxide based sol-gel processes in organic solvents.[6,7] An important disadvantage of alkoxides however is that they are scarcely available and quite expensive. Moreover, they are extremely reactive towards humidity making them difficult to characterize and great care in processing circumstances is desired (inert atmosphere — glove box). The main reason for this is the difference in electronegativity between the metal ions and therefore hydrolysis rates of different ions vary substantially.[8] An alternative is aqueous sol-gel chemistry, starting with stable, rather cheap and easily available inorganic salts.

Aqueous sol–gel synthesis of ceramics containing group Vb metals (like Ta in SBT) is however very complicated, since very few salts are water soluble. Although Ta oxalate is water soluble, it is not suitable for gel formation. However, this compound is a perfect starting material since we managed to synthesize a water soluble peroxo–citrato Ta(V) precursor out of the Ta oxalate, as is shown here.

2. Experimental

2.1. Materials and reagents

The following materials and reagents were used: citric acid (Aldrich, 99% $C(OH)(COOH)(CH_2COOH)_2$), ammonia (UCB, p.a. NH_3 ca 25% in H_2O), tantalum oxalate (H.C. Starck, aqueous solution), hydrogen peroxide H_2O_2 (Acros Organics, 35 wt.% solution in water,

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PII: S0955-2219(01)00169-8

stabilized), strontium acetate (Aldrich, 99.995%, ($CH_3CO_2)_2Sr$), bismuth acetate (Aldrich, 99.99+%, ($CH_3CO_2)_3Bi$) and acetic acid (UCB, 99–100%, p.a., 1.049 kg/l, CH_3COOH).

2.2. Preparation of Ta(V) precursor solution

The flow diagram of the synthesis of the Ta(V) precursor is illustrated in Fig. 1. In the first synthesis step hydrolysed Ta is precipitated out of the oxalate solution by addition of NH_3. After filtration the Ta hydroxide is dissolved in an aqueous solution of citric acid and hydrogen peroxide. The H_2O_2:oxalate ratio amounted to 13:1, the citric acid:Ta ratio was 3:1. After refluxing the solution at 60°C during 16 h, the pH is raised until 6.8 by addition of ammonia. The resulting Ta(V) precursor solution was poured out on a Petri vessel and the solvent was evaporated in an oven under dry air at 60°C.

2.3. Synthesis of SBT

SBT was prepared by adding the Ta(V) precursor, Bi acetate (dissolved in water/acetic acid) and Sr acetate (dissolved in water) in stoichiometric amounts to the suitable quantity of citric acid (citric acid:metal ion ratio was approximately 2:1). By heating the resulting solution in an oven at 185°C a brown powder is formed. This powder is analysed by means of HT–XRD. For HT–XRD measurements a modified Siemens D-5000 powder diffractometer with CuK_α as the radiation source was used. The configuration consisted of a Göbel mirror ($K_{\alpha 1+2}$, Huber), a high temperature device with a Pt rod (Anton Paar, HTK 10) and a position sensitive detector (Braun). The Pt rod also contributes to the diffraction pattern (peaks at 39.76, 46.24 and 67.45° 2θ). For this study the equipment was operated in the hot-stage mode. It is then possible to take diffractograms in situ during heating of the sample in static air. For HT–XRD measurements a heating rate of 10°C/min was considered.

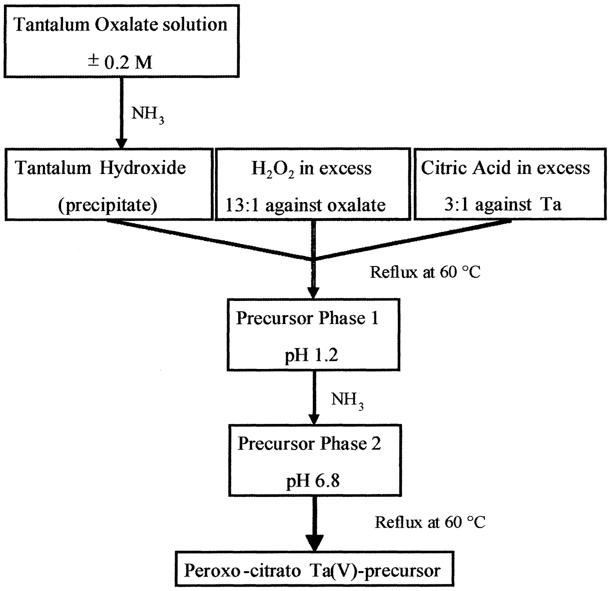

Fig. 1. Flow diagram for the synthesis of the peroxo–citrato Ta(V) precursor.

3. Results and discussion

The flow diagram presented in Fig. 1 is based on the synthesis of a Nb(V) precursor presented by Narendar et al.,[9] however, the procedure is slightly modified: the addition of HNO_3 was avoided, preventing the precipitation of nitrates and reducing the release of NO_x gasses.

Addition of ammonia to the starting solution of Ta oxalate results in an excessive hydrolysis and the precipitation of Ta hydroxide. After addition of citric acid and H_2O_2 the pH of the Ta(V) precursor solution is raised until 6.8 by addition of ammonia. The reason for this is that at that pH most of the carboxylate groups of citric acid are deprotonated (pK_{a3} of citric acid is 6.39). The citrate-groups ($C_6H_4O_7^{4-}$) are now assumed to co-ordinate the metal ions Ta^{5+} and to form a peroxo–citrato complex. The addition of ammonia not only raises the pH, but also promotes the decomposition of the excess H_2O_2 in solution.[9] After evaporation of the solvent we obtained a colorless and homogeneous gel. An XRD measurement was performed in order to distinguish any crystalline precipitate during gel formation. No diffraction peaks were observed. Therefore, it can be stated that the precursor gel is amorphous. The supposed structure of the Ta complex in the precursor solution, based on the characterization of an analogue peroxo-citrato Nb(V) precursor of Narendar et al.,[9] is illustrated in Fig. 2.

The phase formation of SBT was investigated by means of HT–XRD (Fig. 3). A diffuse XRD-spectrum is observed for the powder at 400°C, indicating the synthesized precursor is amorphous up to that temperature. When the powder is heat-treated at 500°C the intermediate fluorite phase is formed. This fluorite phase is converted into the ferroelectric perovskite phase at 725°C. At 800°C the fluorite phase has totally disappeared and only

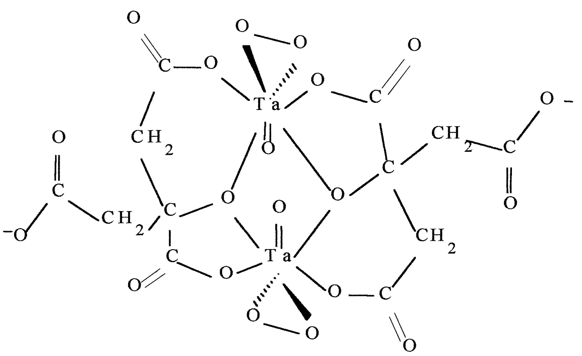

Fig. 2. Supposed structure of the peroxo–citrato Ta(V) precursor, similar to the Nb–peroxo–citrato complex of Narendar et al.[9]

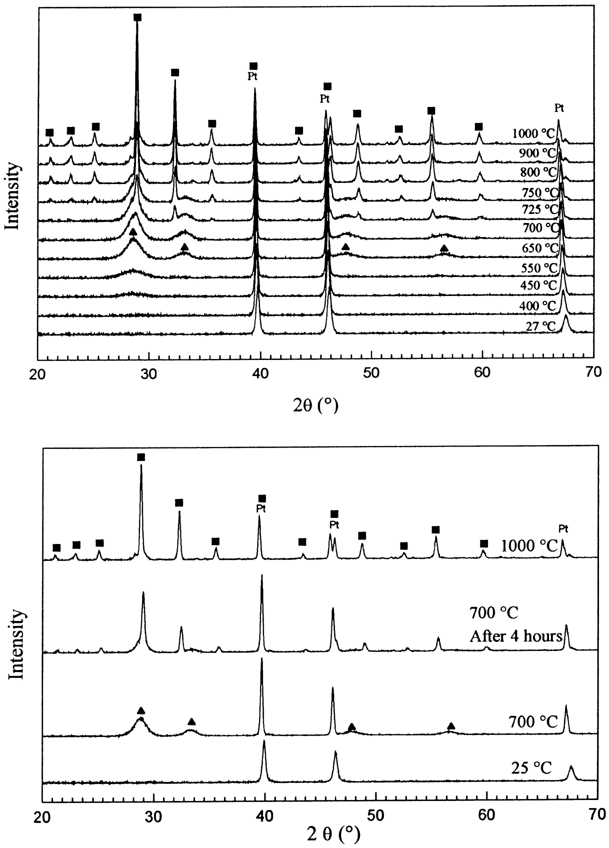

Fig. 3. HT–XRD patterns of SBT: ■, perovskite–SBT; ▲, fluorite–SBT.

perovskite SBT remains. Therefore, one can state that the perovskite phase is formed out of the fluorite phase. When the powder is heated until 700°C and maintained at this temperature during 4 h, one can clearly distinguish the presence of perovskite SBT. The fluorite phase has almost completely turned into the perovskite SBT, though a small fraction of fluorite phase remains present.

4. Conclusions

It was reported that a chemical aqueous solution method can be applied for the preparation of SBT. We succeeded in synthesizing a water soluble peroxo–citrato Ta(V) precursor by a new aqueous sol-gel method. This precursor can be succesfully used for the synthesis of SBT. Indeed, HT–XRD experiments showed that the ferroelectric perovskite phase can be formed at a temperature of approximately 700°C, out of an intermediate fluorite phase.

Acknowledgements

D.N. and G.V. are financed by the Fund for Scientific Research Flanders, Belgium (FWO). M.K.V.B. is a post doctoral fellow of the Fund for Scientific Research Flanders, Belgium (FWO). K.V.W. is indebted to the 'Vlaams instituut voor de bevordering van het wetenschappelijk technologisch onderzoek in de industrie' (IWT). The authors wish to thank H.C. Starck for the supply of the tantalum oxalate solution.

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