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Electron microscopy studies on the formation and evolution of sodium niobate nanoparticles from a polymeric precursor

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Abstract

The objective of this communication is to study by means of electron microscopy the formation of reactive sodium niobate nanoparticles obtained by a novel polymeric precursor route using DL-malic acid as chelating agent. Conventional electron microscopy and electron-diffraction were used to investigate the crystallization, the particle size evolution and the formation of nanoparticle agglomerates.

Keywords: $NaNbO_3$; Nanocrystallites; Electron microscopy (TEM, ED); Polymeric precursor synthesis; Amorphous complex method

1. Introduction

Sodium niobate, $NaNbO_3$, is a dielectric material with a perovskite-type structure. At room temperature, it has an orthorhombic structure, space group Pbma, and shows antiferroelectric behavior, with a Curie temperature of 360 °C [1]. In solid solution with $LiNbO_3$ can exhibit piezoelectric, ferroelectric, pyroelectric and electro-optic behavior [2,3].

The chemical and microstructural homogeneity of alkali metal niobates affects critically the electro-optic behavior, and therefore the synthesis of ceramics powders with good stoichiometry, homogeneity and sinterability are necessary to develop $NaNbO_3$ ceramics [4]. Traditional solid state preparation methods lead to poor compositional homogeneity, especially because of the easy volatilization of the alkali metal, since high temperatures are required for synthesis and sintering. Powder synthesis using solution techniques allow a better mixing of the constituent elements and thus a better reactivity of the mixture to obtain pre-reaction products at lower temperatures [5], and can produce chemically homogeneous powders with fine particle size and high reactivity, suitable for the preparation of dense ceramics with homogeneous microstructure. One such technique for the low temperature synthesis of oxides is the so-called amorphous complex method [6]. This technique is based mainly on the formation of soluble complexes in solution, followed by elimination of the solvent, resulting in a gel that keeps the random distribution of cations of the starting solution. The organic fraction of this gel is removed by heat process, resulting in a very fine, homogeneous and reactive crystalline oxide powder at temperatures lower than those used in the solid-state reaction. However, few studies have been reported on the synthesis of $NaNbO_3$ powders, or the preparation of $NaNbO_3$ polycrystalline ceramics using wet chemical methods: a polymeric precursor route using Pechini method [4], or preparation from solution using oxalic acid [7]. There is almost no study on the crystallization process,

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nucleation and growth of $NaNbO_3$ from amorphous precursors.

Traditionally, citric acid has been used as chelating agent to stabilize Nb in water [8]. Recently, we proposed the use of DL-malic acid (MA) as chelating agent, a smaller molecule than citric acid [9]. The amorphous complex method using DL-MA as chelating agent and water as solvent has been successfully used to synthesize $NaNbO_3$ powders [10]. The main contribution of the present research is to study, using electron microscopy techniques, the solid reaction products at different temperatures, the nucleation of sodium niobate nanoparticles from the polymeric precursor during thermal treatment and the formation of grain boundaries and local sintering behavior above the crystallization temperature.

2. Experimental

The powder preparation method has been described elsewhere [10]. Niobic acid was obtained by precipitation from an aqueous solution of pentahydrated niobium oxide and oxalic acid by adding ammonia. The precipitated and washed niobic acid was dissolved in a DL-MA solution. Sodium carbonate was added to a second DL-MA solution. The solutions of Na-malic and Nb-malic were mixed at molar ratio of [Na]:[Nb] = 1:1 and the temperature of the (Na–Nb) malic solution was increased to 70 °C and kept at this temperature until the formation of a viscous and transparent lightly yellow gel. The beaker was transferred to a mantle-heater, and the temperature increased and kept at 300 °C for 3 h. The heated product, thereafter called as “precursor”, was ground and calcined in air in the temperature range from 400 to 900 °C, at a heating rate of 10 °C min^{-1}, for 5 min to 8 h, using sintered alumina boats.

The precursor and the calcined $NaNbO_3$ powders were characterized by XRD, in a 2θ range from 15° to 75° with scanning speed of 0.75° min^{-1}, at room temperature using Cu Kα radiation (MXP^{3va}, MAC-Science, Japan). The powder morphology was observed by transmission electron microscopy (TEM) (Hitachi H9000NAR, Japan).

3. Results and discussion

The ash of the gel after thermal treatment at 300 °C in the mantle-heater or “precursor” material shows an amorphous character. Fig. 1A shows the XRD pattern

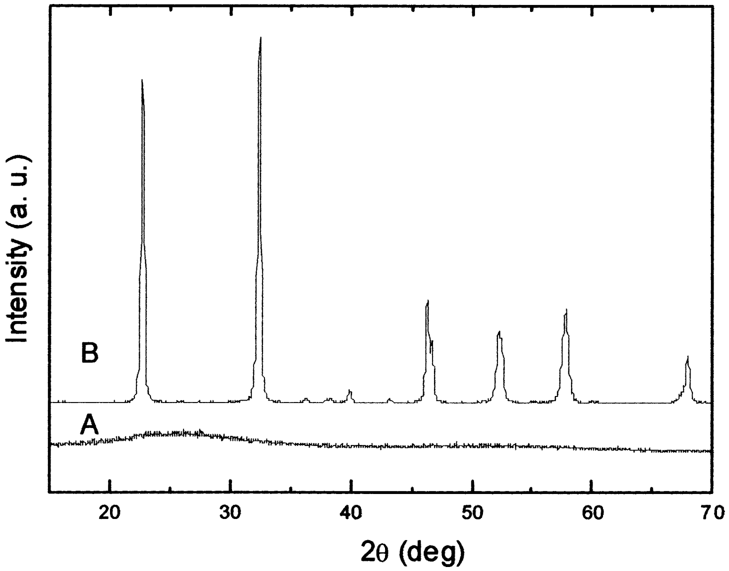

Fig. 1. (A) XRD pattern of the amorphous precursor and (B) the $NaNbO_3$ nanoparticles after thermal treatment of the polymeric precursor at 900 °C for 1 h.

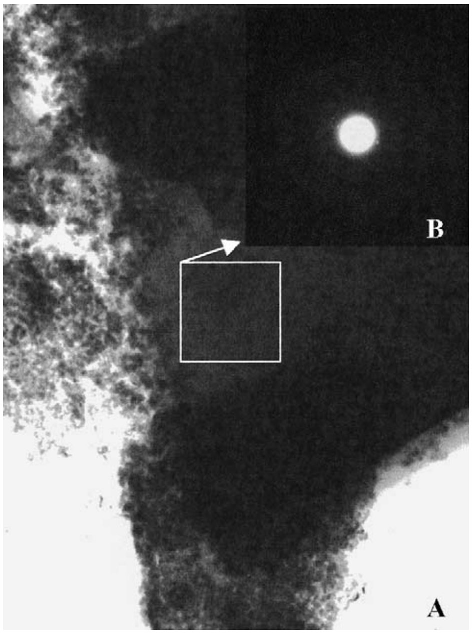

Fig. 2. (A) TEM micrograph showing the precursor calcined at 450 °C; (B) the ED pattern from the amorphous part of the flake-like material, where no crystalline seed or internal structure could be observed, shows a single diffuse ring.

of the amorphous precursor. After thermal treatment of the precursor, the formation of $NaNbO_3$ nanocrystalline powders was observed. Fig. 1B shows the XRD pattern of $NaNbO_3$ nanoparticules calcined at 900 °C for 1 h. The pattern matches with the powder diffraction file card (JCPDS) 33-1270.

The lowest calcination temperature to obtain the $NaNbO_3$ phase is 450 °C. Fig. 2 shows a TEM micrograph of the precursor after thermal treatment at 450 °C, the crystallization of the $NaNbO_3$ nanopowder is shown by the appearance of $NaNbO_3$ crystallites embedded in the amorphous precursor. No crystalline seed or internal structure could be observed in the remaining amorphous part of the flake-like material, the amorphous flakes kept similar irregular shapes than before the thermal treatment. The ED pattern from the amorphous showed a single diffuse ring (Fig. 2B).

Fig. 3 shows in detail the formation of nanocrystallites. The ED pattern (Fig. 3B) from the analyzed area in Fig. 3 showed the characteristic rings of polycrystalline $NaNbO_3$. The density of $NaNbO_3$ crystallites varied between the flakes. The crystallites have

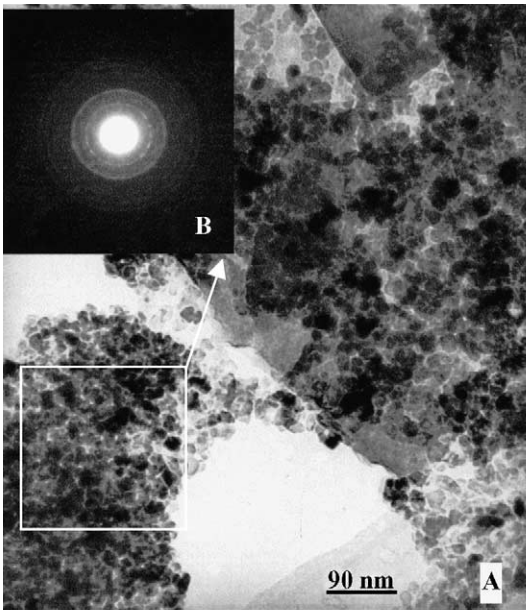

Fig. 3. (A) TEM micrograph of the $NaNbO_3$ nanocrystallites calcined at 450 °C for 1 h. (B) The electro-diffraction pattern shows clear diffraction rings of orthorhombic $NaNbO_3$. The particle size of the nanocrystallites is ∼25 nm.

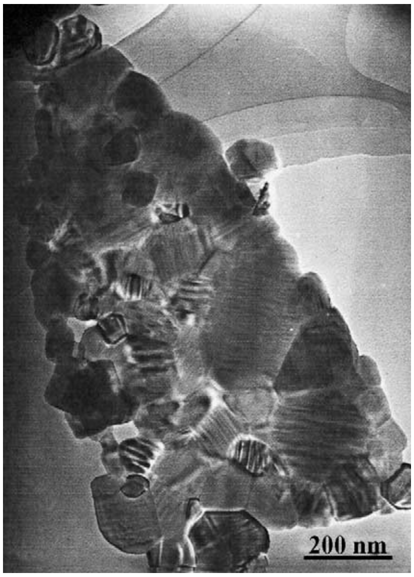

Fig. 4. TEM micrograph of the $NaNbO_3$ nanoparticles calcined at 700 °C for 1 h, showing partial sintering by the formation of grain boundaries and grain boundary networks; the internal features inside the grains indicate defects associated with grain boundaries and the formation of domains inside the grains.

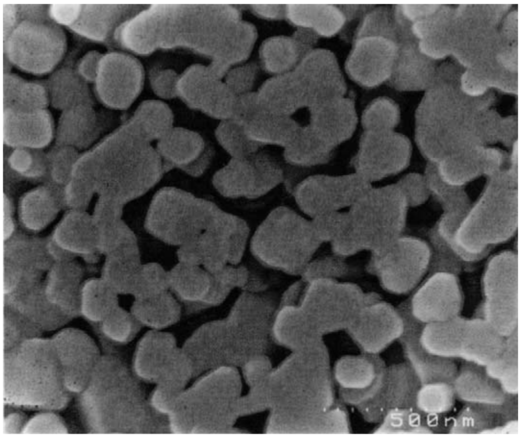

Fig. 5. SEM micrograph of $NaNbO_3$ nanoparticules calcined at 900 °C for 1 h. The particle size has increased to ∼130 nm.

typical sizes between 15 and 40 nm, with a mean particle size of 25 nm, calculated from over 200 $NaNbO_3$ nanocrystals.

Increasing calcination temperatures led to the formation of grain boundaries and sintering. Although the relative low calcination temperature, it is possible to observe in the TEM images (Fig. 4) of the sample calcined at 700 °C that the powder was partially sintered. The beginning of grain growth was also observed at 600 °C.

Fig. 5 shows a SEM micrograph and the XRD pattern of $NaNbO_3$ nanoparticules calcined at 900 °C for 1 h. After calcination at this temperature the crystallite size increased to ∼130 nm.

4. Conclusions

The amorphous complex method using DL-MA as chelating agent and water as solvent has been successfully used to provide very homogenous, single-phase ultra-fine $NaNbO_3$ powders. Crystallization of $NaNbO_3$ nanopowders from the amorphous precursor occurs at ∼450 °C in a single step process. $NaNbO_3$ crystallites with an average particle size ∼25 nm are obtained at this temperature. Formation of grain boundaries, sintering and grain growth begins at 600 °C, but grain growth is slow. The average grain size reaches ∼130 nm after successive thermal treatments of 1 h at 600, 700 and 900 °C.

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