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Journal of the European Ceramic Society 26 (2006) 409–415
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Formation and micro-Raman spectroscopic study of Aurivilius and fluorite-type $SrBi_2Nb_2O_9$ nanocrystallites obtained using an 'amorphous citrate' route

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Available online 2 November 2005

Abstract

The crystallization of a $SrBi_2Nb_2O_9$ gel-glass obtained using the amorphous citrate method was studied by micro-Raman scattering, X-ray diffraction, and electron microscopy techniques. A citric acid–ethanolamine gel with the stoichiometric proportion of the metallic cations was prepared as polymeric precursor and calcined to obtain the amorphous complex. Nanocrystallites with a metastable fluorite-type structure nucleate from the amorphous complex below 500 °C, as shown by X-ray scattering and confirmed by electron microscopy. The morphological study by scanning electron microscopy revealed the nucleation of nanocrystals in the glass-like amorphous powder after thermal treatment at 500 °C. Raman features characteristic of the stable Aurivillius nanocrystals can be detected after thermal treatment at 550 °C, while using X-ray diffraction the crystallization of the Bi-layered perovskite phase is observed only after treatment at 625 °C or higher temperatures. Both X-ray and Raman scattering detected single phase nanocrystallites with Aurivillius structure above 650 °C. The distinctive Raman features of the different $SrBi_2Nb_2O_9$ nanocrystallites and its evolution with thermal treatment is presented.

Keyword: Powders-chemical preparation; Precursors-organic; Raman spectroscopy; $SrBi_2Nb_2O_9$ nanocrystallites

1. Introduction

$SrBi_2Nb_2O_9$ (SBN) is an $n = 2$ member of the Aurivillius family of layered perovskites. It is orthorhombic at room temperature, with a Curie temperature ~430 °C. SBN presents interest as lead-free high temperature piezoelectric with very high resistance to electrical fatigue during ferroelectric switching, i.e. for applications substituting PZT.

SBN ceramics are normally prepared by solid state methods,[1] but the loss of Bi at high temperature promotes the formation of an undesirable non-ferroelectric Bi-deficient pyrochlore phase.[2] Bulk powders can be prepared by low temperature methods, i.e. aqueous solution,[3] or combustion synthesis.[4] The preparation of SBN thin films has been reported both by 'chemical' methods, i.e. using an aqueous solution gel route,[5,6] or by sol–gel[7] and by 'physical' methods: pulsed laser ablation.[8] Advantages of a polymeric precursor water route include an excellent control of the stoichiometry, good structural homogeneity of nanocrystalline powders (i.e. control of particle size, absence of agglomerates) difficult to achieve by other low temperature methods, i.e. combustion synthesis; the use of simpler equipment and cheap reagents compared to physical methods and the use of moderate temperatures, thus avoiding the formation of the unwanted pyrochlore phase.

Compared to other Bi-layered perovskite oxides, such as $SrBi_2Ta_2O_9$ (SBT),[9,10] SBN offers the advantage of a lower preparation temperature. However, the nucleation process of SBN powders is not well known. The crystallization

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doi:10.1016/j.jeurceramsoc.2005.07.049

of metastable phases with fluorite structure at low temperature has been reported, but there is no study on the experimental conditions, i.e. thermal treatment, particle size, which lead to the formation of the intermediate fluorite SBN.

The present study aims to investigate the crystallization from an amorphous complex with SBN stoichiometry of Bi-layered perovskite-type nanocrystallites of the Aurivillius phase via an intermediate fluorite-SBN phase. Raman scattering has been used prominently to determine the nucleation of the different phases. The different Raman features characteristic of each phase and its evolution with thermal treatment and microstructural changes are presented. The use of a Raman microprobe allows the local study of the nanocrystallites in the analyzed areas ($\sim 2\ \mu m^2$).

2. Experimental

2.1. Preparation of the Nb-precursor

The preparation of aqueous Nb-, Bi-, and Sr-precursors have been described previously.[11–15] Aqueous solution–gel synthesis of ceramics containing group Vb metals (like Nb in SBN) is very complicated since very few salts are water-soluble because of the high valency and the subsequent fast hydrolysis. Nevertheless, a stable aqueous Nb-precursor can be prepared starting from Nb-oxalate.[12] A peroxo-citrato-niobium(V) precursor solution is prepared by a synthesis route similar to that of Narendar et al.[13] Although Nb-oxalate is water-soluble, it is however not suitable for gel formation. The first synthesis step comprises the dissolution of niobium(V) ammonium oxalate in an aqueous solution of citric acid and hydrogen peroxide. After heating this mixture at 150 °C, a yellow precipitate of niobic acid is formed. After isolating it by filtration, this Nb-compound is used as Nb-source for synthesis.

2.2. Preparation of the Bi-precursor

An aqueous Bi-precursor is obtained by dissolution of Bi-citrate in water and ethanolamine.[14,15]

2.3. Preparation of the SBN-precursor

The three-metallic SBN-solution is prepared by the addition of Sr-acetate to a mixture of the Nb- and the Bi-precursor solutions in stoichiometric amounts. In order to obtain a stable solution, an excess of citric acid has to be added.

2.4. Thermal treatments

To induce the formation of SBN crystallites, we used thermal treatment at 550, 650, 700 and 750 °C for 2 h at a rate of 5 °C/min.

2.5. Powder X-ray diffraction

The crystalline structure and phase purity of the obtained samples were characterized the X-ray powder diffraction (XRD), using a Siemens D5000 diffractometer with Cu Kα radiation. The XRD patterns were collected with an angle step of 0.01 for all measurements.

2.6. Raman

Raman spectra of all the samples were recorded at room temperature on a Jobin Yvon T64000 Raman microspectrometer equipped with a triple monochromator and a coupled-charge device detector.

2.7. SEM

Samples were observed in an JEOL apparatus after Pt–Pd coating.

3. Results

X-ray diffraction. The evolution of XRD patterns after different thermal treatments is shown in Fig. 1. Patterns 1a and b, measured after thermal treatment up to 400 °C, clearly reveal the amorphous nature of the SBN precursor. The XRD patterns 1c and d, after treatment up to 600 °C, show characteristic peaks corresponding to the planes (1 1 1), (2 0 0), (2 2 0) and (3 1 1) of a SBN-fluorite phase. The patterns have broad diffraction peaks, attributed to a very small crystallite size of the SBN fluorite nanocrystallites. The crystallite size calculated using the Scherrer equation

$$L = \frac{0.9\lambda}{\beta \cos \theta}$$

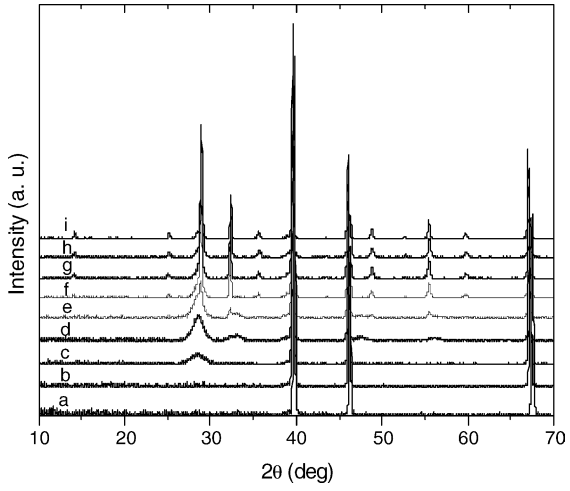

Fig. 1. XRD pattern after thermal treatment at 25 °C (a), 400 °C (b), 500 °C (c), 600 °C (d), 625 °C (e), 650 °C (f), 700 °C (g), 800 °C (h) and 900 °C (i).