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Ceramics International 30 (2004) 613–617

CERAMICS
INTERNATIONAL

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Low temperature preparation of strontium barium niobate powders from metal carboxylate gels

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Received 28 April 2003; received in revised form 8 May 2003; accepted 28 July 2003

Abstract

$Sr_xBa_{1-x}Nb_2O_6$ ($x = 0.4, 0.5, 0.6$) ceramic powders have been synthesized by using the aqueous organic gel routes. The desired metal cations are chelated in a solution using citric acid and ethylenediaminetertraacetic acid (EDTA) as the chelating agents. The thermal decompostion of the metal carboxylate precursors gels have been studied by TG/DTA and the products derived from calcinations of the gels at different temperatures have been characterized by XRD and TEM. The results reveal that tetragonal tungsten–bronze-type SBN with fine particle size could be achieved at 800 °C. The pH 8 used during the preparation of Sr–Ba–Nb precursor gels is determined by calculation of the conditional formation constants K_{cf} of Sr–EDTA and Ba–EDTA complexes. The influences of the pH and the molar ratio of citric acid:Nb cation on the formation of homogeneous Sr–Ba–Nb precursor gels are also studied.

Keywords: A. Powders: chemical preparation; D. Niobates; Metal carboxylate

1. Introduction

Strontium barium niobate $Sr_xBa_{1-x}Nb_2O_6$, SBN, ($0.25 < x < 0.75$) is a ferroelectric solid solution between $BaNb_2O_6$ and $SrNb_2O_6$ which has a tetragonal tungsten–bronze type structure [1]. SBN single crystal has many technological applications such as electro-optic, pyroelectric, piezoelectric, and photorefractive devices because of its excellent pyroeletric and linear electro-optic effects with low half-wave voltage and photo refractive sensitivity [2–4]. In addition, it has advantage with lead-free composition which is concerned with environment, safety and health.

In recent years, SBN ceramics has been receiving great attentions due to the advantages of its low cost, easy fabrication, large size, complex shape and high stress resistance compared with the SBN single crystal. SBN powders are traditionally prepared by the solid state reaction of oxides and carbonates at ∼1050 °C [5]. But the requirements for low processing temperature, higher purity, precisely controlled stoichiometry and optimal powder characteristics particularly need non-conventional powder preparation techniques. Wet chemical routes, which makes the above requirements possible are used to synthesize the SBN powders [6,7]. Among the various wet chemical powder preparation methods, the aqueous organic gel route is becoming increasingly important. The process produces inorganic powders using polyfunctional carboxylic acid and metal salts to form soluble metal carboxylate complexes in amorphous solid precursor which can form the desired compound after firing at elevated temperatures. The advantages of the aqueous organic gel methods are homogeneous mixing at molecular level, good stoichiometric control, low processing temperature, use of an aqueous based processing system and the production of active powders. Although there have been some reports about the preparation of powders of several ferroelectrics ceramics powders such as lead magnesium niobate (PMN), $SrTiO_3$, PZT, $SrBiNb_2O_9$ by organic-gel methods [8–11], systematic studies about the SBN powders synthesized by this method have not yet been reported in the literature to our knowledge. Moreover, there are several processing parameters deserving studying, such as, the pH value of the precursor solution, the molar ratio of cations and the polyfunctional carboxylic acid which would influence the chelation between the cations and the associated acid ions, and affect the thermal decompositon of the precursor gel.

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doi:10.1016/j.ceramint.2003.07.007

The aim of this work was to determine the feasibility of utilizing aqueous organic gel route to produce SBN ceramic powders and to investigate the process of gel conversion. In addition the effect of the pH and the molar ratio of metal cations and carboxylic acid on the stability of Sr-Ba-Nb precursor metal carboxylate gel was also investigated.

2. Experimental procedure

The starting materials used were $Ba(NO_3)_2$, $Sr(NO_3)_2$, Nb_2O_5, EDTA, ammonia solution, citric acid, and ethylenediaminetertraacetic acid (EDTA). we used the citric acid and EDTA as the chelating agents. For preparation of Ba–EDTA and Sr–EDTA complexes, the barium nitrate and strontium nitrate were separately dissolved in deionized water and mixed with aqueous EDTA. The required amount of ammonia solution was added to achieve $pH > 7$ to form transparent Ba–EDTA and Sr–EDTA complexes. Then the pH of the solution was adjusted to 7 by using nitric acid.

The procedure for preparation of Nb–citrate complex was similar to that of the Nb–tartarate complex which was reported previously [12]. Nb_2O_5 was dissolved in HF to form ${NbOF_5}^{2-}$ or ${NbF_7}^{2-}$ complexes by heating for 48 h. Aqueous solution of ammonium oxalate was added to the solution, keeping the oxalate ions in excess. Then ammonia solution was added with continuous stirring to form a precipitation of hydrous niobium oxide ($Nb_2O_5{\cdot}nH_2O$). The precipitation was aged at 80 °C for 12 h, after which it was filtered and washed with water to make the fluoride free. The hydrous niobium oxide was then dissolved in aqueous solution of citric acid by continuous stirring and heating at 60 °C to form a transparent pale yellow Nb–citrate complex. The concentrations of metal ions in the solution were determined by using inductively coupled plasma (ICP) emission spectrochemical analysis.

For preparation of $Sr_xBa_{1-x}Nb_2O_6$ ($x = 0.4, 0.5, 0.6$) ceramic powders, stoichiometric amounts of Ba–EDTA, Sr–EDTA, and Nb–citrate solutions were mixed together, followed by addition of citric acid in the molar ratio of citric acid:Nb = 3:1. The pH was adjusted to 8 by the addition of ammonia solution and then a clear transparent Sr–Ba–Nb precursor solution had high stability and no precipitation for several months after preparation was obtained with continuous stirring.

The Sr–Ba–Nb precursor solution was heated at 80 °C for 24 h to produce a gelatinous precursor which was then calcined between 400 and 800 °C for 2 h in air to form the SBN powders. The procedure for preparation of SBN powders is shown in Fig. 1.

Thermal analysis and thermogravimetric analysis were used to analyze the thermal decomposition behavior of the gelatinous precursor with a heating rate of 10 °C min^{-1} in air up to 800 °C. The phase compositions of the heat-treated

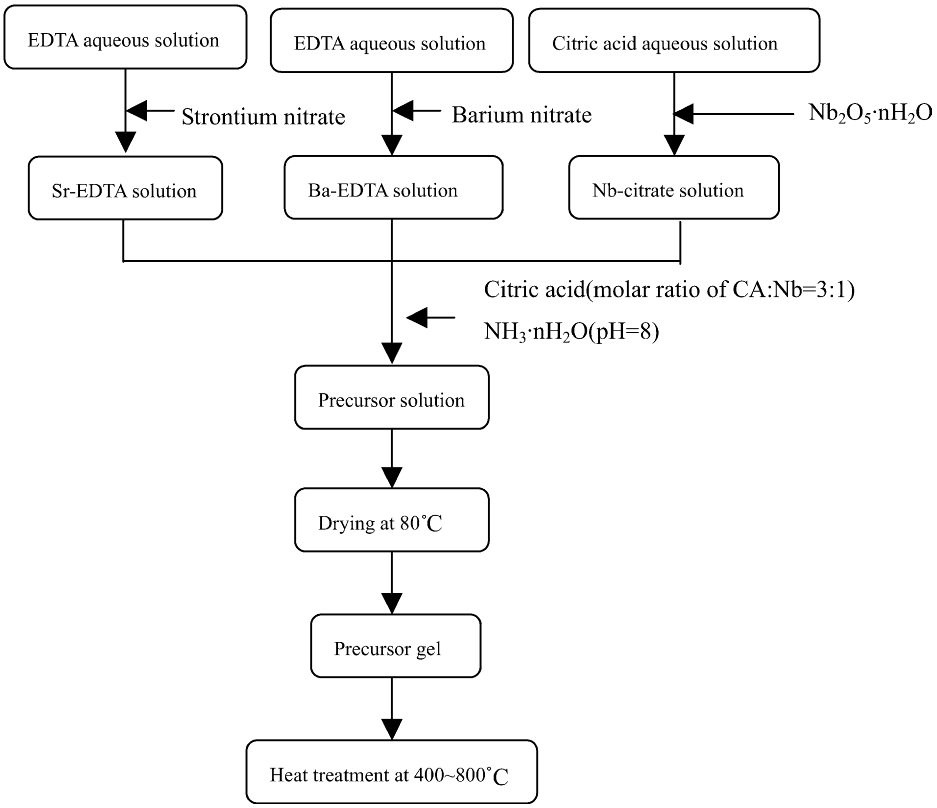

Fig. 1. Flow chart for preparation of SBN powders from the metal carboxylate gels.

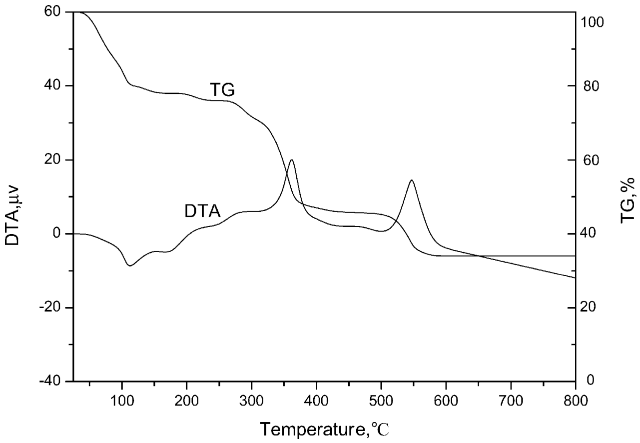

Fig. 2. TG/DTA curves of the Sr–Ba–Nb precursor gel (pH8).

powders were analyzed by using X-ray diffraction. The microstructure and the particle distribution studies were performed on a transmission electron microscope (TEM, Philips CM12/STEM, Holland).

3. Results and discussion

Fig. 2 shows the DTA and TG curves of the precursor gel of SBN. The TG–DTA curve involves three primary stages. The first stage weight loss of ~22% corresponding to a broad endothermic event occurs between 50 and 200 °C, which can be attributed to the loss of free and bound water from the gels. The second stage weight loss of 25% between 300 and 400 °C corresponds to an exothermic peak. This can be attributed to the decomposition of the metal carboxylate gels and liberation of NO_2, CO_2, and H_2O. The third weight loss of 12% between 500 and 600 °C corresponding to another exothermic peak may be due to the oxidation of the residual organic groups in the gel. No further weight loss up to 800 °C, and no clear exothermic peak corresponding to SBN crystallization was found.

Fig. 3 shows XRD patterns of the samples obtained by heating the precursor gels in air at 400–800 °C for 2 h. A clear transition from amorphous state to crystalline state could be noticed in Fig. 3. The precursor was amorphous in structure, as shown by the broad continuum in Fig. 3a, which required to be calcined at elevated temperature to yield SBN powder. We detected the first appearance of tetragonal tungsten–bronze phase SBN in the sample heated at 500 °C. As the temperature increased, the intensities of the diffraction peaks were strengthened and until the temperature raised to 800 °C, a single SBN phase was completely synthesized. The precursor completely transformed into SBN after 2 h at 800 °C. The diffraction of the powders is somewhat complex because of the complex structure of tungsten–bronze-type compounds. From the XRD results, it can be shown that crystalline SBN phase was derived from the amorphous metal carboxylate gel by calcining without passing through any intermediate metal-oxide phases which indicates that appropriate chemical homogeneity in the amorphous precursors.

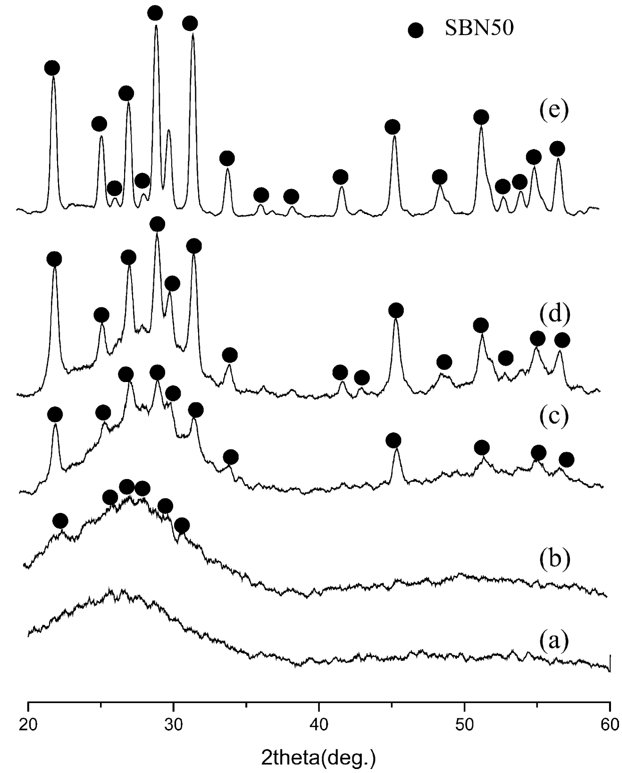

Fig. 3. X-ray diffractograms of the products calcined at (a) 400 °C, (b) 500 °C, (c) 600 °C, (d) 700 °C, and (e) 800 °C.

It suggests that pH value might affect the chelation between the cation and the associated carboxylate acid ion. In this work, the pH value of 8 was used during the synthesis of SBN powders which was determined by calculation of the conditional formation constants K_{cf} of Sr–EDTA and Ba–EDTA complexes, where K_{cf} represents the modified formation constant for the following complexing reactions:

$$M^{2+}+Y^{4-} \Leftrightarrow MY^{2-} \tag{1}$$

where M^{2+} is divalent metal ions, such as Ba^{2+}; Sr^{2+}; $Y^{4-} = (CH_2N)_2(CH_2COO)_4{}^{4-}$. And the formation constant for reaction (1) is given by

$$K_f = \frac{[MY^{2-}]}{[M^{2+}][Y^{4-}]} \tag{2}$$

In aqueous solution, EDTA can remain as the compound H_4Y or disassociate increasing numbers of protons to form the species H_3Y^-, H_2Y^{2-}, HY^{3-} or Y^{4-} with the proportions of these species varying with pH values [13]. Since the anion Y^{4-} is the ligand species in complex formation, the complexation equilibria (Eq. (1)) affected markedly by the pH is shifted to left as hydrogen ion concentration increases, due to competition for the chelating anion by hydrogen ion. Taking into account the competing reactions for the formation of the alternatively protonated forms of EDTA as a function of pH according to the following:

$$K_{\mathrm{cf}} = \alpha_4 K_{\mathrm{f}} \tag{3}$$

$$\frac{1}{\alpha_4} = \frac{\mathrm{C_{H_4Y}}}{[\mathrm{Y^{4-}}]} = 1 + \frac{[\mathrm{H^+}]}{\mathrm{K_{a_4}}} + \frac{[\mathrm{H^+}]^2}{\mathrm{K_{a_3}K_{a_4}}} + \frac{[\mathrm{H^+}]^3}{\mathrm{K_{a_2}K_{a_3}K_{a_4}}} + \frac{[\mathrm{H^+}]^4}{\mathrm{K_{a_1}K_{a_2}K_{a_3}K_{a_4}}}$$

where α_4 is the fraction of the total EDTA species that exists as $\mathrm{Y^{4-}}$. $\mathrm{C_{H_4Y}}$ represent the total concentration of all forms of uncomplexed EDTA, it can be given by

$$\mathrm{C_{H_4Y}} = [\mathrm{Y^{4-}}] + [\mathrm{HY^{3-}}] + [\mathrm{H_2Y^{2-}}] + [\mathrm{H_3Y^{-}}] + [\mathrm{H_4Y}]$$

K_{a_i} ($i = 1, 2, 3, 4$) are the dessociation constants of the variously protonated $\mathrm{H_3Y^-}$, $\mathrm{H_2Y^{2-}}$, $\mathrm{HY^{3-}}$, and $\mathrm{Y^{4-}}$ forms of EDTA in aqueous solution, with the value 1.0×10^{-2}, 2.2×10^{-3}, 6.9×10^{-7} and 5.5×10^{-11}, respectively [13]. Moreover, the formation constants of Ba–EDTA and Sr–EDTA chelates are 5.75×10^7 and 4.26×10^8, respectively [14], then the values of K_{cf} for various pH values can be calculated according to Eq. (3) and are shown in Table 1. The data show that with the increase of the pH, both the value of α_4 and K_{cf} increase indicating that more EDTA is ionized and more carboxylic groups can be available to chelate the metallic ions in the solution at higher pH conditions. When the pH value is above 8, the conditional formation constant is high enough to form stable metal EDTA complexes. In addition, Narendar and Messing [15] reported that the citrate–niobium bond is unstable at pH < 5, and the precipitation of niobium hydrate is observed. Consequently, the stable Sr–Ba–Nb gels should be synthesized at pH > 8 to ensure complete chelation of all the cations according to the above results.

In order to evaluate the calculation results, the stability of the Sr–Ba–Nb precursor solution and precursor gel at various pH values are investigated in the experiment. The results are illustrated in Table 2. It shows that the calculation results are consistent with the observations, that is, obtaining clear precursor gel without precipitation depends on the pH of the solution and no precipitations occurred at pH > 8 when the molar ratio of citric acid:Nb = 3:1 in this investigation. While at lower pH value, white colored precipitates which might be nitrates and niobium hydrate were formed indicating that incomplete complexation of the metal ions took place in a acid medium.

Table 1
Conditional formation constants K_{cf} of Ba–EDTA, Sr–EDTA complexes at different pHs

pH	α_4	Ba–EDTA	Sr–EDTA
2	4.1×10^{-14}	2.36×10^{-6}	1.75×10^{-5}
3	6.3×10^{-11}	3.62×10^{-3}	2.68×10^{-2}
4	3.6×10^{-9}	2.07×10^{-1}	1.53
5	3.5×10^{-7}	2.01×10	1.49×10^{2}
6	2.2×10^{-5}	1.27×10^{3}	9.37×10^{3}
7	4.8×10^{-4}	2.76×10^{4}	2.04×10^{5}
8	5.4×10^{-3}	3.11×10^{5}	2.30×10^{6}
9	5.2×10^{-2}	2.99×10^{6}	2.22×10^{7}
10	3.5×10^{-1}	2.01×10^{7}	1.49×10^{8}
11	8.5×10^{-1}	4.89×10^{7}	3.62×10^{8}
12	9.8×10^{-1}	5.64×10^{7}	4.17×10^{8}

Table 2
Experimental parameters and stability of the Sr–Ba–Nb precursor solutions and gels

pH	Molar ratio of citric acid/Nb	State of precursor solution	State of gel
2	1:1	White precipitate	Muddy gel
2	3:1	White precipitate	Muddy gel
4	1:1	White precipitate	Muddy gel
4	3:1	White precipitate	Muddy gel
6	1:1	White precipitate	Muddy gel
6	3:1	Yellowish clear solution	Muddy gel
8	1:1	Yellowish clear solution	Muddy gel
8	3:1	Yellowish clear solution	Transparent gel
10	1:1	Yellowish clear solution	Transparent gel
10	3:1	Yellowish clear solution	Transparent gel
12	1:1	Yellowish clear solution	Transparent gel
12	3:1	Yellowish clear solution	Transparent gel

To facilitate the formation of stable Sr–Ba–Nb precursor solution, ammonia additions were used in this work as an easily removed pH modifier to obtain larger pH value. And then ammonium nitrate was produced by reaction of the ammonia with the $\mathrm{NO_3}$ groups from the barium nitrate and strontium nitrate. This compound greatly accelerates the decomposition of the gel precursors on heating, producing strongly exothermic reactions.

The DTA curves (Fig. 4) of the samples obtained at different pH values showed that the exothermic peaks for the thermal decomposition reaction changes with the pH of the solution. The sharp decomposition of the precursor gel at pH 12 leads to generation of large amount of heats, while the exothermic peaks of the other pHs are relatively weak.

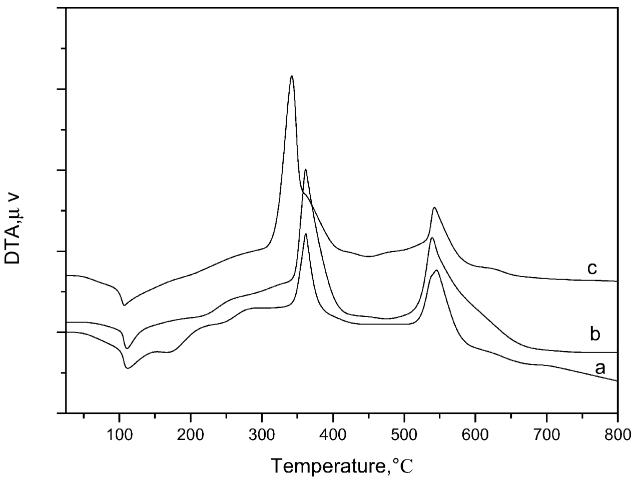

Fig. 4. DTA curves of the Sr–Ba–Nb precursor gel obtained at different pH values.

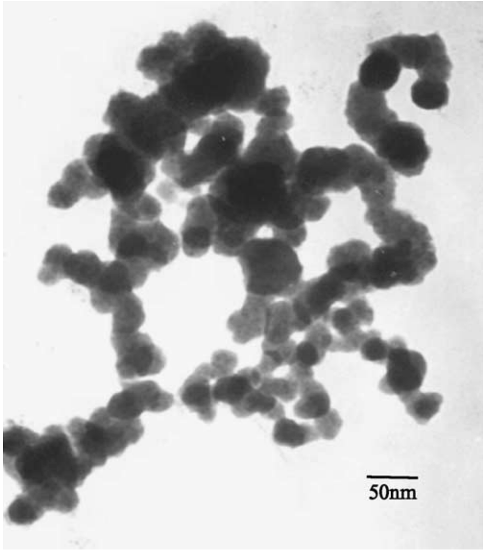

Fig. 5. TEM micrograph of SBN powder obtained at 800 °C.

The strongly exothermic reactions can result in coarsening of the resultant particles due to the generated heat [16]. Consequently, the addition of excess of ammonia is generally deleterious and to be avoided in the synthesis of SBN by using the organic gel routes. So the optimum pH value for the formation of clear homogeneous precursor gel is 8.

TEM was used to estimate the particle size and morphology for metal carboxylate gel derived powders heated for 2 h at 800 °C (Fig. 5). It clearly shows uniform sized and weakly agglomerated SBN particles have an average size of about 30–50 nm.

The concentration of citric acid also has an influence on the chelation of metal cations. The effect of the citric acid is also shown in Table 2. It can be seen that the citric acid also plays an important role in forming stable Sr–Ba–Nb precursor solution and gel, which are generally stabilized in excess of citric acid. The precipitates can be circumvented in the precursor solution as the molar ratio of citric acid:Nb increases from 1:1 to 3:1 at pH = 6. However, precipitation and an unclear gel were observed during the thickening of the solution upon drying. Consequently, the optimum molar ratio of citric acid:Nb cations for obtaining homogeneous Sr–Ba–Nb precursor gel is 3:1.

4. Conclusions

(1) $Sr_xBa_{1-x}Nb_2O_6$ ($x = 0.4, 0.5, 0.6$) ceramic powders have been prepared from the metal carboxylate gel annealing at a low temperature of 800 °C. XRD and TEM studies have shown that tetragonal tungsten–bronze-type SBN powders with nanoparticle size could be achieved.

(2) The pH of the precursor solution and molar ratio of citric acid and metal cations plays an important role in the formation of stable metal carboxylate gels. Increasing the concentration of citric acid and pH values can circumvent the precipitate in the precursor gel and ensure complete chelation of all the cations.

(3) A homogeneous Sr–Ba–Nb precursor gel with no precipitate was formed at pH 8 and the optimum molar ratio of citric acid and the metal cations for obtaining is 3:1.

Acknowledgements

This work was financially supported by the National Nature Science Foundation of China under Grant No. 20171015 and the Multidisciline Scientific Research Foundation of Harbin Institute of Technology (HIT.MD.2002.03). The first author is gratefully acknowledged.

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