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Low temperature preparation of nanocrystalline $Sr_{0.5}Ba_{0.5}Nb_2O_6$ powders using an aqueous organic gel route

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Abstract

Nano-sized $Sr_{0.5}Ba_{0.5}Nb_2O_6$ (SBN50) ceramic powders have been synthesized by an aqueous organic gel route. Homogeneous Sr–Ba–Nb precursor gels are prepared with Ba–EDTA, Sr–EDTA, and Nb–citrate complex as source of Sr, Ba, and Nb, respectively. Citric acid and ethylenediaminetetraacetic acid (EDTA) were used as the chelating agents. The structural variation of the SBN powder with annealing temperature was studied by TG–DTA, FT-IR and XRD. The precursor gel on calcination at 800 °C for 2 h produces a pure tungsten bronze SBN phase and the corresponding average particle size is 30–50 nm. The influences of the pH and the molar ratio of citric acid:Nb cation on the formation of homogeneous Sr–Ba–Nb precursor gels were also studied. The results show that a homogeneous Sr–Ba–Nb precursor gel with no precipitate is formed at pH 8 and the optimum molar ratio of citric acid and the metal cations is 3:1.

Keywords: A. Metals; A. Oxides; B. Chemical synthesis

1. Introduction

$Sr_xBa_{1-x}Nb_2O_6$ (SBN, where $0.25 < x < 0.75$) ceramics are ferroelectric materials with tungsten bronze-type structure [1], which have excellent electro-optic, pyroelectric, photorefractive, and pyroelectric properties [2–4]. The chemical and microstructural homogeneity of alkali-earth metal niobates affects critically the electro-optic behavior, and therefore the synthesis of ceramics powders with good stoichiometry, homogeneity, and sinterability is necessary to develop SBN ceramics. Traditional solid state preparation method leads to poor compositional homogeneity and high sintering

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temperature. In resent years, several wet chemical processing techniques, have been used to synthesize the SBN powders [5,6].

Among the various wet chemical powder preparation methods, the aqueous organic gel route is becoming increasingly important. The advantages of this method are homogeneous mixing at molecule-level, good stoichiometric control, low processing temperature, use of an aqueous based processing system, and the production of active powders. Aqueous organic gel method has been applied for a range of materials such as lead magnesium niobate (PMN), $SrTiO_3$, PZT, and $SrBiNb_2O_9$ [7–10], but has so far been not applied for the SBN powders.

In the present work, we reported the preparation of $Sr_{0.5}Ba_{0.5}Nb_2O_6$ (SBN50) using aqueous organic gel method. The process produces inorganic powders by 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. In addition, the effect of several processing parameters such as, the pH value of the precursor solution, the molar ratio of metal cations and the carboxylic acid on the stability of Sr–Ba–Nb precursor gel was also investigated.

2. Experimental procedure

2.1. Preparation of SBN powders

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 [11]. 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. 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.

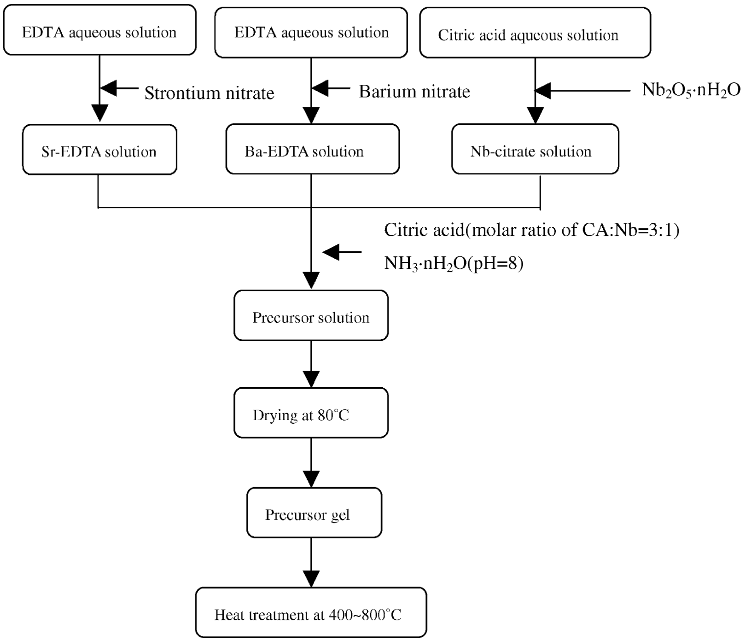

Fig. 1. Flow chart for preparation of SBN powders from the metal carboxylate gels.

2.2. *Characterization of SBN precursors and powders*

To study the decomposition behavior of SBN precursors, each precursor solution was dried at 80 °C for 24 h and the obtained precursor powders were ground gently. Differential thermal analysis (DTA) and thermogravimetry (TG) (TG–DTA 2000, Japan) were used to analyze the thermal decomposition behavior of the powdered precursors with a heating rate of 10 °C min^{-1} in air up to 800 °C. The crystallization process of the SBN gel powders was studied by Fouries trasform infrared (FT-IR) spectroscopy (Nicolet 520 FT-IR spectrometer) and X-ray diffractometry (Siemens 5000). 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.

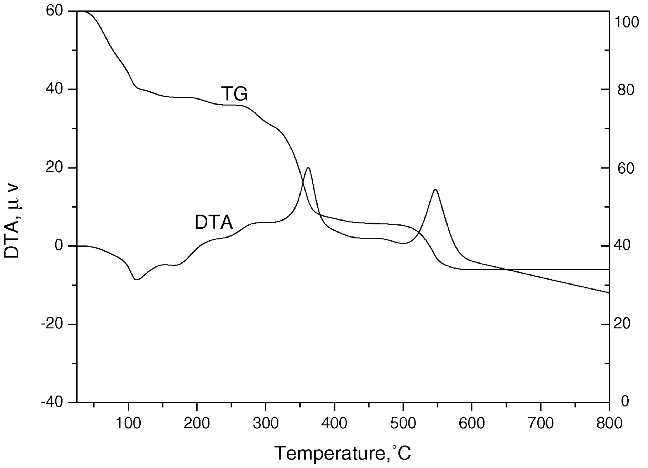

Fig. 2. TG–DTA curves of the Sr–Ba–Nb precursor gel pH 8).

Fig. 3 shows the FT-IR spectra of gel powders annealed for 2 h at various temperatures. The spectrum of the gel powder as prepared indicates a COO^- group with vibrations at 1418 and 1589 cm^{-1} (Fig. 3(a)). These absorption bands remain in the spectrum of the powders heat-treated at 500 °C, but reduce with heat treatment at higher temperatures. When the annealing temperature reaches 600 °C, the absorption peaks associated with the COO^- groups disappear due to the decomposition of the organic compounds and the band of Sr–O, Ba–O, and Nb–O between 500 and 850 cm^{-1} becomes prominent. In the spectra of the powders heat-treated at 500–600 and 800 °C, the 2337 cm^{-1} band corresponds to carbon dioxide (O=C=O). The O=C=O absorption bands appear in the spectra because the carboxylic group present in the powder burn to CO_2 during heating and some of the CO_2 molecules are adsorbed on the powders. The ~3400 cm^{-1} absorption band could be from the water molecules in the powders.

Fig. 4 shows XRD patterns of the precursor gel powder and the products calcined in air at a series of increasing temperatures. A clear transition from amorphous state to crystalline state could be noticed in Fig. 4. The basic gel is amorphous but contains a small amount of NH_4NO_3 as a minor phase. The NH_4NO_3 minor phase decomposes when heated to 400 °C and the diffraction peaks of NH_4NO_3 disappear. The product calcined at 400 °C is amorphous in structure, which required to be calcined at elevated temperature to yield SBN powder. We detect 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 are strengthened and after the temperature is raised to 800 °C, a single SBN phase is completely synthesized. This indicates that the SBN phase, which usually forms at high temperatures in conventional method (~1050 °C) [12], has been formed at a lower temperature by using organic gel method. The diffraction pattern of the SBN phase 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 is 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 has been achieved.

The pH value should affect the degree of 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

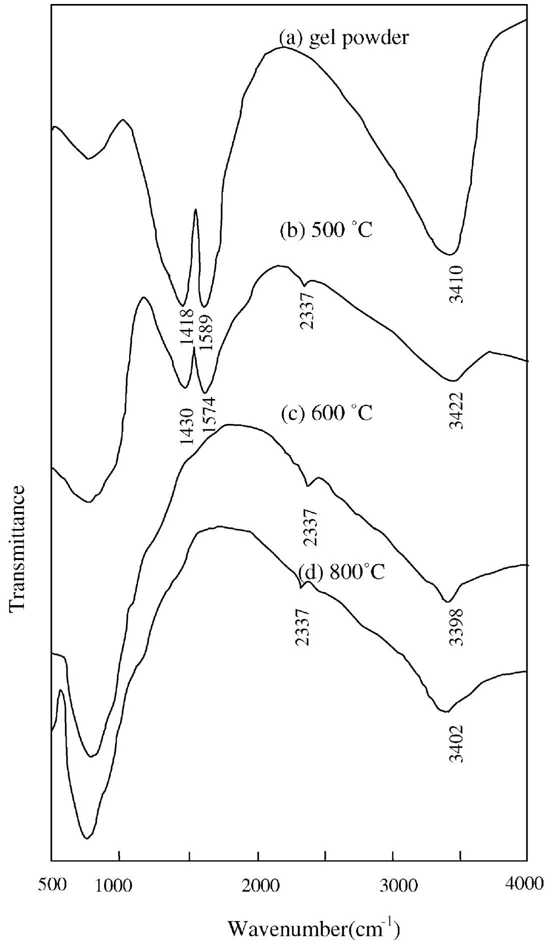

Fig. 3. Changes in FTIR spectra of gel powders with heat treatment at various temperatures.

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+}; $Y^{4-} = (CH_2N)_2(CH_2COO)_4^{4-}$. 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

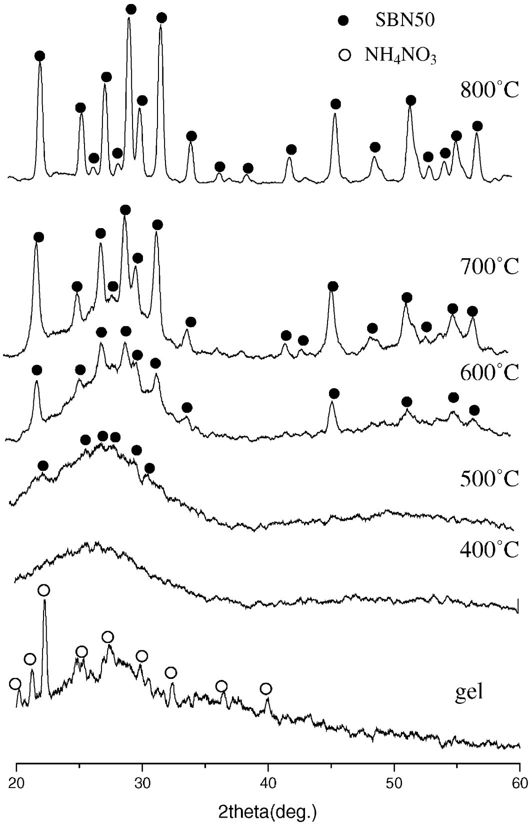

Fig. 4. X-ray patterns of the precursor gel powder and the products calcined in air at a series of increasing temperatures.

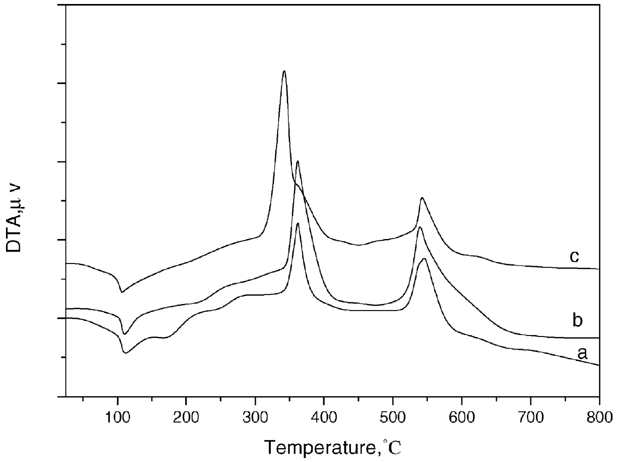

Fig. 5. DTA curves of the Sr–Ba–Nb precursor gel obtained at different pH values.

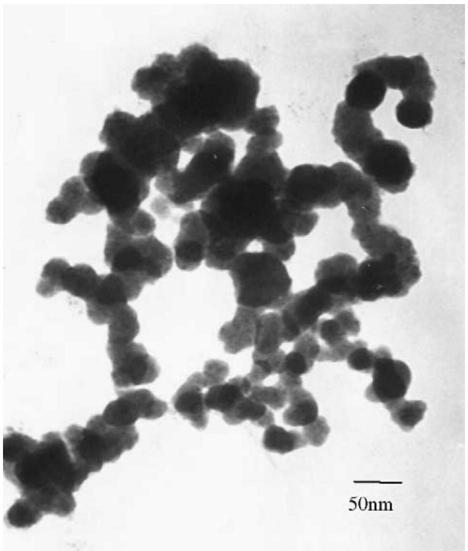

Fig. 6. TEM micrograph of SBN powder obtained at 800 °C.

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:

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

$$\frac{1}{\alpha_4} = \frac{\mathrm{C}_{\mathrm{H_4Y}}}{[\mathrm{Y}^{4-}]} = 1 + \frac{[\mathrm{H}^+]}{\mathrm{K}_{a4}} + \frac{[\mathrm{H}^+]^2}{\mathrm{K}_{a3}\mathrm{K}_{a4}} + \frac{[\mathrm{H}^+]^3}{\mathrm{K}_{a2}\mathrm{K}_{a3}\mathrm{K}_{a4}} + \frac{[\mathrm{H}^+]^4}{\mathrm{K}_{a1}\mathrm{K}_{a2}\mathrm{K}_{a3}\mathrm{K}_{a4}}$$

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

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

K_{ai} ($i = 1,2,3,4$) are the dissociation constants of the variously protonated $\mathrm{H_4Y}$, $\mathrm{H_3Y}^-$, $\mathrm{H_2Y}^{2-}$ and HY^{3-} forms of EDTA in aqueous solution, with the values of 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 [15] has reported that the citrate–niobium bond is unstable at $\mathrm{pH} < 5$, and the precipitation of hydrous niobium oxide is observed. Consequently, the stable Sr–Ba–Nb gels should be synthesized at $\mathrm{pH} > 8$ to ensure complete chelation of all the cations according to the above results.

Table 1
Conditional formation constants K_{cf} of Ba, 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}

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. At lower pH values, white precipitates, which might be nitrates and niobium hydrate were formed indicating that incomplete complexation of the metal ions took place in a acid medium.

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 higher pH values. Further, ammonium nitrate will be produced by reaction of the ammonia with the NO_3^- groups from the barium nitrate and strontium nitrate as water is removed. This compound greatly accelerates the decomposition of the gel precursors on heating, producing strongly exothermic reactions.

The DTA curves (Fig. 5) 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

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

decomposition of the precursor gel at pH 12 leads to generation of a large amount of heat, while the exothermic peaks of the other pHs are relatively weak. 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. 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. 6). It clearly shows uniform sized and weakly agglomerated SBN particles having 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

Strontium barium niobate ($Sr_{0.5}Ba_{0.5}Nb_2O_6$) powders have been synthesized by using an aqueous organic gel route. XRD and FT-IR studies have shown that tetragonal tungsten bronze-type SBN powders with nano particle size could be achieved from the metal carboxylate gel annealing at a low temperature of 800 °C. The pH of the precursor solution and molar ratio of citric acid and metal cations play an important role in the formation of stable Sr–Ba–Nb precursor gels. 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 is 3:1.

Acknowledgements

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