Ceramics International 32 (2006) 475–477

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Short communication

A co-precipitation technique to prepare $CaNb_2O_6$

V. Ravi [a,*], S.C. Navale [b]

[a] *Physical and Materials Chemistry Division, National Chemical Laboratory, Pune 411008, India*
[b] *Polymer Science and Engineering Division, National Chemical Laboratory, Pune 411008, India*

Received 5 February 2005; received in revised form 28 February 2005; accepted 15 March 2005

Abstract

A mixture of ammonium oxalate and ammonium hydroxide was used to co-precipitate calcium and niobium ions as calcium oxalate and niobium hydroxide under basic conditions. This precursor yielded $CaNb_2O_6$ (CN) ceramics on calcining at 750 °C, i.e. at a temperature much lower than 900 °C, reported for the formation of $CaNb_2O_6$ prepared by the traditional solid state method. Transmission electron microscope (TEM) investigations revealed an average particle size 100 nm for the calcined powders. The room temperature dielectric constant at 1 kHz was found to be 100. The ferroelectric hysteresis loop parameters of these samples were also studied.

Keywords: A. Powders: chemical preparation; B. X-ray methods; B. Electron microscopy

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1. Introduction

ANb_2O_6 (A = Ba, Sr and Ca) compounds find wide applications in electro-optic, pyroelectric and photorefractive applications [1–3]. The microwave dielectric properties of $CaNb_2O_6$ were also reported in the literature [4,5]. Since, the microstructure of the alkali-earth metal niobates affects critically the optical properties, synthesis of these ceramic powders with good sinterability and compositional homogeneity is needed. The traditional solid state method leads to poor compositional homogeneity and high sintering temperatures. Chemical methods, e.g. co-precipitation, sol–gel, hydrothermal and colloid emulsion have been confirmed to efficiently control the morphology and chemical composition of prepared powder. Recently, a organic gel route has been reported for the strontium barium niobate [6]. We have also reported a low temperature synthesis route for the preparation of $BaNb_2O_6$ powders [7]. Here we communicate a simple co-precipitation procedure to prepare $CaNb_2O_6$ ceramics at low temperature. Co-precipitation is one of the more successful techniques for synthesizing ultrafine ceramic powders having narrow particle size distribution [8–10]. This process can avoid complex steps such as refluxing of alkoxides, resulting in less time consumption compared to other techniques. The limitation of this process is that cations should have similar solubility.

2. Experimental

For preparing $CaNb_2O_6$, niobium(V) oxide and calcium chloride were used as the starting materials (AR grade). Nb_2O_5 was dissolved in minimum amount of HF after heating in a hot water bath for 10 h. To this NbF_5 solution, the required quantity of $CaCl_2{\cdot}2H_2O$ was added and accurately mixed. A mixture of ammonium oxalate and ammonium hydroxide was added dropwise to precipitate niobium and calcium as hydroxide and oxalate, respectively. The pH was maintained around 9 to ensure completion of the reaction. Then, the precipitated precursor powder was filtered and oven dried, then calcined at different temperatures from 400 to 1000 °C for 6 h. XRD (Philips PW 1710 Diffractometer) and TEM were used to characterize the powders. For lattice parameter and interplanar distance (d) calculation, the samples were scanned in the 2θ range of 10–80° for the period of 5 s in the step scan mode. Silicon was

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[*] Corresponding author. Tel.: +91 20 5893300; fax: +91 20 5893044.
E-mail address: ravi@ems.ncl.res.in (V. Ravi).

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doi:10.1016/j.ceramint.2005.03.027

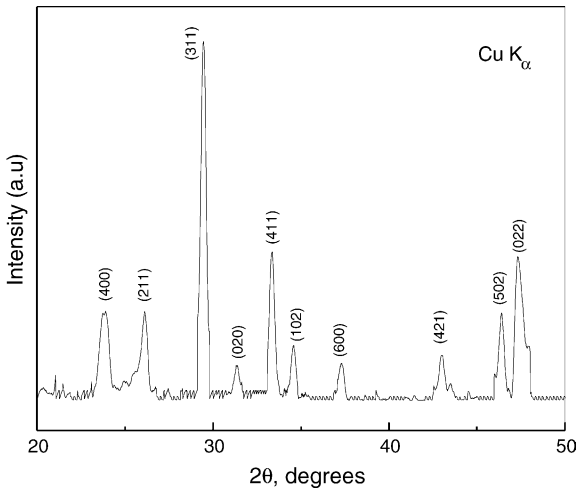

Fig. 1. XRD of calcium niobate after annealing the precursor at 750 °C.

used as an internal standard. Least squares method was employed to determine the lattice parameters. The TEM picture was recorded with JEOL model 1200 EX instrument at the accelerating voltage of 100 kV. The fine powders were dispersed in amyl acetate on a carbon coated TEM copper grid. For comparison, calcium niobate samples were also prepared by the ceramic method. The corresponding oxides or carbonates are taken in stoichiometric ratio and mixed, ground several times and heated at 900 °C for 72 h. The calcined powders (from both precursor derived and ceramic method) were mixed with few drops of 1 wt.% solution of poly vinyl alcohol and pelletized at 1–2 t. The green pellets were sintered at 1300 °C for 2 h. The densities of the sintered samples were measured by Archimedes technique. The surfaces of the sintered pellet were polished and electroded with low-temperature curing silver paint. The ferroelectric hysteresis loop parameters were measured with the aid of a home-built Sawyer-Tower circuit. A LCR meter was used to measure the dielectric constant at 1 kHz.

3. Result and discussion

Fig. 1 shows the XRD pattern of the $CaNb_2O_6$ powder formed after calcining the precursor at 750 °C. The crystal structure of $CaNb_2O_6$ is orthorhombic and all the *d*-lines match with reported values (JCPDS: 31-289). The calculated lattice parameters by least square fit (two decimal

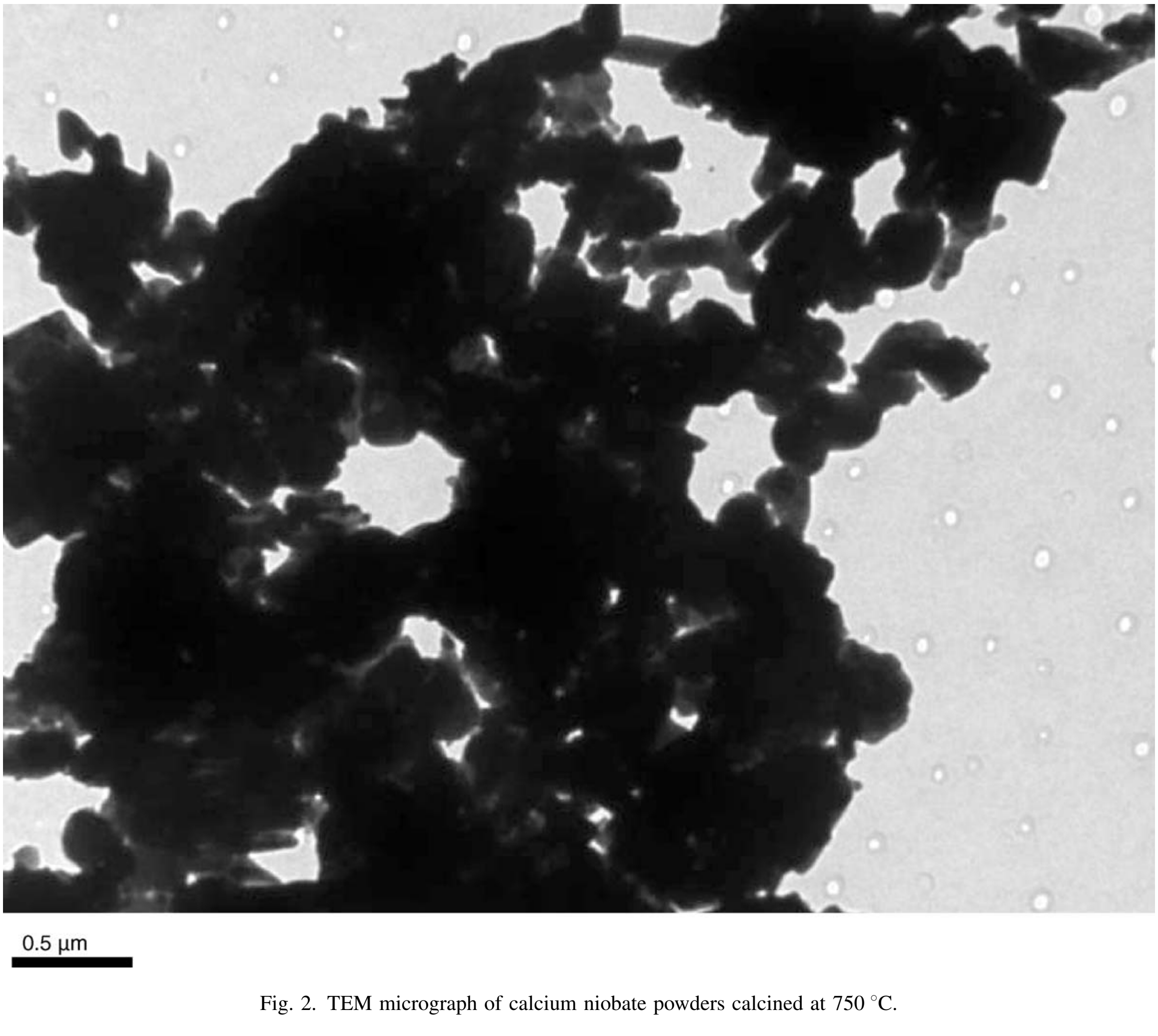

Fig. 2. TEM micrograph of calcium niobate powders calcined at 750 °C.

accurate) are $a = 15.023(1)$ Å, $b = 5.71(5)$ Å and $c = 5.24(2)$ Å. Seven hundred and fifty degree Celsius is the lowest temperature reported so far for the formation of $CaNb_2O_6$ by the coprecipitation technique. Few extra lines (low intensity) may arise from unknown impurities present or intermediate phase formed in the samples. The EDX analysis performed on these sample show the atomic percentage for Ca: 0.48 and Nb: 0.52 which may be a reason for minor difference in the observed unit cell parameters from that of reported (in JCPDS: 31-289). The particle size and morphology of the calcined powders were examined by transmission electron microscopy. The particle morphology of the calcined powder (750 °C for 6 h) prepared by this technique was irregular in shape and agglomerated, with an average primary particle size around 100 nm (Fig. 2). The particle size calculated from Scherrer's formula ($t = K\lambda/B\cos\theta_B$), where t is the average size of the particles, assuming particles are spherical, $K = 0.9$, λ the wavelength of X-ray radiation, B the full width at half maximum of the diffracted peak and θ_B is the angle of diffraction) is 120 nm. Conventional solid state method also forms the $CaNb_2O_6$ phase at 900 °C [5] after prolonged heating (72 h) with comparatively larger particle size of ~1 μm. The densities of all the sintered samples are above 92% of the single crystal values. The density of the samples prepared by the coprecipitation technique was always greater than those of prepared by the solid state method. The XRD of the sintered samples do not show any difference from that of powders indicating that phase contents remain the same. The ferroelectric hysteresis loop parameters for the present sample sintered at 1300 °C showed the values of remnant polarization $P_r = 0.8\ \mu C/cm^2$ and coercive field, $E_C = 25$ kV/cm at an applied voltage of 40 kV/cm without electric breakdown of the sample. It is well known that the ferroelectric properties obtained depends on density, grain size and defects present in the sample. The samples prepared by the ceramic technique have remnant polarization $P_r = 0.5\ \mu C/cm^2$ and coercive field, $E_C \sim 30$ kV/cm at an applied field of 50 kV/cm with no electric breakdown. The average grain size for the coprecipitation derived samples was ~2 μm whereas for the samples prepared by ceramic method was 4 μm. The room temperature dielectric constant measured at 1 kHz is 100 for the specimens prepared by the wet chemical method as compared to 90 for specimens prepared by the traditional solid state method.

4. Conclusions

A simple co-precipitation process was adopted for the preparation of ultrafine powders of $CaNb_2O_6$. The dielectric and ferroelectric properties of calcium niobate prepared by this process are also reported.

Acknowledgement

One of the authors (V.R.) acknowledges the Department of Science and Technology, (DST) India, grant no. SP/S1/H-19/2000 for financial assistance.

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