Bull. Mater. Sci., Vol. 28, No. 2, April 2005, pp. 121–123. © Indian Academy of Sciences.

Preparation of nanocrystalline ferroelectric $BaNb_2O_6$ by citrate gel method

S P GAIKWAD, VIOLET SAMUEL[†], RENU PASRICHA[‡] and V RAVI*

Physical and Materials Chemistry Division, [†]Catalysis Division, [‡]Centre for Materials Characterization, National Chemical Laboratory, Pune 411 008, India

MS received 7 April 2004; revised 3 February 2005

Abstract. A gel was formed when a aqueous solution of $BaCl_2$, NbF_5 and citric acid in stoichiometric ratio is heated on a water bath. This gel on decomposition at 600°C yielded the nano crystallites of $BaNb_2O_6$, as confirmed by X-ray diffraction study (XRD). This is a much lower temperature as compared to that prepared by traditional solid state method (1000°C) as reported for the formation of $BaNb_2O_6$. Transmission electron microscopic (TEM) investigations revealed that the average particle size is 50 nm for the calcined powders. The room temperature dielectric constant at 1 kHz is found to be 1000. The ferroelectric hysteresis loop parameters of these samples were also studied.

Keywords. Ceramics; electronic material; oxides; chemical synthesis; ferroelectricity.

1. Introduction

$Sr_xBa_{1-x}Nb_2O_6$ ($0{\cdot}25 < x < 0{\cdot}75$) (SBN) ceramics are ferroelectric materials with tungsten bronze type structure, which have excellent electro-optic, pyroelectric and photo-refractive applications (Ewbank *et al* 1987; Xu 1991; Huang 2002). Although single crystals of varying chemical compositions of SBN find applications, there are still restrictions because of high cost and difficult to fabricate (Duran *et al* 2002). In contrast, polycrystalline SBN ceramics can be made with a larger size and more complex shape. Since microstructure of the alkali-earth metal niobates affect critically the optical properties, the synthesis of SBN ceramic powders with good sinterability and compositional homogeneity is necessary. Traditional solid state method leads to poor compositional homogeneity and high sintering temperatures (Dhespande *et al* 1992). The properties of ceramics are greatly affected by the characteristics of the powder, such as particle size, morphology, purity and chemical composition. Using chemical methods, the co-precipitation, sol–gel, hydrothermal and colloid emulsion techniques have been confirmed to efficiently control the morphology and chemical composition of prepared powder. Recently, a low temperature organic gel route has been reported for strontium barium niobate (Li *et al* 2004). The purpose of this study was to prepare ultrafine $BaNb_2O_6$ powder using citrate gel technique from simple inorganic salts. This process can avoid complex steps such as refluxing of alkoxides, resulting in less time consumption compared to other techniques. The citrate gel process offers a number of advantages for the preparation of fine powders of many complex oxides as quoted in the literature (Dhage *et al* 2003). This simple procedure can be extended to the preparation of SBN ceramics.

2. Experimental

For preparing $BaNb_2O_6$, niobium (V) oxide, barium chloride and citric acid were used as starting materials, which were of AR grade (LOBA chemie). A stoichiometric amount of $BaCl_2{\cdot}6H_2O$ was dissolved in distilled water and Nb_2O_5 was dissolved in minimum amount of HF after heating in hot water bath for 20 h. An excess quantity of concentrated HCl was added to the above solution to dissolve the barium fluoride formed by mixing of NbF_5 and $BaCl_2{\cdot}6H_2O$. The above mixture was mixed with required quantity of citric acid. Since there was no precipitation during mixing, pH of the solution was not varied. On heating in a water bath at 373 K a light yellowish gel was formed after evaporation of water. Subsequently, the gel was decomposed at various temperatures ranging from 200–800°C. The gel initially started to swell and filled the beaker producing a foamy precursor. This foam consisted of very light and homogeneous flakes of very small particles. Various techniques such as XRD (Philips PW1710 Diffractometer) and TEM surface area measurements (Nova 1200 instrument) were employed to characterize these powders. For lattice parameter and interplanar distance (d) calculation, the samples were scanned in the $2q$ range 10^o–80^o for a period of 5 s per step in the step scan

*Author for correspondence (ravi@ems.ncl.res.in)

mode. Silicon was used as an internal standard. Least squares method was employed to determine the lattice parameters. The TEM picture was recorded with JEOL model 1200EX instrument at the accelerating voltage of 100 kV. The fine powders were dispersed in amyl acetate on a carbon coated TEM copper grid. The samples were analysed for the presence of carbon by microanalysis technique on a CARLO ELBA EA-1108 analyser. For comparison, $BaNb_2O_6$ samples were also prepared by ceramic method. The corresponding oxides or carbonates were taken in stoichiometric ratio and mixed, ground several times and heated at 1000°C for 72 h. The calcined powders were mixed with few drops of 1 wt% solution of poly vinyl alcohol and pelletized at 1–2 tons. The green pellets were sintered at 1300°C for 2 h. 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 room temperature dielectric constant of the samples.

3. Results and discussion

Figure 1 shows the XRD pattern of $BaNb_2O_6$ powder formed after calcining the citrate precursor powder at 600°C. The crystal structure of $BaNb_2O_6$ is orthorhombic and all the *d*-line patterns match with reported values (JCPDS: 14–27). The calculated lattice parameters by least square fit are a = 12·201 Å, b = 10·275 Å and c = 7·872 Å. Conventional solid state method also forms $BaNb_2O_6$ phase at 1000°C after prolonged heating (72 h) with a comparatively larger particle size of ~ 1 μm. The particle size and morphology of the calcined powders were examined by transmission electron microscopy. Particle morphology of calcined powder (600°C for 6 h) prepared by this technique was irregular in shape and agglomerated, with an average primary particle size around 50 nm (figure 2). The particle size calculated from Scherrer's formula

$$t = K\,l/B\cos q_B, \quad (1)$$

where t is the average size of the particles, assuming particles are spherical, K = 0·9, l the wavelength of X-ray radiation, B the full width at half maximum of the diffracted peak and q_B the angle of diffraction, is 65 nm. The densities of all the sintered samples are above 92% of the single crystal values. The ferroelectric hysteresis loop parameters for the present sample sintered at 1300°C showed the values (figure 3) of remnant polarization, P_r = 1·8 μC/cm^2 and coercive field, E_c = 25·2 kV/cm at an applied voltage of 60 kV/cm without occurrence of an electric breakdown of the sample. The reported values of these parameters vary as E_c ~ 10–120 kV/cm and P_r ~ 6–10 μC/cm^2 depending on preparative conditions

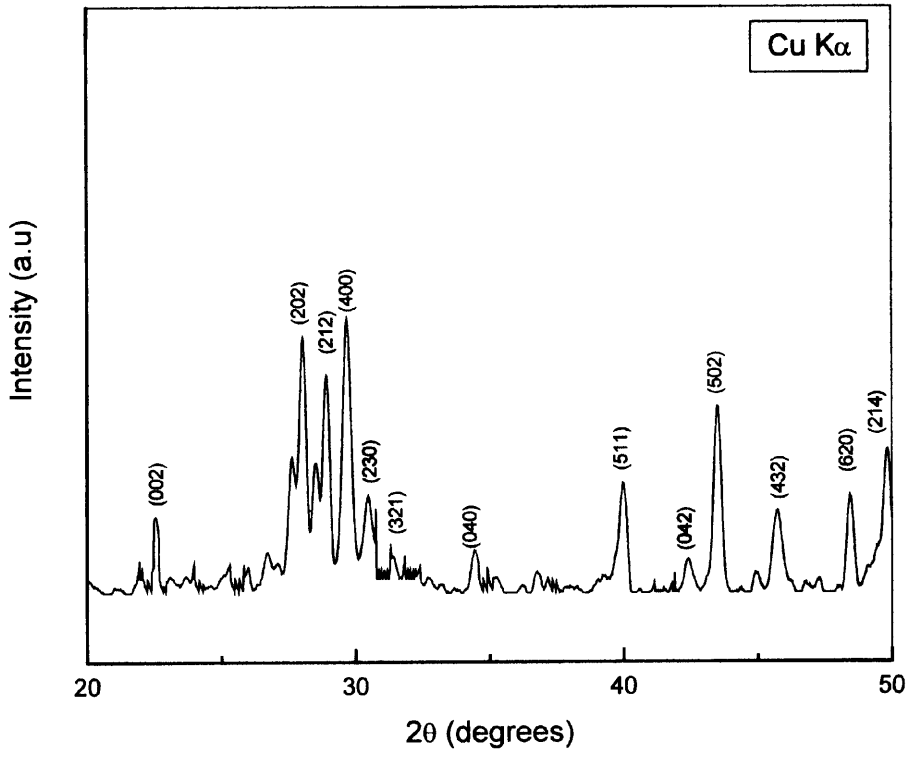

Figure 1. XRD of BN powder calcined at 600°C.

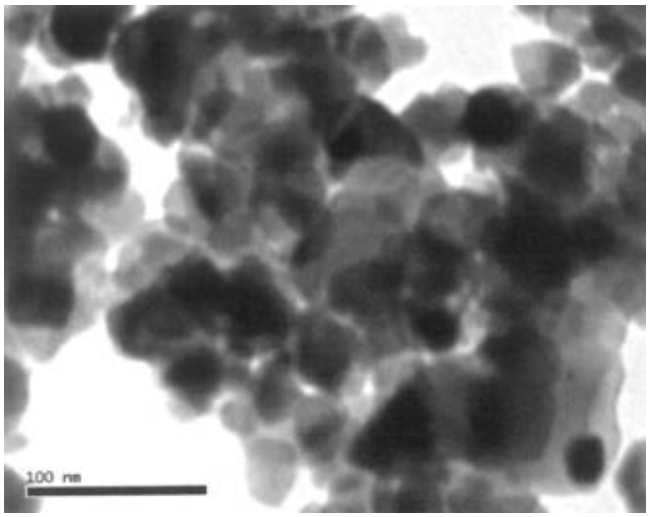

Figure 2. TEM of BN powder calcined at 600°C.

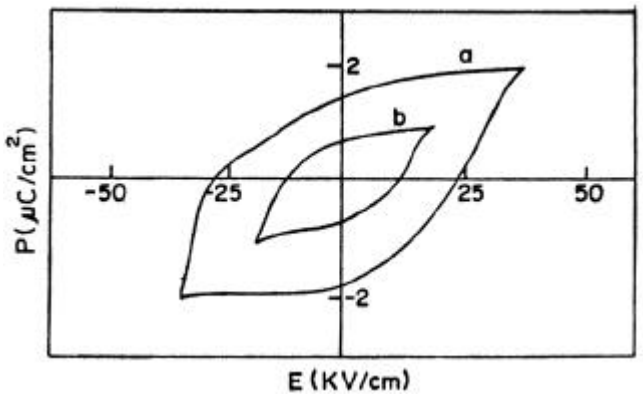

Figure 3. P/E loop measurements for (**a**) citrate derived and (**b**) solid state method derived samples.

(Dhespande *et al* 1992). It is well known that the ferroelectric properties obtained depends on sinter-density, grain size and defects present in the sample. The samples prepared by the ceramic technique have remnant polarization, $P_r = 0{\cdot}5$ μC/cm^2 and coercive field, $E_c \sim 12$ kV/cm at an applied field of 45 kV/cm without occurrence of an electric breakdown. The room temperature dielectric constant measured at 1 kHz is 1000 for these samples.

4. Conclusions

A simple citrate gel method was used to prepare ultrafine particles of $BaNb_2O_6$. The barium niobate phase was found to be formed at 600°C with an average particle size of 50 nm.

Acknowledgement

One of the authors (VR) acknowledges DST, New Delhi (grant no. SP/S1/H-19/2000), for financial assistance.

References

Dhage S R, Pasricha R and Ravi V 2003 *Mater. Res. Bull.* **38** 1623

Dhespande S B, Potdar H S, Godbole P D and Date S K 1992 *J. Am. Ceram. Soc.* **75** 2581

Duran C, Mckinstry S T and Messing G L 2002 *J. Mater. Res.* **17** 2399

Ewbank M D, Neurgaonkar R R, Copy W K and Feinberg J 1987 *J. Appl. Phys.* **62** 374

Huang Q W, Wang P L, Cheng Y B and Yan D S 2002 *Mater. Lett.* **56** 915

Li Y, Zhao J and Wang B 2004 *Mater. Res. Bull.* **39** 365

Xu Y 1991 *Ferroelectric materials and their applications* (Amsterdam: North Holland) p. 254