ZnO as Sintering Additive in Sr$_2$Nb$_2$O$_7$

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Abstract. The effect of 0.3wt% ZnO addition on phase, microstructure and properties of Sr$_2$Nb$_2$O$_7$ was investigated. X-ray diffraction (XRD) of samples calcined at 1000°C revealed the formation of the major Sr$_2$Nb$_2$O$_7$ phase along with Sr$_5$Nb$_4$O$_{15}$ as second phase. After sintering at 1300°C, 1350°C and 1400°C, a two phase ceramic developed comprising Sr$_3$Zn$_{0.33}$Nb$_{4.67}$O$_{15}$ and Sr$_2$Nb$_2$O$_7$. The addition of ZnO resulted in the reduction of grain size by ~50% and an optimum sintering temperature reduced by ~50°C that yielded 95% of the theoretical density of Sr$_2$Nb$_2$O$_7$. Preliminary results of dielectric properties are presented and compared with previous studies.

1. Introduction

Sr$_2$Nb$_2$O$_7$ belongs to the homologous series of A$_n$B$_n$O$_{3n+2}$ type compounds with A=Sr, B=Nb and n = 4 [1]. Its Curie temperature is 1342°C, below which it is ferroelectric and possesses interesting piezoelectric and electro-optic properties [2]. Sr$_2$Nb$_2$O$_7$ with certain substitutions, e.g. in the form of important solid solutions such as, Sr$_2$(Nb, Ta)$_2$O$_7$ and (Sr, Ba)$_2$Nb$_2$O$_7$, is used for ferroelectric memory storage devices based on field effect transistors and capacitors [3]. Its crystal structure is orthorhombic with lattice parameters a = 3.97Å, b = 26.86Å and c = 5.72Å, and its space group is Pna2$_1$ [4]. The structure of Sr$_2$Nb$_2$O$_7$ comprises slabs, each slab extending parallel to (010) planes and consisting of 4NbO$_6$ octahedra with Sr atoms occupying the space between them. These NbO$_6$ octahedra are known to distort and tilt upon cooling and consequently Sr$_2$Nb$_2$O$_7$ undergoes three phase transitions from Cmcm → Cmcm$_{21}^1$ → Pb11 at 1342°C, 215°C and -156°C respectively [5].

Most ceramic compounds require high sintering temperatures and therefore, various processing methods are being investigated to reduce the sintering costs and improve the density and hence electrical properties of functional ceramics. These new routes include i) chemical synthesis [6], ii) use of initial materials with fine particle size [7] and iii) addition of low melting fluxes [8]. The high costs and / or laborious processing procedures involved in the first two methods preclude the use of these routes for commercial production of technical ceramics; however, the addition of low melting fluxes in small percentages has been investigated in an attempt to achieve the above targets [9]. For example, La$_2$O$_3$ has been used as a sintering aid and highly dense Sr$_2$Nb$_2$O$_7$ with 99% of its theoretical density has been fabricated [10]. La doping has been reported to reduce the dielectric loss but resulted in the formation of a second phase, obviously deteriorating the properties. Similarly, the addition of V$_2$O$_5$ in low concentrations has been reported to improve the piezoelectric properties of Sr$_2$Nb$_2$O$_7$ [11]. ZnO has been found to enhance the density and dielectric properties of other compounds like 0.95MgTiO$_3$.
0.05 CaTiO$_3$ and BaZn$_{1/3}$Nb$_{2/3}$O$_3$ [12-13] and here we describe our preliminary results regarding the effect of 0.3wt% ZnO on the phase, microstructure and dielectric properties of Sr$_2$Nb$_2$O$_7$.

2. Experimental

A 50g batch of Sr$_2$Nb$_2$O$_7$ was prepared by mixing reagent grade SrCO$_3$ and Nb$_2$O$_5$ and milling in disposable plastic jars using Y-toughened ZrO$_2$ balls as grinding media in 2-propanole for 24 h. The slurry was dried at ~90°C overnight and calcined at 1000°C at a heating / cooling rate of 10°C/min for 2h. 0.3wt% of ZnO was added to the calcined powders prior to re-milling for 40min. After drying the slurry, the powders were again sieved and pressed into 13 mm diameter pellets at 130 MPa in a tool steel die. The pellets were sintered at 1300°C, 1350°C and 1400°C for 2h at 10°C/min. An electronic densimeter (MD-300S) was used for density measurement. Phase analysis of fired samples was carried out using a JEOL JDX 3500 X-ray diffractometer operating at 30 mA and 40 kV with CuK$_\alpha$ radiation from 2$\theta$ =10 to 70$^\circ$ (step size 0.03$^\circ$) at 2s/step. Microstructure of polished, thermally etched and gold-coated samples was investigated using a JEOL JSM 5910 SEM operating at 15-20 keV. Electrical properties of gold-coated pellets were measured using an LCR meter (4287A) at 1 to 100MHz.

3. Results and Discussion

The lattice spacings (d) corresponding to major XRD peaks (labelled as ‘▲’ in figure 1a) from the sample calcined at 1000°C matched JCPDS card# 70-114 for Sr$_2$Nb$_2$O$_7$ with maximum intensity peak at 2$\theta$=29.35$.^\circ$. A few low intensity peaks labelled as ‘■’ matching JCPDS card# 480421 for Sr$_5$Nb$_4$O$_{15}$ indicated the formation of the second phase as observed previously for samples calcined and sintered at 850°C and 1100°C respectively but for prolonged periods [14]. The d-values corresponding to XRD peaks from samples sintered at 1300°C (figure 1b), 1350°C (figure 1c) and 1400°C (figure 1d) matched JCPDS card# 511868 for Sr$_3$Zn$_{0.33}$Nb$_{4.67}$O$_{15}$ labelled as ‘●’ with maximum intensity peak at 2$\theta$=32.41$^\circ$ and JCPDS card# 70-114 labelled as ‘▲’ for Sr$_2$Nb$_2$O$_7$. Note the decrease in the intensity of major Sr$_2$Nb$_2$O$_7$ peak at 29.35$^\circ$ accompanied by an increase in the intensity of major Sr$_3$Zn$_{0.33}$Nb$_{4.67}$O$_{15}$ peak at 32.41$^\circ$ with sintering temperature up to 1350$^\circ$C indicative of second phase formation. At 1400$^\circ$C, the intensity of major Sr$_2$Nb$_2$O$_7$ peak increases again. Although the authors could not find previous studies regarding the addition of ZnO to Sr$_2$Nb$_2$O$_7$, ZnO has been reported to react with the base composition such as LnTiNbO$_6$ (Ln = Sm or Dy), forming second phase(s) [15].

**Figure 1.** XRD patterns from ZnO-added Sr$_2$Nb$_2$O$_7$ samples, a) calcined at 1000°C, and sintered at b) 1300°C, c) 1350°C and d) 1400°C showing the formation of Sr$_2$Nb$_2$O$_7$, Sr$_3$Nb$_3$O$_{15}$ and Sr$_3$Zn$_{0.33}$Nb$_{4.67}$O$_{15}$ phases.

The highest apparent density measured for ZnO-added Sr$_2$Nb$_2$O$_7$ sintered at 1400°C was ~95% of its theoretical density. The achievement of the same density required attrition milling as well as ~50°C higher sintering temperature for Sr$_2$Nb$_2$O$_7$ [1].
Secondary electron SEM images of sintered microstructures from pure and 0.3 wt\% ZnO-added Sr$_2$Nb$_2$O$_7$ samples are compared in figure 2. The observed grain morphology was rod-like and almost similar on the surface and in the bulk for samples without ZnO. The observed grain size varied from ~1×1 to 6×70 $\mu$m$^2$ on the surface and from ~1×1 to 1.5×20 $\mu$m$^2$ in the bulk (figure 2 a-b). The morphology of grains in ZnO-added Sr$_2$Nb$_2$O$_7$ sintered at 1300°C appeared as a mixture of irregularly shaped grains and rods with grain size ranging from ~0.5×1 to 1.5×12 $\mu$m$^2$ on the surface and ~0.5×0.5 to 2×10 $\mu$m$^2$ in the bulk (not shown). In the sample sintered at 1400°C, the grain size varied from ~0.8×1.5 to 4×40 $\mu$m$^2$ on the surface and from ~0.5×0.5 to 1.5×5 $\mu$m$^2$ in the bulk (figure 2c-d). This indicated an increase in the grain size with increase in sintering temperature at the surface of the sample only. The average grain size in the bulk did not change much, indicating the influence of ZnO in suppressing the grain growth. A comparison of the microstructures of pure and ZnO-added Sr$_2$Nb$_2$O$_7$ demonstrated that the addition of ZnO resulted in a visibly dense microstructure with reduced grain size by at least more than 50%. It is noticeable that the optimum sintering temperature of ZnO-added sample was ~50°C lower than that for pure Sr$_2$Nb$_2$O$_7$ which might be a reason for the observed small grain size in addition to the effect of ZnO in suppressing the grain growth.

The dissipation factor or its inverse ($Q_0=1/\tan\delta$) for ZnO-added Sr$_2$Nb$_2$O$_7$ is given in table 1 where $\delta$ is the phase angle between voltage and current in the capacitor. The dielectric loss decreased with increase in sintering temperature from 1300°C to 1350°C, obviously due to increased density at high temperature. Upon further increase in sintering temperature to 1400°C, a further decrease in dielectric loss was observed. The maximum value of ‘$Q_0$’ was 1687 at 80 MHz. This indicated that $Q_0$ value was higher for the denser sample and was dependent upon the frequency which may be due to a decrease
in friction among the dipoles at higher frequencies [16]. Similarly, as expected, the dielectric constant increased with increase in sintering temperature from 1300°C to 1400°C and a consequent increase in density (table 1), however, at a constant temperature, it decreased with increase in frequency. The dielectric constant of samples sintered at 1400°C was lower than that sintered at 1350°C. This unexpected decrease may be due to the increase in ZnO-containing phase at 1400°C than that sintered at 1350°C as evident from XRD (figure 1b-c). The previously reported high dielectric constants of 48 at 10kHz and 42 at 100kHz for Sr$_2$Nb$_2$O$_7$ [1, 17] suggests that at lower frequencies the electronic, ionic, dipolar and extrinsic effects contribute to the dielectric constant, however, at relatively higher frequencies, the contribution from interfacial/surface polarization get minimized [18]. The presence of second phase in the samples with 0.3wt% ZnO may also be a reason for the observed decrease in $\varepsilon_r$.

Table 1. Dielectric properties of 0.3wt% ZnO-added Sr$_2$Nb$_2$O$_7$ at 80 MHz

| Temp (°C) | $\rho$ (gcm$^{-3}$) | $\varepsilon_r$ at 25°C | $Q_o$ Value | $\tan\delta$ |
|----------|---------------------|------------------------|-------------|--------------|
| 1300     | 4.64                | 13                     | 273         | 0.0037       |
| 1350     | 4.7                 | 17                     | 714         | 0.0014       |
| 1400     | 4.98                | 14                     | 1687        | 0.0006       |

4. Conclusions
The effect of addition of 0.3 wt% ZnO on the phase, microstructure and properties of Sr$_2$Nb$_2$O$_7$ was investigated. Pure samples calcined at 1000°C were multiphase containing Sr$_2$Nb$_2$O$_7$ and Sr$_3$Nb$_4$O$_{15}$. The addition of 0.3wt% of ZnO resulted in the formation of highly dense ceramics at lower temperatures than that for pure Sr$_2$Nb$_2$O$_7$. The final ceramic was two-phase comprising Sr$_3$Zn$_{0.33}$Nb$_{4.67}$O$_{15}$ and Sr$_2$Nb$_2$O$_7$ crystalline grains. The lowest dielectric loss angle corresponded to the sample sintered at 1400°C. Preliminary observations revealed that the dielectric constant decreased with increase in frequency whereas the dielectric loss angle decreased with increase in frequency which is being investigated.

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