THE EFFECT OF CALCINATION TEMPERATURE ON THE MICRO-STRUCTURE OF \( \text{Sr}_5\text{Nb}_4\text{TiO}_{17} \)

Abdul Manan\(^1\), Yaseen Iqbal\(^1\), Ibrahim Qazi \(^2\)

\(^1\) Materials Research Laboratory, Department of Physics, University of Peshawar Pakistan.
\(^2\) Faculty of Engineering Sciences, Ghulam Ishaq Khan Institute of Science & Technology, Topi, NWFP Pakistan

Corresponding Author: Abdul Manan, Material Research Laboratory, Department of Physics, University of Peshawar, Pakistan. Email: Abdul_Manan_sher@yahoo.com, Mobile: 00 92 (0302) 576 2708

ABSTRACT
The properties of dielectric materials are directly related to the microstructure, grain size and density. In the present study stoichiometric quantities of AR-grade raw powders of SrCO\(_3\), Nb\(_2\)O\(_5\), TiO\(_2\) (Anatase) were used to synthesize \( \text{Sr}_5\text{Nb}_4\text{TiO}_{17} \) by solid-state sintering route. The reaction mixture was characterized by TGA/DTA to locate the formation temperature of \( \text{Sr}_5\text{Nb}_4\text{TiO}_{17} \) and to determine the phase transitions. The milled mixture was calcined at two different temperatures i.e. 990°C and 1350°C. Pellets of the calcined powders were made and sintered at 1500°C in air. The X-ray diffraction was used to identify the phase or phases present in the calcined powder as well as in the sintered samples. Micro-structural study of calcined powders as well as sintered samples, through SEM revealed Variation in the size and shape of the grains. The material sintered at 1500°C with calcination temperature of 990°C is more compact as compared to the sintered material with calcination temperature of 1350°C.

INTRODUCTION
Electro-ceramics materials are widely used in telecommunication and electronic industry. The application potential of a material depends on the relevant properties which have a direct relationship with its density and hence grain size and microstructure of the final product\(^1\). Some of the important processing parameters that greatly influence the microstructure and grain size of materials\(^2\) prepared via solid state sintering route include, doping, substitution of cations\(^3\) - \(^4\), milling\(^5\) - \(^6\), and calcination and and sintering temperature\(^7\). Thus optimization of these parameters is very crucial in the engineering of materials for electronic applications\(^8\) - \(^9\).

Compounds belonging to the \( \text{AnB}_{n}\text{O}_{3n+2} \) homologous series (where \( \text{A}=\text{La, Sm, Sr, Na, Cd, and B}=\text{Ti, Nb, Ta, Ga, Fe, Cr, Al} \)) possess interesting ferroelectric, piezoelectric, magnetic, electric and optical properties\(^10\) - \(^12\). The crystal structure of \( \text{A}_n\text{B}_n\text{O}_{3n+2}=\text{ABO}_n \) (with \( n=3+2/n \)) type compounds consists of infinite two-dimensional slabs of BO\(_6\) octahedra sharing their corners having \( \text{A} \) cations in the cavities created by the BO\(_6\) octahedra. The slabs are separated by inter-slab regions. The octahedra on opposite sides of the inter-slab region do not share oxygen atoms and thus leave an extra layer of oxygen atoms with respect to the ideal perovskite structure. This results in an irregular coordination of \( \text{A} \) cations in these regions. Each slab is nBO\(_6\) octahedra thick and is extended parallel to the direction of ideal perovskite structure. Consecutive slabs are shifted with respect to each other by half of the body diagonal of the octahedron i.e. by the vector \( \frac{1}{2}(a+c) \). The ideal perovskite structure corresponds to the limiting value \( n=\infty \) i.e. with a single infinitely thick slab of octahedra.

The lower limit is \( n=4 \). Pasero \textit{et al}\(^14\), Levin \textit{et al}\(^15\) - \(^16\), and Iqbal and Reaney\(^17\) found a homologues series of single phase compounds of the type \( \text{Sr}_n\text{Nb}_n\text{Ti}_{4-n}\text{O}_{3n+2} \), where \( n=4, 4.33, 4.5, 5, 6 \) and 7 along the \( \text{Sr}_4\text{Nb}_4\text{O}_{17} \)-SrTiO\(_3\) tie line. These compounds have been reported to resonate poorly at MW frequencies because of high losses\(^15, 17\). The compound with \( n=5 \) i.e. \( \text{Sr}_5\text{Nb}_4\text{TiO}_{17} \) processed via attrition milling has dielectric constant \((\varepsilon_r)\) 57, temperature coefficient of dielectric constant \((T\varepsilon_r)\) of \(-7\times10^{-4}\) and \(Q_{\text{xf}}\sim10^{70} \). Its behavior is antiferroelectric at \( T_c \geq 860K \). The crystal structure of \( \text{Sr}_5\text{Nb}_4\text{TiO}_{17} \) is orthorhombic with lattice parameters \( a=5.6614(4), b=32.515(7) \) and \( c=3.9525(3) \) Å with space group \( \text{Pnmm} \) and is iso-structural with \( \text{Ca}_5\text{Nb}_4\text{TiO}_{17} \). In the present study, we have investigated the effect of calcination temperature on the grain size and microstructure of the...
compound Sr$_5$Nb$_4$TiO$_{17}$ prepared by mixed oxide route using horizontal ball milling for extended period instead of an attrition mill.

EXPERIMENTAL PROCEDURE

The samples were prepared using the conventional mixed oxide route in Materials Research Laboratory, University of Peshawar. Laboratory grade SrCO$_3$, Nb$_2$O$_5$ and TiO$_2$ were weighted in stoichiometric ratios. The batch was milled for 60 h in 2-praponal in a disposable polyethylene mill jar in a horizontal ball mill (Cole-Parmer Lab mill-8000) at 200 rpm using Yt-toughened ZrO$_2$ as grinding media. The slurry was dried in oven at ~90°C overnight and calcined for 2 h at 990°C and 1350°C at a heating/cooling rate of 10°C/min in an electric furnace (Nabertherm Model LHT04/18). The calcined powders were ball milled for 30 min. to disassociate agglomerate and dried. After sieving, the powder were pressed into 13 mm diameter pellets at 140 MPa using Carver Pellet Press (Model 4350L). The pellets were then sintered at 1500°C for 2h at heating/cooling rate of 10°C/min. Sample were prepared for powder XRD via cutting the pellets into pieces using a Diamond cutting Saw (Allied Tech Cut 4$^TM$) and grinding in a pestle and mortar. TG/DTA of as mix-milled powder was performed from room temperature to 1200°C at 5°C/min using TG/DTA unit (Perkin Elmer Diamond TG-DTA) at Centralized Resource Laboratory, University of Peshawar. XRD of samples after various treatments was performed using a JDX 3500, JEOL Diffractometer operating at 30 mA and 40 KeV with CuK$_\alpha$ radiation ($\lambda = 1.5418\text{Å}$) from 2θ=10 to 70°, with step size 0.03° and count time of 2s/step. For Scanning Electron Microscopy (SEM), small pieces of the sintered samples were cut and polished finely using Polishing Machine (Allied Twinprep$^TM$). The polished samples were then thermally etched at 1360°C for 30 min. at a heating/cooling rate of 10°C/min. The etched samples were then mounted on aluminum stubs using silver paste to provide conduction path to electrons. Finally, the samples were gold-coated to avoid charging in the SEM. A JEOL JSM5910 SEM operating at 15-20 KeV was used for micro-structural examination of the samples.

RESULTS AND DISCUSSION

The TG/DTA curves for as-mix-milled powder are shown in Figure 1. Three exothermic peaks were observed on the DTA curve at ~340°C, ~875°C and ~980°C. The peak at ~980°C is due to the formation of Sr$_5$Nb$_4$TiO$_{17}$ as confirmed by XRD while the other two peaks may be due to decomposition of initial ingredients which requires further work for characterization. In the TGA curve, a

![Figure 1: TGA/DTA curves for as mix-milled powder showing exothermic peaks at ~340°C, ~875°C and ~980°C.](image-url)
continuous weight loss was observed at ~640 to 870°C, which may be due to the decomposition of SrCO$_3$. 19.958% of the total weight was lost from room temperature to 1200°C. This is consistent (within ~3 wt%) with the theory which shows that ~17 wt% of the initial ingredients comprise of gases to be evolved upon reaction.

XRD patterns of samples subjected to various heat treatments are shown in Figure 2. The d-values corresponding to XRD peaks from sample calcined at 990°C matched with ICDD card#521486 for Sr$_5$Nb$_4$TiO$_{17}$ labeled as “S”. A couple of peaks with relatively lower intensity matching ICDD card#281246 for Sr$_2$Nb$_2$O$_7$ (labeled as “Sn”) were also observed showing the presence of second phase after calcination at 990°C. Similarly, the d-values corresponding to the XRD peaks from the sample calcined at 1350°C matched the ICDD card#521486 for Sr$_5$Nb$_4$TiO$_{17}$ and ICDD card#281246 for Sr$_2$Nb$_2$O$_7$. This again indicated the presence of second phase even at 1350°C but much lower in intensity than those observed at 990°C. The d-values corresponding to the XRD peaks from the sintered samples after calcination at 990°C and 1350°C matched with ICDD card#521486 for Sr$_5$Nb$_4$TiO$_{17}$ only. However, d-spacings corresponding to a couple of low intensity peaks labeled as (*) in Figure 2 which could not be identified were also observed.

Secondary electron SEM image from the calcined powder (Figure 3a) shows that the grain size of powder calcined at 990°C (Figure 3a) ranges from ~1-2µm while that of calcined at 1350°C (Figure 3b), ranges from ~1-4µm. The grain morphology of the sample calcined at 990°C and sintered at 1500°C is plate like (Figure 3c) while the microstructure of the sample calcined at 1350°C and sintered at the same temperature comprised of elongated rod-shaped grains (Figure 3d). The sintered sample with calcination temperature of 990°C is well compacted with very low apparent porosity in comparison to the sintered sample with calcination temperature of 1350°C. SEM image of the sintered sample with calcination temperature of 1350°C shows variation in the grain size. As a result there will be much difference in the dielectric properties of the materials with the two different calcination temperatures.

CONCLUSIONS
The major phase crystallized in both the samples calcined at 990°C and 1350°C was identified as Sr$_5$Nb$_4$TiO$_{17}$, however, a few minor XRD peaks probably due to Sr$_2$Nb$_2$O$_7$ were also
present. Similarly, the major phase observed in both the sintered samples was Sr$_5$Nb$_4$TiO$_{17}$, along with a couple of XRD peaks yet to be identified were also present. The microstructure of sample calcined and sintered at 990°C and 1500°C respectively appeared more compact than the one calcined and sintered at 1350°C and 1500°C respectively. The sintered microstructure of sample calcined at 990°C comprised plate-like grains and the one calcined at 1350°C and sintered at 1500°C comprised elongated rod-shaped grains. Although, density and property measurements are underway, these preliminary results show that the calcination temperature greatly influence the final microstructure of the body.

Acknowledgement
The authors acknowledge the financial support (through NRPU 569) of the Higher Education Commission of Pakistan.

REFERENCES
4. Xu ZY, Chen XM. Effects of Ca and Sr substitution on dielectric properties in Ba$_2$Sm$_5$Ti$_5$Ta$_3$O$_{30}$ ceramics. J Mat Scien: Materials in electronics. 2000; 11: 219 - 23.

7. Cheng CM, Chen YC, Yang CF, Chan CC, Sintering and compositional effects on the microwave dielectric characteristics of Mg(Ta$_x$Nb$_{1-x}$)$_2$O$_6$ ceramics with 0.25$\leq x \leq$0.35. J Electroceram. 2007; 18: 155 - 60.


