# COMPLEX METAL NIOBATES AND TANTALATES: SYNTHESIS, PHASE RELATIONS, MICROSTRUCTURE AND DIELECTRIC PROPERTIES

BY

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To my mother
to whom I shall remain indebted
for setting the foundation

# CERTIFICATE

This is to certify that the thesis entitled, " **COMPLEX METAL NIOBATES AND TANTALATES: SYNTHESIS, STRUCTURE, PHASE RELATIONS, MICROSTRUCTURE AND DIELECTRIC PROPERTIES**" , being submitted by Mr. **M.THIRUMAL**, to the Indian Institute of Technology, Delhi for the award of the degree of Doctor of Philosophy in chemistry is a record of bonafide research work carried out by him. Mr. M. Thirumal has worked under my guidance and supervision, and has fulfilled the requirements for the submission of this thesis, which to my knowledge has reached the requisite standard.

The results contained in this dissertation have not been submitted in part or full to any other university or institute for award of any degree or diploma.

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## Abstract

Synthesis and characterization of new materials enables structure – property correlations which provide directions for tailoring materials. This thesis deals with synthesis and characterization of new dielectric oxides related to the perovskite ($ABO_3$) and columbite ($AB_2O_6$) structures. These oxides have unique dielectric properties and have a large market as passive ceramic components for mobile communications and satellite broadcasting. More Specifically, they are used as resonators for stabilization of oscillators and for frequency filters.

Chapter I describes a brief overview of the research activity that has taken place in the area of dielectric oxides, in particular those having applications as dielectric resonators at microwave frequencies. The structure and properties of the various oxides that have been developed so for have been discussed. Different methodologies of obtaining these materials have also been outlined. Factors influencing the dielectric properties, like cation ordering have been discussed. The perovskite and columbite structures allow a variety of substitutions and the scope of such a study has motivated this thesis.

In chapter II we discuss the detailed substitution studies at A, B, and $B^1$ sites in the perovskite related structures, of the type $A_3BB^1{}_2O_9$. Strontium substitution at the A site (Ba) in $Ba_3MgNb_2O_9$ leads to ordered hexagonal structures at 1300°C. For the analogous Zinc compound ($Ba_3ZnNb_2O_9$) monophasic cubic phases could be obtained for the entire range of 'x' in $Ba_{3-x}Sr_xZnNb_2O_9$. Dielectric constant for oxides of the type,

$Ba_{3-x}Sr_xMgNb_2O_9$ ranges from 25 (x = 0) to 60 (x = 3) at 500 kHz. At GHz frequencies the dielectric constant increases with strontium substitution and is in the range of 21 to 37. The dielectric loss is quite low ( 0.0003 to 0.0005). Some of the above oxides have low temperature coefficient of resonant frequencies ( -12 ppm/ °C ).

B - site substitution has been carried out in $Sr_3MgNb_2O_9$, $Sr_3ZnNb_2O_9$, $Ba_3MgNb_2O_9$ , $Ba_3ZnNb_2O_9$ , $Ba_3MgTa_2O_9$, $Ba_3ZnTa_2O_9$ families. We have substituted transition metal ions like Co, Ni, Cu, Zn and main group ions like Mg and Cd. We find that Co stabilizes the cubic structure for the entire range of solid solution in almost all the above families of oxides (typical lattice parameters, a = 4.100A°). On the other hand Mg tends to stabilize the hexagonally ordered structure (a = 5.8A°; c = 7.1A°). The Cu - substituted phases be monophasic at lower temperatures (1000°C). However, the Cu- rich phases tend to disproportianate to biphasic mixtures at higher temperatures(> 1200°C). The range of solid solution is limited in the Ni - substituted oxides single phases existing for $x \leq 0.5$ for all the families of oxides studied. In $Sr_3Zn_{1-x}Mg_xNb_2O_9$ the dielectric constant varies between 20 to 30 depending on 'x' at 500 kHz. These oxides also have good dielectric properties at microwave frequencies (5.4 to 6 GHz). The x = 0.5 composition has a dielectric constant of 22.3 and dielectric loss of 0.0006 and temperature coefficient of resonant frequency of + 4.4 ppm/ °C. These samples had a density of around 97 %(sintered at 1425°C) and had grain size of around 5 –6 μm.

Most of the substituted oxides belonging to other families had dielectric constant in the range of 20 to 30 at 500 kHz with loss in the range of 0.01 to 0.002. However, there were compositions which showed high dielectric constant and higher losses ( 0.1 to 0.4). These samples were multiphasic in all the cases.

Pure cubic phases could be obtained for $Ba_3ZnTa_{2-x}Nb_xO_9$ and $Ba_3MgTa_{2-x}Nb_xO_9$ ($B^1$- substitution) at 1300°C. The former had a dielectric constant of around 25 to 30 and the latter had values of 15 to 20 at 500 kHz. The dielectric loss (0.02) was an order of magnitude lower for oxides of the type, $Ba_3ZnTa_{2-x}Nb_xO_9$. At GHz frequencies too, the Zn containing family of oxides had higher dielectric constants and lower dielectric loss compare to the Mg containing analogues.

Attempts to synthesize oxides with simultaneous substitution of **B** and **B**$^1$ sites, like in $Ba_3Mg_{1-x}Al_xNb_{2-x}Zr_xO_9$, lead to limited success in most of the families studied. Monophasic oxides were obtained upto x = 0.1 or in some cases till x = 0.25.

We have also obtained several dielectric oxides like $Ba_3ZnTa_2O_9$, $Ba_3MgNb_2O_9$, $Ba_3ZnNb_2O_9$ as single phases by the flux method at low temperature (900°C) using NaCl /KCl eutectic mixtures. These oxides have large grain size of 7 to 10 μm when sintered at 1300°C.

In chapter III, we have discussed the synthesis and characterization of solid solutions related to the $AB_2O_6$ (columbite) oxides. In $MgNb_{2-x}Ta_xO_6$ oxides prepared by the solid state route, we find nearly 5 to 15 % of $Nb_2O_5$/ $Ta_2O_5$ in addition to the orthorhombic columbite structure. The pure tantalum phase crystallizes in a tetragonal tri-rutile structure. The dielectric constant of these oxides are around 15 at 500 kHz with the dielectric loss of around 0.03. At 14.5 GHz the dielectric constant is 21 for the x = 0 compositon and 18 for the x = 2 composition. Pure $AB_2O_6$ type of phases could be obtained using $MgNO_3$ as starting material instead of MgO for the above family of oxides. The dielectric constant (23 to 28) for these oxides is nearly constant over the entire frequency (100 kHz to 500 kHz) range. The dielectric constant is also highly stable with temperature, the temperature coefficient of dielectric constant being +3 ppm / °C , over the temperature range of 50°C to 300°C. Monophasic oxides of the type $ZnNb_{2-x}Ta_xO_6$ could also be obtained. These oxides were found to have a dielectric constant of around 20 at 500 kHz. Solid solutions of the type $Zn_{1-x}Ca_xNb_2O_6$ and $Mg_{1-x}Ca_xNb_2O_6$ were attempted. However, in both the cases biphasic mixtures of the end members (x = 0 and x = 1) could only be obtained.

In chapter IV, lead based dielectric materials having loaded compositions 3PbO – MgO/ZnO –$Nb_2O_5$ have been attempted by using different processing conditions. The ceramic method leads to a mixture of two phases, the cubic pyrochlore $Pb_3Nb_4O_{13}$ and the columbite (Mg/Zn)$Nb_2O_6$ phase. High temperatures leads to a decrease in the pyrochlore phase and an increase in the cubic perovskite phase and $PbNb_2O_6$ which shows that there is reaction of the pyrochlore phase and the columbite phase, (Mg/Zn)$Nb_2O_6$, to yield the cubic perovskite phase. The reactivity of the columbite phase depends crucially on an optimum Mg : Zn ratio. Molten salt synthesis of similar compositions in NaCl – KCl (900°C for 6 hours) leads to a biphasic mixture with a significant increase in the perovskite Pb(Mg/Zn)$_{1/3}Nb_{2/3}O_3$ phase for Mg- rich compositions. The dielectric constant is quite low (14 to 18) for the composites prepared by the ceramic route whereas, the composites (pyrochlore + perovskite) obtained by the molten salt method have much larger dielectric constant. Large dielectric constant of ~ 1800 could be obtained in some of the composites prepared under different flux conditions.

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