Synthesis, Characterisation and Properties of $(Ba_{1-x}Sr_x)(Nd_{1/2}Nb_{1/2})O_3$ Ceramics for Application as Dielectric Resonators in Microwave Circuits

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(Received 1 August 1994; accepted 10 February 1995)

Abstract: The $(Ba_{1-x}Sr_x)(Nd_{1/2}Nb_{1/2})O_3$ ceramics have been prepared by the conventional ceramic route for different values of x. Addition of a small amount of CeO_2 (1 wt%) as a sintering aid increased the density of the samples. The structure and microstructure of the sintered samples are studied by X-ray diffraction and SEM methods. The dielectric properties of the samples are measured in the microwave frequency region as a function of composition. The dielectric constant decreases as x increases. The coefficient of thermal variation of resonant frequency decreases as the Sr content increases and goes to the negative side. The dielectric properties of $(Ba_{1-x}Sr_x)(Nd_{1/2}Nb_{1/2})O_3$ are in the range suitable for application as dielectric resonators in microwave circuits.

1 INTRODUCTION

It was shown by Richtmyer[1] in 1939 that a dielectric material of suitable shape can act as an electromagnetic resonator. The most striking advantage of dielectric resonators (DR) is their reduced size by a factor of the order of $\sqrt{\epsilon_r}$ (ϵ_r = dielectric constant) compared to conventional metallic cavity resonators. Moreover, DRs possess excellent integrability. With the recent advances in microwave communication, especially in direct broadcast satellite communication and cellular mobile telephones, DRs find extensive use as frequency determining components in filters and oscillators. Consequently there has been an increasing demand for DR materials for the microwave frequency region and intensive search for new high quality resonator materials is in progress.[2-7] Three important requirements of these materials are (1) a high dielectric constant (ϵ_r), (2) a high quality factor (Q) and (3) a very small coefficient of thermal variation of the resonant frequency (τ_f).

Complex perovskite oxides form a large class of materials, many of them having interesting dielectric properties.[6-10] $Ba(Zn_{1/3}Ta_{2/3})O_3$ and $Ba(Mg_{1/3}Ta_{2/3})O_3$ are known as good dielectric resonator materials with high Q and low τ_f.[6,7] However, their dielectric constants are relatively low (29 and 25, respectively). Agranovskaya[8] has outlined the dielectric properties of many complex perovskite materials and suggested the possibility of $A(B^{3+}_{1/2}B^{5+}_{1/2})O_3$ as excellent microwave resonator materials. Recently Takata and Kageyama[9] and Sreemoolanadhan *et al.*[10] have reported the microwave characteristics of

Ceramics International. 0272-8842/95/$9.50

$A(B^{3+}_{1/2}B^{5+}_{1/2})O_3$ ceramics where A = Ba, Sr, Ca, B^{3+} is a trivalent rare earth ion and B^{5+} = Nb, Ta, with ϵ_r ranging up to 40. It was found[9,10] that most of the Ba compounds have positive τ_f, while Sr and Ca compounds have negative τ_f. Their results indicate that a partial substitution of Sr or Ca for Ba reduces the value of τ_f. The structure, properties and preparation of several complex perovskite compounds are described by Galasso in his book.[11] In the present paper we report the synthesis and microwave characteristics of $(Ba_{1-x}Sr_x)(Nd_{1/2}Nb_{1/2})O_3$ ceramics and discuss their usefulness as dielectric resonator materials.

2 EXPERIMENTAL PROCEDURE

The samples were prepared by the conventional solid state ceramic route.[9,11] The oxides were weighed in the appropriate molar ratio and thoroughly mixed in an agate mortar using acetone as the mixing medium. The powder was dried and calcined at 1250°C for 10 h in air. The calcined powder was again ground well, along with 1 wt% CeO_2 added as a sintering aid, and pressed in the form of thick pellets of 10 mm diameter and 5–10 mm height by applying a pressure of 4 tonnes. The pellets were then sintered at 1440°C for 10 h in air.

The crystal structure and phase purity of the sintered samples were examined by X-ray powder diffraction analysis. The polished surfaces of the sintered pellets were observed by scanning electron microscopy (SEM) after etching the sample surface thermally at 1100°C for 6 h. The microwave measurements were carried out using a Network Analyser (HP 8510 B), reflection transmission test unit and a sweep oscillator with an RF plug-in. The dielectric constant was measured by the Hakki-Coleman method[12] with the dielectric placed between two conducting plates. The Q factor was measured by the microstripline method of Khanna and Garault[13] and is the Q that can be achieved in an actual working environment. The coefficient of thermal variation of resonant frequency, τ_f, is measured by noting the temperature variation of the resonant frequency of TE_{011} mode in the reflection configuration over a range of temperature 25–70°C.

3 RESULTS AND DISCUSSION

The X-ray powder diffraction patterns recorded from $(Ba_{1-x}Sr_x)(Nd_{1/2}Nb_{1/2})O_3$ ceramics for three different values of x are shown in Fig. 1. They have a face centred cubic structure like $[(NH_4)]_3FeF_6$ [11](also refer to JCPDS File No. 14–116). The

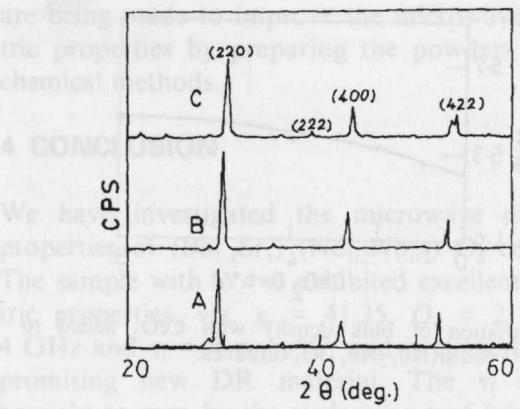

Fig. 1. X-ray powder diffractometer record of intensity vs 2θ using CuKα radiation using $(Ba_{1-x}Sr_x)(Nd_{1/2}Nb_{1/2})O_3$ ceramics. (a) $x = 0$, (b) $x = 0{\cdot}5$ and (c) $x = 1$.

lattice parameter decreases steadily with increase in strontium content (x) (see Fig. 2) as one would expect, since the size of the strontium ion is smaller than that of barium. The smooth variation of lattice constant indicates the formation of solid solution phases.

The Ba $(Nd_{1/2}Nb_{1/2})O_3$ ceramic, when sintered at 1480°C without any additive, showed a bulk density less than 90% of theoretical density. Addition of 1 wt% of CeO_2 helped to achieve a density of 94% TD. Hence, about 1 wt% of CeO_2 is used as the sintering aid for all the ceramics in this system. Addition of a higher amount of CeO_2 adversely affects the τ_f. Since the melting point of CeO_2 is >2000°C, liquid phase sintering is not expected. The role of CeO_2 on the densification of $(Ba_{1-x}Sr_x)(Nd_{1/2}Nb_{1/2})O_3$ ceramics is expected to be by the solid solution effect. The cation vacancies formed due to the substitution of Ce^{4+} on Nd^{3+} sites enhances the bulk material transport.[14,15] The cation vacancies render the diffusion coefficient extrinsic by making the thermal vacancy concentration insignificant up to a certain temperature.[15] The rate of material transport can be appreciably changed through solid phase itself by adding a

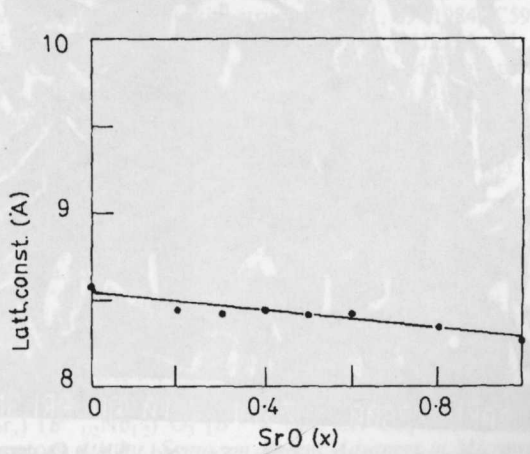

Fig. 2. Variation of lattice constant with strontium content (x).

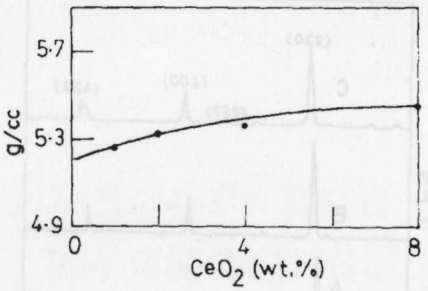

Fig. 3. Variation of bulk density with CeO_2 added to $Sr(Nd_{1/2}Nb_{1/2})O_3$ ceramics.

sufficient quantity of CeO_2. Figure 3 shows the variation of bulk density with respect to the quantity of CeO_2 added to the $Sr(Nd_{1/2}Nb_{1/2})O_3$ ceramic. The density increases with CeO_2 addition, which is in agreement with a similar finding[16] on Mn addition in $Ba(Mg_{1/3}Ta_{2/3})O_3$. Figures 4 (a) and (b) show the SEM photographs of $(Ba_{1-x}Sr_x)(Nd_{1/2}Nb_{1/2})O_3$ ceramics for $x = 0{\cdot}3$ and 1. The sintered pellets are polished and thermally etched at 1100°C for 6 h before recording the SEM pictures.

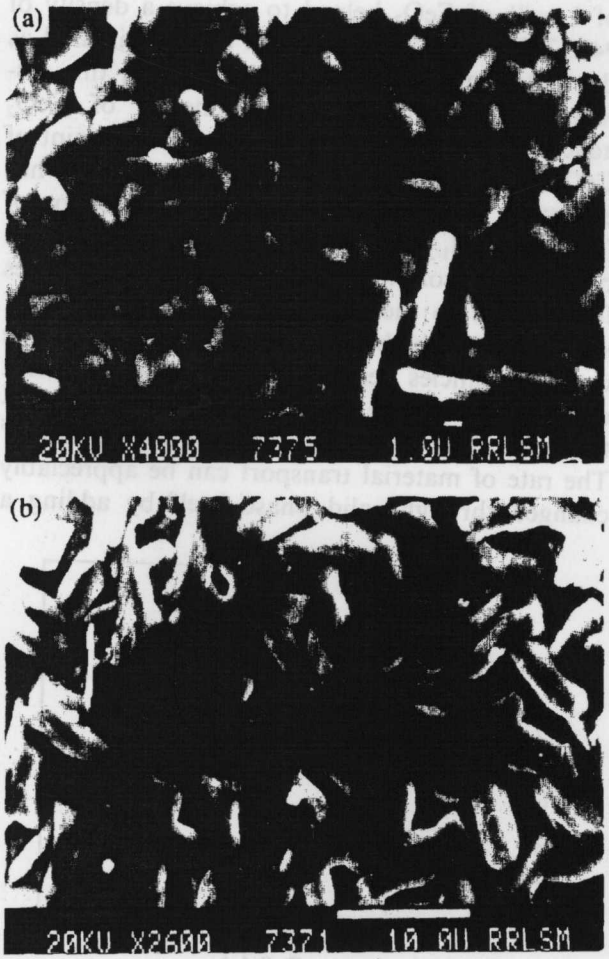

Fig. 4. SEM photographs of $(Ba_{1-x}Sr_x)(Nd_{1/2}Nb_{1/2})O_3$ ceramics. (a) $x = 0{\cdot}3$ and (b) $x = 1$.

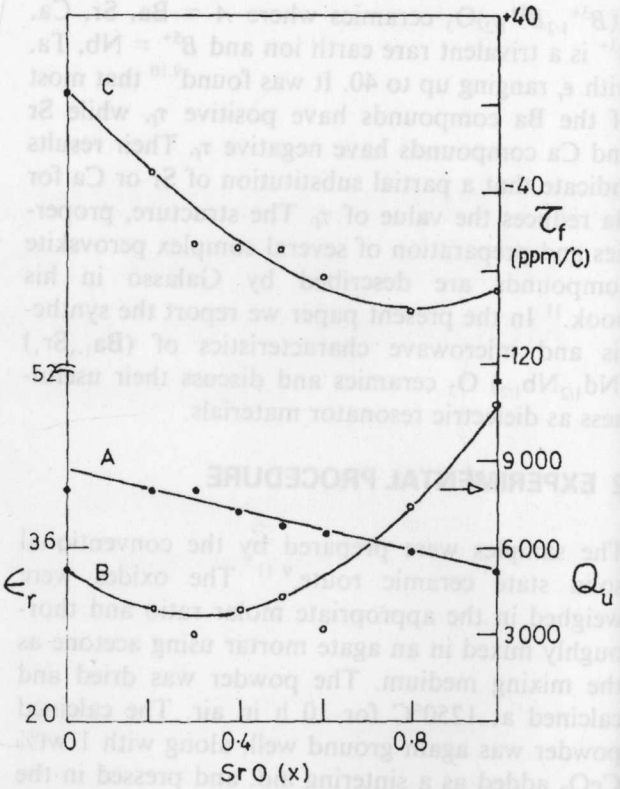

Fig. 5. Compositional variation of microwave dielectric properties of $(Ba_{1-x}Sr_x)(Nd_{1/2}Nb_{1/2})O_3$ ceramics. (A) ϵ_r vs x, (B) Q_u vs x and (C) τ_f vs x.

The microwave dielectric properties of $(Ba_{1-x}Sr_x)(Nd_{1/2}Nb_{1/2})O_3$ ceramics are shown in Fig. 5. The dielectric constant ϵ_r decreases with increase in strontium content (Fig. 5(A)). The substitution of an Sr^{2+} ion at the Ba^{2+} site decreases the unit cell size and hence the polarisation is reduced. However, the reduction in ionic mass of the A^{2+} site lowers the anharmonicity in the potential energy of the mean separation between ions which is responsible for the loss factor (tan δ).[17] The lighter Sr^{2+} ion substituting for the heavier Ba^{2+} ion results in the increase of the RF response of ionic polarisation, thereby decreasing tan δ. Hence the quality factor Q_u, which is the inverse of tan δ, increases with strontium substitution (Fig. 5(B)). A similar result is obtained for $(A^{1+}_{1/2}A^{3+}_{1/2})TiO_3$ {where A^{1+} is an alkali metal ion and A^{3+} is a lanthanide} ceramics by Takahashi *et al.*[18] In their study, the ϵ_r of $(A^{1+}_{1/2}A^{3+}_{1/2})TiO_3$ increased with the increase in ionic radius of the substituent lanthanide at the A^{3+} site. Correspondingly, the quality factor decreased with increase in A^{3+} ionic radius. It should be noted that the sinterability of $(Ba_{1-x}Sr_x)(Nd_{1/2}Nb_{1/2})O_3$ ceramics is unaffected by strontium substitution. Figure 6 shows that the theoretical, as well as bulk, densities decrease with increase in strontium content (x), which rules out

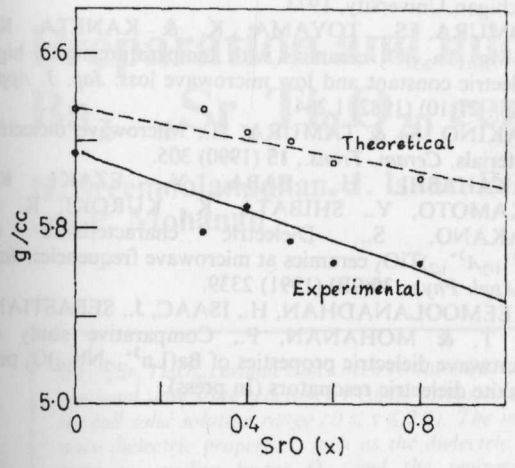

Fig. 6. Variation of theoretical and bulk densities of $(Ba_{1-x}Sr_x)(Nd_{1/2}Nb_{1/2})O_3$ ceramics with strontium content, x.

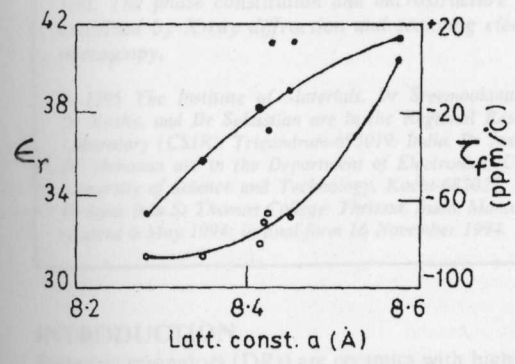

Fig. 7. Dependence of ϵ_r (upper curve) and τ_f (lower curve) on lattice constant of $(Ba_{1-x}Sr_x)(Nd_{1/2}Nb_{1/2})O_3$ ceramics.

the possible explanation for increase in Q factor by increase in sinterability due to strontium substitution.

The coefficient of thermal variation of resonant frequency τ_f, decreases with increase in strontium content (Fig. 5(C)). In general, a progressive decrease in ϵ_r is reflected in τ_f also. The τ_f decreases with decrease in lattice constant (Fig. 7). Such a decrease in ϵ_r and τ_f with decrease in lattice constant or ionic radii has recently been reported for $Ba(Ln^{3+}_{1/2}Nb_{1/2})O_3$ ceramics.[19] The τ_f is related to τ_ϵ and α (coefficient of thermal expansion) by the relation.

$$\tau_f = -\frac{\tau_\epsilon}{2} - \alpha$$

It is evident from the above equation and Fig. 5(C) that τ_ϵ changes from a negative value to a positive value since τ_f changes sign at about $x = 0{\cdot}25$. A detailed investigation is needed to understand the mechanism of the change in sign of τ_f by strontium substitution.

The dielectric resonator properties are tunable by strontium substitution for barium. Attempts are being made to improve the microwave dielectric properties by preparing the powders by wet chemical methods.

4 CONCLUSION

We have investigated the microwave dielectric properties of $(Ba_{1-x}Sr_x)(Nd_{1/2}Nb_{1/2})O_3$ ceramics. The sample with $x = 0$ exhibited excellent dielectric properties, viz. $\epsilon_r = 41{\cdot}35$, $Q_u = 2,600$ at 4 GHz and $\tau_f = 4$ ppm/°C, and is suggested as a promising new DR material. The τ_f can be brought to zero by the replacement of barium by a very small amount of strontium.

ACKNOWLEDGEMENTS

The authors are grateful to Dr A. D. Damodaran and Prof. K. G. Nair for their keen interest and encouragement given to the work and to Dr H. Tamura and Dr P. Laffez for supplying samples for standardising the measurement system. One of the authors [HS] is grateful to CSIR for financial support.

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