Synthesis, characterization and properties of 
\([\text{RE}_{1-x} \text{RE}'_x] \text{TiNbO}_6\) dielectric ceramics

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Abstract

Dielectric ceramics based on solid solution phases of \([\text{RE}_{1-x} \text{RE}'_x] \text{TiNbO}_6\), where \(\text{RE}_{1-x} = \text{Nd, Pr, Sm}\) and \(\text{RE}'_x = \text{Dy, Gd and Y}\), were prepared by the conventional solid-state ceramic route for values of \(x\). The ceramic samples are characterized by X-ray diffraction and microwave methods. Ceramics based on RE (Pr, Nd and Sm) belonging to aeschynite group shows positive value of \(\tau_f\) and those based on RE (Gd, Dy and Y) belonging to euxenite group show negative value of \(\tau_f\). The solid solution phases between the aeschynite and the euxenite group shows intermediate dielectric constant and \(\tau_f\) values. The results indicate the possibility of tailoring the dielectric properties by varying the composition of the solid solution phases. The range of solid solubility of euxenite in aeschenite and aeschenite in euxenite are different for different rare earth ions. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

With the recent advances in microwave telecommunication and satellite broadcasting, a variety of microwave devices have been developed using dielectric resonators as the frequency determining components. Dielectric resonators (DRs) provide significant advantages in terms of compactness, light weight, temperature stability and relatively low cost in the production of high frequency devices. The important characteristics required for a DR are high dielectric constant for miniaturization, high quality factor for selectivity and low temperature variation of resonant frequency for stability. Several DR materials have been investigated \([1–9]\) for microwave applications. Still the search for new materials having these properties is in progress. Recently RETiNbO\(_6\) (RE: rare earth ion) is reported as a useful ceramic material for dielectric resonator applications \([10–12]\). Single crystals of these groups of materials are recently reported as useful for miniature solid state and diode pumped lasers \([13,14]\) because of their interesting optical properties. In 1963, Komkov \([15]\) synthesized RETiNbO\(_6\) compounds by hydrothermal synthesis from equivalent mixtures of \(\text{RE}_2\text{O}_3\), \(\text{TiO}_2\) and \(\text{Nb}_2\text{O}_5\).

The RETiNbO\(_6\) compounds with atomic number of the rare earth ion in the range of 57–63 are known \([13–15]\) to crystallize with orthorhombic aescynite crystal structure with four formula units per unit cell and space group Pnma. Compounds with atomic number of the rare earth ion in the range of 64–71 have euxenite structure. The euxenite structure is also orthorhombic but of a different symmetry with space group Pcan. The members of aescynite group are known \([10–12]\) to have positive \(\tau_f\) with high \(\varepsilon\) and that of euxenite group have negative \(\tau_f\) with relatively low \(\varepsilon\) (see Table 1). Hence by preparing the solid solution phases between positive and negative \(\tau_f\) materials it may be possible to tailor microwave dielectric properties. This paper discuss the synthesis characterization and microwave dielectric properties of solid solution phases in \([\text{RE}_{1-x} \text{RE}'_x] \text{TiNbO}_6\).

2. Experimental

The \([\text{RE}_{1-x} \text{RE}'_x] \text{TiNbO}_6\), where \(\text{RE}_{1-x} = \text{Nd, Pr, Sm}\) and \(\text{RE}'_x = \text{Dy, Gd and Y}\), were prepared by the conventional solid-state ceramic route. The oxides of the rare earths, titanium and niobium were weighed in the appropriate molar ratio and thoroughly mixed in an agate mortar using acetone as mixing medium. The powder was dried and calcined at 1260°C for 4h in air. The calcined powder was again ground well and 5% polyvinyl alcohol was added as binder and the mixture was again ground before being pressed to cylinders of 10 mm diameter and 7–8 mm length at about 150 MPa pressure. The pellets were sintered at 1360–1400°C
GdTiNbO₆ dissolves in PrTiNbO₆ up to 80 mol% to form solid solution phases in the aeschynite group for \( x < 2 \). The solid solution phases have the symmetry \( F \) of the aeschenite group. For \( x < 0.2 \), the structure changes to that of the euxenite group. The \( \tau_f \) values of solid solution phases for \( x < 0.2 \) have negative values. Further work is needed to know the exact value of \( x \) at which the aeschenite to euxenite transition occurs and to obtain a zero \( \tau_f \) material. Table 3 shows the dielectric properties of Sm₁₋ₓYₓTiNbO₆ ceramics. The YTiNbO₆ forms solid solution phases in SmTiNbO₆ for \( x > 0.8 \) with the structure and symmetry of the aeschynite group. For \( x < 0.8 \), it forms solid solution phases with the structure and symmetry of the euxenite group and have negative \( \tau_f \). The dielectric constants of the phases in the euxenite group are relatively low as compared to those in the aeschynite group. In Nd₁₋ₓDyₓTiNbO₆, the solid solution phases have the aeschynite structure up to \( x > 0.7 \) with a high dielectric constant and positive \( \tau_f \) (Table 4). For \( x < 0.5 \), they are euxenite with negative \( \tau_f \).

### 3. Microwave characterization

The microwave characterization of the samples was done using a network analyzer (HP 8510 C). The dielectric constant was measured by Hakki and Coleman method [16] with the dielectric placed in between two conducting plates. The \( Q \) factor was measured by the microstripline method of Khanna and Garault [17]. The coefficient of thermal variation of resonant frequency \( (\tau_f) \) was measured by noting the temperature variation of resonant frequency of TE₀₁₁ mode over the range of temperature 25–80°C.

### 4. Results and discussion

Table 2 shows the microwave dielectric properties of Pr₁₋ₓGdₓTiNbO₆ samples. The substitution of Gd at the Pr site decreases the dielectric constant and the \( \tau_f \) value as a function of \( x \). The solid solution phases have the symmetry and structure of the aeschynite group for \( x > 0.2 \). The GdTiNbO₆ dissolves in PrTiNbO₆ up to 80 mol% to form Pr₁₋ₓGdₓTiNbO₆. For \( x < 0.2 \), the structure changes to that of the euxenite group. The \( \tau_f \) values of solid solution phases for \( x < 0.2 \) have negative values. Further work is needed to know the exact value of \( x \) at which the aeschenite to euxenite transition occurs and to obtain a zero \( \tau_f \) material. Table 3 shows the dielectric properties of Sm₁₋ₓYₓTiNbO₆ ceramics.

<table>
<thead>
<tr>
<th>( x )</th>
<th>( \varepsilon )</th>
<th>( Q \times F ) (GHz)</th>
<th>( \tau_f ) (ppm per °C)</th>
<th>Sintering temperature (°C)</th>
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<tr>
<td>1.0</td>
<td>53</td>
<td>12400</td>
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<td>1370</td>
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<tr>
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<td>9000</td>
<td>−52</td>
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</tbody>
</table>

Table 3 shows the dielectric properties of Sm₁₋ₓYₓTiNbO₆ for different values of \( x \).

### 5. Conclusions

Solid solution phases of \( [\text{RE}_{1-x}\text{RE'}_x]\text{TiNbO}_6 \), where \( \text{RE}_{1-x} = \text{Nd, Pr, Sm and } \text{RE'}_x = \text{Dy, Gd, Y} \), respectively, were synthesized for different values of \( x \) by the conventional solid-state ceramics route and were characterized by microwave methods. The dielectric properties vary linearly as a function of \( x \) until a phase transition (aeschenite–euxenite) occurs. Again the dielectric properties vary linearly as a
function of $x$ in the new phase. The range of solid solubility of aescynite in euxenite and euxenite in aescynite depend on the rare earth ions. The $\tau_f$ of the materials are improved by the solid solution formation. Further work is in progress to understand the mechanism of phase transition, dielectric properties of the ceramics near the transition point, to find the exact values of $x$ at which the transition occur and to know whether it is possible to get zero $\tau_f$ materials.

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References