June 2004

Effect of V$_2$O$_5$ Doping on the Sintering and Dielectric Properties of $M$-Phase Li$_{1+x-y}$Nb$_{1-x-3y}$Ti$_{x+4y}$O$_3$ Ceramics

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Effect of $V_2O_5$ Doping on the Sintering and Dielectric Properties of $M$-Phase $Li_{1+x-y}Nb_{1-x-3y}Ti_{x+4y}O_3$ Ceramics

Abstract
The effect of the addition of $V_2O_5$ on the structure, sintering and dielectric properties of $M$-phase ($Li_{1+x-y}Nb_{1-x-3y}Ti_{x+4y}O_3$) ceramics has been investigated. Homogeneous substitution of $V^{5+}$ for $Nb^{5+}$ was obtained in $LiNb_{0.6(1-x)}V_{0.6x}Ti_{0.5}O_3$ for $x \leq 0.02$. The addition of $V_2O_5$ led to a large reduction in the sintering temperature and samples with $x = 0.02$ could be fully densified at $900^\circ C$. The substitution of vanadia had a relatively minor adverse effect on the microwave dielectric properties of the $M$-phase system and the $x = 0.02$ ceramics had $\varepsilon_r = 66$, $Q \times f = 3800$ at $5.6$ GHz, and $\tau_f = 11$ ppm/$^\circ C$. Preliminary investigations suggest that silver metallization does not diffuse into the $V_2O_5$-doped $M$-phase ceramics at $900^\circ C$, making these materials potential candidates for low-temperature cofired ceramic (LTCC) applications.

Comments
Effect of V₂O₅ Doping on the Sintering and Dielectric Properties of M-Phase Li₁₊ₓ₋ₓNB₁₋ₓ₋₃ₓTiₓ₋₄ₓO₃ Ceramics

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I. Introduction

LOW-TEMPERATURE cofired ceramics (LTCC) are receiving increased attention in the research community because of their potential for novel multilayer communication modules involving the integration of passive components. The major requirements for these materials are sinterability below the Ag/Cu metallization melting temperature (~900°C), chemical compatibility with the metallization material within the temperature and time scale of the sintering process, as well as good microwave properties. Three classes of LTCC compositions have been investigated.¹ The first includes "low-fire materials," generally Bi-based, such as Bi pyrochlores (e.g., Ref. 2) and sillenites (e.g., Ref. 3). The second type includes glass-ceramic composites with high glass contents (~45%). These two approaches are combined in the third class, which uses ceramics with relatively low sintering temperatures (1100°C–1150°C) and small amounts of glass or sintering aids (e.g., Ref. 4). This paper reports on a new family of low-sintering temperature dielectric compositions based on the M-phase system Li₁₊ₓ₋ₓNB₁₋ₓ₋₃ₓTiₓ₋₄ₓO₃.

The so-called M-phase compounds in the Li₂O–Nb₂O₅–TiO₂ system were first reported by Villafuerte-Castrejon et al.³ as forming a solid solution, Li₁₊ₓ₋ₓNb₁₋ₓ₋₃ₓTiₓ₋₄ₓO₃, with 0.05 ≤ x ≤ 0.3, 0 ≤ y ≤ 0.182. Recent studies of the structure of the M-phase system⁶,⁷ have shown that it is best described as a homologous series of compounds with a layered structure comprised of LiNbO₃-type (LN) blocks separated by single corundum-type [Ti₄O₇]₂⁺ layers. The charge of the layers is compensated by partial Ti⁴⁺/Nb⁵⁺ substitution within the LN blocks. The thickness of the LN block, which is determined by the Ti content, varies from 4 (at the Ti-rich end) to ~50 cation layers (at the LiNbO₃-rich end).

The microwave dielectric properties of the M-phase system have also been investigated.⁶ The relative permittivity ranged from 78 at the LN-rich end of the system to 55 for the Ti-rich compositions. All of the phases exhibited good Q values in the microwave region with the value of Q×f approaching 9000. The temperature coefficient of resonant frequency, ν, changed sign from negative (for LiNbO₃-rich compositions) to positive (Ti-rich compositions) with a zero value in the intermediate region. Because these studies also showed that the M-phase Li₁₊ₓ₋ₓNB₁₋ₓ₋₃ₓTiₓ₋₄ₓO₃ system could be sintered to essentially full density at relatively low temperatures, 1100°C–1150°C, additional investigations were initiated to identify methods for reducing their sintering temperature to a range appropriate for LTCC applications.

V₂O₅ was chosen as a candidate sintering aid because of its low melting point (680°C) and the chemical similarity of V⁵⁺ to Nb⁵⁺. The choice of V₂O₅ was also guided by its successful application in lowering the sintering temperatures of several other niobate (e.g., SrBi₂Nb₅O₁₅) and titanate (e.g., BaBi₂Ti₄O₁₃) ceramic compositions. While a certain degree of homogeneous V⁵⁺/Nb⁵⁺ substitution in the M-phase is possible, differences in ionic radii and the potential formation of compounds with reduced oxidation states usually preclude complete compatibility and often result in low solid solubilities of V-based compounds in their Nb analogues. For example, the structure of LiVO₃ is very different from that of LiNbO₃ and contains tetrahedrally coordinated V⁵⁺ ions;¹⁰ similarly, solid solution of LiVO₃ in LiNbO₃ can be obtained only at high pressure.¹¹ Thus it was expected that any solid solubility of V⁵⁺ in M-phase would be very limited.

The present study details the results on the effect of the addition of V₂O₅ on the structure, sintering, and dielectric properties of the niobate M-phases and explores their compatibility with Ag metal. LiNb₀.₆Ti₀.₅O₃, which has a τₚ close to zero, was chosen as the base composition.

II. Experimental Procedure

The samples for the dielectric property measurements were prepared from dried powders of Li₂CO₃ (Baker, 99.95%), Nb₂O₅ (Ceracl, 99.95%), TiO₂ (Ceracl, 99.9%), and V₂O₅ (Baker, 99.95%). The mixing ratio was chosen to give the desired level of substitution of Nb by V according to the formula LiNb₀.₆₋ₓ₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋_-...
in sacrificial powder of the same composition. The sintered ceramics were light brown with the shade intensifying with V content, and their density was between 94% and 98% of the theoretical value. Electron spin resonance spectra of selected powders were acquired using a Bruker ESP-300 spectrometer in the field range chosen to include the reported values for V$^4^+$ (Ref. 12) and Ti$^3^+$ (Ref. 13) ions in a similar coordination.

The relative permittivity, $\varepsilon_r$ (calculated from the capacitance assuming room-temperature dimensions), and dielectric loss tangent, $\tan \delta$, were measured in the 100 Hz to 1 MHz frequency range from $-100^\circ$C to 200$^\circ$C by the parallel-plate method using an HP 4284A precision LCR meter and a Delta 9920 environmental chamber. The temperature coefficient of capacitance $\tau_C$ was calculated for $-20^\circ$C to 80$^\circ$C from linear fits of the permittivity data. Microwave measurements were performed via the cavity reflection method using an HP 8719C network analyzer. Ceramic cylinders with a height-to-diameter ratio of $\sim 0.4$ were placed into a gold-plated resonant cavity, and their permittivities and $Q$ values were calculated at the resonant conditions from the $S_{11}$ reflection coefficients. The temperature coefficient of the resonant frequency ($\tau_f$) was determined in the temperature range $0^\circ$C–$80^\circ$C by inserting the test cavities into a temperature-controlled chamber. The setup and methodology are described in detail in Ref. 14.

To investigate the compatibility of the ceramics with silver metal the $x = 0.02$ powders were processed to give an average particle size of 0.87 $\mu$m. Pellets were pressed as described above and coated with silver paste (Heraeus ST1601-14). After a 15 min treatment at 530$^\circ$C to expel volatile components in the silver paste, the compact was heated for 1 h at 900$^\circ$C.

The SEM studies were conducted at 20 kV using a JEOL 6300F scanning electron microscope equipped with a PGT energy dispersive X-ray detector. Specimens for TEM/STEM studies were prepared from pellets by conventional polishing, dimpling, and ion milling. To eliminate the possibility of water leaching any of the unreacted components, all polishing, slicing, etc., were conducted with kerosene as a lubricant with subsequent washing in hexane. Specimens were examined at 200 kV using a JEOL 2010F microscope equipped with a PGT energy dispersive X-ray detector.

### III. Results and Discussion

For the phase analysis studies, samples were formulated for 1%–5% substitution of Nb by V in LiNb$_{0.6}$Ti$_{0.5}$O$_3$ (LiNb$_{0.61-x}$V$_{x}$Ti$_{0.5}$O$_3$ with $x = 0.01$ to 0.05), processed as described in Section II, and then annealed at 1000$^\circ$C to obtain higher-quality XRD patterns by increasing the grain size. Pure LiNb$_{0.6}$Ti$_{0.5}$O$_3$ could be indexed as a single-phase $N = 10$ structure with $a = 5.1254(4)$ Å, $c = 23.207(2)$ Å, where $N$ represents the superstructure periodicity. Since the value of $N$ was previously shown to be primarily determined by the Ti content ($N$ decreases as the Ti content increases), no change would be expected for the isovalent substitution of Nb by V. The cell parameters of LiNb$_{0.61-x}$V$_{x}$Ti$_{0.5}$O$_3$ with $x = 0.01$ to 0.05 all gave an excellent fit to the $N = 10$ structure; the $a$ parameter decreased with increasing $x$, while $c$ showed no detectable change (see Fig. 1(a)). These cell parameters are consistent with the expected behavior of a homogeneous solid solution and reflect the decrease in the average ionic radii in the LiNbO$_3$-type blocks due to the smaller size of V$^{5+}$ (0.54 Å) compared with Nb$^{5+}$ (0.64 Å).15

The diffraction patterns of samples with $x = 0.03$ to 0.05 could no longer be accurately indexed by the $N = 10$ cell, and the errors in the cell parameter refinement were unrealistically high. Therefore, the X-ray diffraction patterns of these samples were indexed using a variable value of $N$ (see details in Ref. 6). The variable periodicity model allowed the XRD patterns of all the V$_2$O$_5$-doped samples to be indexed satisfactorily. The data for the average superstructure periodicity are presented in Fig. 1(b). The value of $\langle N \rangle$ is constant (10) for $x = 0$ to 0.02 and then increases steeply for more V-rich compositions, reaching 10.8 for $x = 0.05$. From the correlations observed previously for these systems, an increase in the average periodicity reflects a decrease in the overall Ti content in the $M$-phase. This would imply that for the higher V concentrations some of the Ti content is incorporated into a second phase that could not be detected by XRD, presumably because of its small volume fraction or its amorphous character. The results of the lattice parameter refinements support a very narrow range of solid solubility in the LiNb$_{0.61-x}$V$_x$Ti$_{0.5}$O$_3$ system with the limit lying between $x = 0.02$ and 0.03 at 1000$^\circ$C.

While many reduced compounds of V are stable, the light coloring of the samples and their low dielectric loss (and hence low conductivity; see below) was consistent with V remaining in the +5 state. This speculation was confirmed by an ESR investigation of the $x = 0.02$ powder, which showed no evidence for reduced forms of V or Ti.

The sintering properties of the V-doped samples were investigated on compacts prepared from prereacted (at 800$^\circ$–900$^\circ$C) single-phase powders. The sintering temperature was defined as the lowest temperature that achieved a density of $>90\%$ of the theoretical value after 1–2 h heat treatment. The sintering temperature decreased rapidly with the addition of V$_2$O$_5$ (Fig. 2), and for $x = 0.02$ the samples could be densified at 900$^\circ$C.

Data for the dielectric properties of the sintered pellets at 1 MHz are shown in Fig. 3. The permittivity decreases linearly with increasing V content while the temperature coefficient of capacitance is nonmonotonic and is apparently affected by the transition...
Figure 4(b) shows an SEM micrograph of the cross section of the applied to the green body, which was then sintered at 900 °C, suggesting that the doped material is of prereacted MV investigations were made by examining the XRD patterns of Ag/H11001 MV 2 O 5 capacitance (open dots) of Li(Nb 1-x V x O 3 ceramics at 1 MHz. The measured dielectric loss tangent at 1 MHz was negative, indicating that the precision of the measurement was not high enough to determine the actual loss. The values and trends in the relative permittivity at microwave frequencies were in good agreement with the 1 MHz data (Table I). The observed Q×f values generally decreased with doping level, with the sharpest drop coinciding with the initial introduction of V. The temperature coefficient of resonant frequency behaved irregularly with the level of substitution, although the observed values were quite low for most of the samples. Overall, the system shows excellent promise for liquid-phase sintering temperature of the M-phase is very small, and does not induce any significant deterioration in the dielectric response. The most likely explanation for the reduction in the densification temperature is that the sintering is assisted by liquid-phase transport across the grain boundaries. This explanation would be consistent with the melting point of V 2 O 5, which is lower than the sintering temperature. This mechanism generally manifests itself through the formation of liquid inclusions in the grain boundaries and triple points. A study of the microstructure was conducted to find direct evidence for a liquid-phase-assisted mechanism. The x = 0.02 composition was used for the study as it exhibits the most promising dielectric properties. SEM analyses revealed no evidence for liquid-phase formation perhaps due to the limited resolution of this technique or the difficulty in the observation of the associated features on the surface of a thick specimen. Therefore, further observations were made on thinned specimens using TEM/STEM.

To maximize the potential role of a liquid-phase sintering mechanism a new sample was made in which V 2 O 5 was added to preformed M-phase samples of LiNb 0.6 Ti 0.5 O 3. The sample was prepared from ball-milled powders of LiNb 0.6 Ti 0.5 O 3, with a comparatively large grain size, mixed with V 2 O 5 powder to give the same weight percentage of V 2 O 5 (0.82%) as in the previously prepared x = 0.02 samples. A series of pellets prepared from this mixture were annealed at 900 °C for 0 to 80 min, characterized by X-ray diffraction, and examined by TEM and STEM. The sintering proceeded rapidly, though the highest density (84%) achieved after annealing this composite for 80 min is somewhat lower than those (91%–95%) obtained after a 1 h treatment of the prereacted x = 0.02 powder. This decrease can be attributed to the difference in grain size.

The microstructure study provided evidence for liquid inclusions in all of the investigated samples. Figure 5(a) shows an example of a liquid-phase layer wetting a grain boundary in a sample sintered for 30 min. The small thickness of the layer (~30 nm) is consistent with the observation that very small amounts of additive are effective in improving the density. EDX microprobe analysis of this and other similar features clearly demonstrated a final product. Compositional imaging using an EDX microprobe (not shown) allowed us to identify a layer denoted as I as Ag metallization. The interface between metatllization layer I and ceramic layer II is quite sharp, suggesting good compatibility. Image contrast associated with the top part of the ceramic layer (IIa) is similar to that of the metallization; however, no traces of Ag were detected by EDX below the I–II interface. The contrast likely arises from the interaction of the ceramic with the glass frit or organic components of the paste, as the thickness of the IIa layer depends strongly on the curing treatment of the silver metallization; exact changes in the ceramic have not been determined. The results of the experiment nevertheless appear promising as there is no Ag diffusion across the interface. It is also possible that a fully compatible metallization could be found by varying the corresponding glass/organic additives.

Table I. Microwave Dielectric Properties of Li(Nb 1-x V x O 3 )

<table>
<thead>
<tr>
<th>x</th>
<th>f (GHz)</th>
<th>εr</th>
<th>Q×f (GHz)</th>
<th>τr (ppm/K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>5.66</td>
<td>65</td>
<td>6400</td>
<td>+8</td>
</tr>
<tr>
<td>0.01</td>
<td>5.41</td>
<td>66</td>
<td>3000</td>
<td>+40.5</td>
</tr>
<tr>
<td>0.02</td>
<td>5.55</td>
<td>66</td>
<td>3800</td>
<td>+11</td>
</tr>
<tr>
<td>0.03</td>
<td>5.61</td>
<td>64</td>
<td>2500</td>
<td>+15.5</td>
</tr>
<tr>
<td>0.04</td>
<td>5.48</td>
<td>64</td>
<td>1900</td>
<td>+12</td>
</tr>
<tr>
<td>0.05</td>
<td>5.74</td>
<td>59</td>
<td>1000</td>
<td>+43</td>
</tr>
</tbody>
</table>

Although the bulk composition of this sample is somewhat different from that of x = 0.02, it is very close, and corresponds to Li 0.989 Nb 0.607 Ti 0.494 O 3 composition within the M-phase field with 2.2% VNb substitution.
higher V concentration in the grain boundary layer compared with the bulk of the surrounding grains in the 30-min-annealed specimen (Fig. 5(b)). However, it should be noted that the EDX data at low V concentrations can be interpreted only qualitatively, as the TiKα line overlaps exactly with VKα, making V undetectable except when the Ti concentration is comparable or less. Thus it was not possible to determine with EDX whether V penetrates into the M-phase grains.

Close examination of the changes in X-ray diffraction patterns in the course of sintering provided evidence for the chemical interaction occurring between the V2O5 liquid-phase and the M-phase grains. While the widths of the peaks associated with the M-phase subcell decreased with time, as expected because of the grain growth, the supercell peak widths increased (Fig. 6). This unusual behavior is also consistent with the preferential leaching of TiO2 into a V2O5-rich liquid phase, as this would increase the periodicity of the superstructure in the vicinity of grain boundaries and thus introduce dispersion in the periodicity within the grains, while the grains continue to grow via a liquid-phase sintering
the most efficient method to sinter the system would be to form the 
V distribution would enhance the sintering properties. Therefore, 
grain sizes of the powder and increased homogeneity in the initial 
solubility. This observation would also imply that smaller initial 
V-rich grain boundaries, which is consistent with the limited 
ceramics the situation is similar, and the transport occurs via 
V-rich grain boundaries, which is consistent with the limited 
solubility. This observation would also imply that smaller initial 
V distribution would enhance the sintering properties. Therefore, 
the most efficient method to sinter the system would be to form the 
M-phase in the presence of V_2O_5 in a pressed compact, an 
approach often referred to as reactive sintering.

To explore the effectiveness of a route using reactive sintering, 
pellets were prepared from prefired (600°C) ball-milled mixtures of 
Li_2CO_3, TiO_2, Nb_2O_5, and V_2O_5 with a stoichiometry ratio 
identical to that of x = 0.02 composition. The XRD pattern of the 
 prefired powder showed a mixture of Li_2TiO_3, LiNbO_3, and TiO_2; 
V_2O_5 could not be detected presumably because of its low mass 
fraction. While the prefire step could decrease the reactivity at 
high temperature, concerns such as excessive Li loss during the 
de decomposition of Li_2CO_3 at 900°C and adverse effects on the 
density produced by the evolution of CO_2 led to its incorporation 
in the processing. The pellets were placed into a furnace preheated 
to 900°C, fired for 10 to 60 min, and then quenched. Figure 7 
shows the change in the XRD patterns as a function of the sintering 
time. It is evident that the M-phase phase forms after only 10 min, 
with the additional heating times only increasing the grain size. 
This time scale is unusually short for a solid-state reaction and 
again suggests that it is assisted by liquid-phase transport. Despite 
the initially inhomogeneous composition of the compacts their 
densification proceeds with formidable speed, rising above 90% of 
their theoretical value in 1 h, similar to the prereacted powder. 
While the absolute value of the density after a 1 h treatment is 
somewhat smaller than that for the original prereacted powder 
route, it should be noted that these samples were quenched to 
ensure the accuracy of the time-dependent measurements.

A TEM study of this series of samples revealed considerably 
 fewer identifiable microstructural features associated with a liquid 
mechanism. Although complete incorporation of V_2O_5 into the 
structure can be expected for this composition, the TiO_2 leaching 
is a kinetic effect caused by the initial inhomogeneous distribution 
of V_2O_5.

From these studies it is concluded that a liquid-phase transport 
mechanism is responsible for the outstanding sintering properties 
of the Nb M-phase with added V_2O_5. While the above-described 
experiment is not strictly equivalent to the sintering of prereacted 
V_2O_5-doped Nb M-phase, it should also be noted that for the 
LiNb_0.6Ti_0.5O_3, the sintering properties of samples within the solid solution limit seem to be just as good as those of 
samples outside. Therefore, one can assume that for the prereacted 
ceramics the situation is similar, and the transport occurs via 
V-rich grain boundaries, which is consistent with the limited 
solubility. This observation would also imply that smaller initial 
V distribution would enhance the sintering properties. Therefore, 
the most efficient method to sinter the system would be to form the 
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somewhat smaller than that for the original prereacted powder 
route, it should be noted that these samples were quenched to 
ensure the accuracy of the time-dependent measurements.

A TEM study of this series of samples revealed considerably 
 fewer identifiable microstructural features associated with a liquid 
phase (Fig. 8(a)). In full agreement with the bulk density data, the 
 micrographs illustrated the development of a dense microstructure 
(Fig. 8(b)). The “reactive sintering” effect was not restricted to 
LiNb_0.6Ti_0.5O_3 but was observed for virtually all M-phase com- 
positions. While the undoped compounds generally take several 
annealing cycles at 1100°C to achieve a single-phase state, with 
1%-2% additions of V_2O_5 they can be obtained in one step at 
significantly lower temperature.

IV. Conclusions

The addition of V_2O_5 to M-phase Li_1+x−xNb_1−x−x/2Ti_x+y/2O_3 
permits the formation of dense low-loss dielectric ceramics at 
temperatures as low as 900°C. Compared with the undoped end 
member, the V_2O_5-doped samples show relatively minor deterio- 
rations in their microwave dielectric response and ceramics of 
LiNb_0.xTi_0.5O_3 with x = 0.02 have εr = 66, Q×f = 3800 
at 5.6 GHz, and τf = 11 ppm/C. Studies of the microstructure 
revealed evidence for a liquid-phase-assisted sintering mechanism, 
and by tailoring the precursor powders single-phase, high-density 
M-phase ceramics could be obtained from the component oxides 
after 1 h of heating at 900°C. Preliminary investigations of the
interaction of V$_2$O$_5$-doped M-phase with silver metallization found no evidence for silver diffusion into the ceramics at 900°C and this system may be a promising candidate for low-temperature cofired ceramics (LTCC) applications.

Acknowledgments

We thank Dr. M. Valant (Institut Josef Stefan, Ljubljana, Slovenia) for measurements of the microwave dielectric properties, Dr. D. Yates (University of Pennsylvania) for assistance with powder processing, and N. Nemes (University of Pennsylvania) for the ESR measurements.

References


L. Farber, I. Levin, A. Borisevich, I. E. Grey, R. S. Roth, and P. K. Davies, “Structural Study of Li$_{1-x}$–$\frac{x}{2}$Nb$_{1-x}$–$\frac{y}{2}$Ti$_{1-x}$–$\frac{3y}{2}$O$_3$ Solid Solutions,” J. Solid State Chem., 166, 81–90 (2002).


