

Microwave properties of doped lead pyroniobate

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Abstract

The microwave dielectric properties of the series $\text{Pb}_n\text{Nb}_2\text{O}_{5+n}$ ($1.3 \leq n \leq 3.0$) have been established in this work. Single-phase cubic pyrochlore was obtained for $n = 1.5$. Compositions for which $n > 1.5$ showed discreet PbO-rich layers between alternating slabs of pyrochlore, similar in appearance to Ruddlesden–Popper phases. These layers have a profound effect on the microwave properties, with $n = 2$ yielding the lowest τ_f (814 ppm/°C) in the series. Attempts were made to reduce τ_f further by both Mg- and Ta-doping. The properties of Mg-doped $\text{Pb}_{1.5}\text{Nb}_2\text{O}_{6.5}$ were investigated for several concentrations of Mg (on the Nb site) up to $\text{Pb}_{1.5}(\text{Mg}_{0.24}\text{Nb}_{1.76})\text{O}_{6.14}$, but none showed great promise. Isovalent doping with Ta, $\text{Pb}_n\text{Ta}_x\text{Nb}_{2-x}\text{O}_{5+n}$, was much more successful. Both the $n = 1.5$ as well as the $n = 2$ compositions showed a marked decrease in τ_f with an increasing amount of Ta. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Dielectric properties; Niobates, *Pyrochlores*; Tantalates

1. Introduction

The pyrochlore structure, space group Fd3m (No. 227), is well-understood. Stoichiometrically it is usually written as $\text{A}_2\text{B}_2\text{O}_7$, consisting of large (radius ≈ 1 Å) A-site cation species in 8-fold co-ordination and a network of oxygen octahedra (actually trigonal antiprisms) enclosing smaller (radius ≈ 0.6 Å) B-site cations. The cubic form of lead pyroniobate is Pb-deficient, with only 75% of A-sites occupied ($\text{Pb}_{1.5}\text{Nb}_2\text{O}_{6.5}$). Introducing more Pb into this structure causes a rhombohedral distortion of the pyrochlore structure, the nature of which is still not completely understood. For this reason, stoichiometric $\text{Pb}_2\text{Nb}_2\text{O}_7$ does not have the cubic pyrochlore structure.

1.1. $\text{Pb}_{1.5}\text{Nb}_2\text{O}_{6.5}$

Cook and Jaffe¹ measured the dielectric properties of the cubic pyrochlore $\text{Pb}_{1.5}\text{Nb}_2\text{O}_{6.5}$ and found $\epsilon_r = 200$ at room temperature (and $\epsilon_r = 500$ at -196 °C). It was subsequently found² to have $\epsilon_r = 259$, $Q_f = 3015$, and $\tau_f = 1239$ ppm/°C. With increasing Pb content, crystallographic layers appear in the structure on {111} planes,

lowering the symmetry of the crystal from cubic to rhombohedral.

1.2. $\text{Pb}_2\text{Nb}_2\text{O}_7$

Cook and Jaffe³ were the first to report the existence of lead pyroniobate, $\text{Pb}_2\text{Nb}_2\text{O}_7$. The electrical properties they measured were $\epsilon_r = 110$ at room temperature with $\tan\delta = 0.004$ at 100 kHz. The temperature dependence of ϵ_r was strongly negative and non-linear. At about the same time, Shirane and Pepinsky⁴ reported that $\text{Pb}_2\text{Nb}_2\text{O}_7$ was probably not ferroelectric, unlike $\text{Cd}_2\text{Nb}_2\text{O}_7$, despite the small maximum observed in dielectric constant at -259 °C. The room-temperature dielectric constant they measured was $\epsilon_r = 185$. Hulm⁵ also studied this dielectric anomaly in $\text{Pb}_2\text{Nb}_2\text{O}_7$ and suggested that it might be attributed to an antiferroelectric transition. Siegarth et al.⁶ used a sulphate route similar to Goodman's⁷ to obtain $\text{Pb}_2\text{Nb}_2\text{O}_7$; but, unlike Goodman, they used no sintering aids and could only obtain samples of approximately 75% of theoretical density. The peak in ϵ_r was observed at -256 °C, but at a value of only 53 due to the poor densification. Based on specific heat measurements, they suggested that the peak was the result of a low-frequency dielectric relaxation and not an antiferroelectric transition. As the frequency of the field increased, the peak decreased and was shifted to higher temperatures- the classic sign of relaxation. While most workers^{4,6,8,9} seem to agree that the

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pyrochlore-type compounds in the system are not ferroelectric, Sekiya et al.¹⁰ have reported that $\text{Pb}_2\text{Nb}_2\text{O}_7$ is ferroelectric.

1.3. Pb-rich phases

The properties of Pb-rich ($n > 2.0$) lead pyrochlores has been previously reported by the present authors.² In addition, Jawahara et al.¹¹ published microwave properties of $\text{A}_{2.5}\text{B}_2\text{O}_{7.5}$ ($\text{A} = \text{Ba}, \text{Sr}, \text{Ca}, \text{Mg}, \text{Zn}$; $\text{B} = \text{Nb}, \text{Ta}$) and found some compositions to have ϵ_r , high Q , and low τ_f .

1.4. Doping studies

In 1971, Krause et al.¹² reported that $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PMN) was a cubic perovskite crystal with $a = 4.049 \text{ \AA}$. Ten years later, Pfoertsch et al.¹³ observed a cubic pyrochlore XRD pattern from a MgO-doped $\text{Pb}_{1.5}\text{Nb}_2\text{O}_{6.5}$ material with an apparent stoichiometry of $\text{Pb}_{1.83}\text{Nb}_{1.71}\text{Mg}_{0.29}\text{O}_{6.39}$. The lattice constant they measured was $a = 10.5988 \text{ \AA}$. The same material was later studied by Shrouf et al.,⁸ who confirmed these findings and reported a room-temperature dielectric constant of 130 with an anomalous peak near 200 at $-253 \text{ }^\circ\text{C}$ due to relaxation. The dielectric loss at room temperature was $\tan\delta < 0.002$.

The solubility of Mg^{+2} in the pyrochlore phase has been studied by several workers. Wakiya et al.¹⁴ found the solubility limit of Mg^{+2} in pyrochlore $\text{Pb}_{(3+3x)/2}\text{Mg}_x\text{Nb}_{(2-x)}\text{O}_{6.5}$ to be $x = 0.24$. Additionally, they measured a gradient in the cubic lattice constant in sintered pellets with depth which indicated that pyrochlores with various compositions must form in the system. Earlier work¹⁵ indicated the existence of a pyrochlore with this composition with a lattice constant of 10.6029 \AA . No cation ordering was found on the A- or B-site. Other workers found pyrochlores containing more Mg^{+2} , including $\text{Pb}_2(\text{Mg}_{0.25}\text{Nb}_{1.75})\text{O}_{6.625}$,¹⁶ $\text{Pb}_{1.83}\text{Mg}_{0.29}\text{Nb}_{1.71}\text{O}_{6.39}$,¹⁷ and $\text{Pb}_2\text{Mg}_{0.32}\text{Nb}_{1.87}\text{O}_7$.¹⁸ The ϵ_r of these pyrochlores is generally reported as 200.

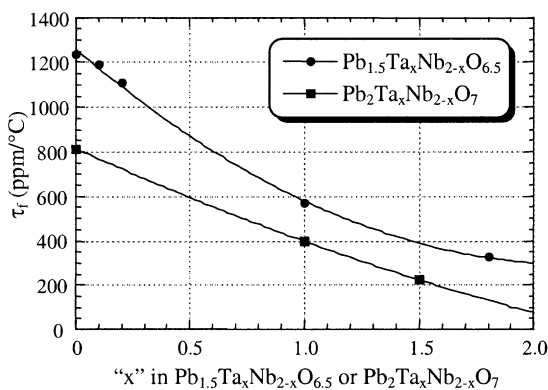


Fig. 1. The effect of Ta^{+5} -doping on the τ_f of $\text{Pb}_{1.5}\text{Nb}_2\text{O}_{6.5}$ and $\text{Pb}_2\text{Nb}_2\text{O}_7$.

Some ceramics have been produced^{9,16,19,20} which have comprised both lead magnesium niobate perovskite (negative τ_f) and pyrochlore (positive τ_f) phases, either by accident or purposely to effect dielectric properties.

To date, very little effort has been expended in studying the tantalate analogues of these niobates, although preliminary work by the present authors seems to suggest it as a more promising avenue. It has been shown² that Ta^{+5} doping on the Nb^{+5} sites can decrease τ_f dramatically, while increasing Q at the expense of ϵ_r .

2. Procedure

Pellets with compositions in the $\text{Pb}_n\text{Nb}_2\text{O}_{5+n}$ system were prepared by a conventional mixed-oxide route as described elsewhere.² Phase assemblages were checked by scanning electron microscopy (SEM, model JSM 6400, Jeol, Tokyo, Japan) and X-ray diffraction (XRD, model PW1730/10, Philips, Holland) using $\text{CuK}\alpha$ radiation from $10^\circ \leq 2\theta \leq 60^\circ$.

Some pellets underwent thinning by conventional ceramographic techniques followed by ion milling (model 600, Gatan, Pleasanton, California, USA) to electron transparency for observation in the transmission electron microscope (TEM, model JEM 3010, Jeol, Japan).

Measurements of Q and τ_f were made at Filtronic Comtek¹ on a vector network analyser (model 8753E, Hewlett Packard, USA). By placing the resonators inside a temperature-controlled chamber, it was possible to calculate accurate values of τ_f from 60 to $-30 \text{ }^\circ\text{C}$ as:

$$\tau_f = \frac{1}{f_o(20^\circ\text{C})} \frac{df_o}{dT} \quad (1)$$

where f_o is the resonant frequency at a given temperature and $df_o = f_o(T) - f_o(20^\circ\text{C})$.

Values of ϵ_r were calculated from the resonant frequency, obtained during the Q measurement, and the dimensions of the sample and cavity by the post-resonator method. The cavity in this case was Ag-coated and many times larger than the pellets being tested, and the support was a hollow cylinder of 30%-glass-reinforced polyetheramide ($\epsilon_r \approx 1$).

3. Results and discussion

3.1. $\text{Pb}_{1.5}\text{Nb}_2\text{O}_{6.5}$

Fig. 1 shows the effect of Ta doping on the τ_f of both the $n = 1.5$ and $n = 2$ compositions. In both cases, a clear trend is obvious, with τ_f decreasing significantly

¹ Measurements courtesy of Filtronic Comtek, Ceramics Division, Wolverhampton, UK.

with increasing Ta content. This can be explained in terms of the crystal chemistry of the system. As the ionic sizes of 6-coordinated Nb^{+5} and Ta^{+5} are virtually identical, the change is associated with a dampening of ionic mobility (rather than octahedral tilting or other effects). The more massive ion, Ta^{+5} , has a lower ionic polarisability than the less massive Nb^{+5} , giving rise to weaker interactions with the microwave field and hence lower permittivity and a flatter ϵ_r vs. temperature curve. In this way, doping with Ta has the effect of dampening τ_{ϵ_r} and thus τ_f . Along with the inevitable decrease in ϵ_r , a corresponding increase in Q was also observed (Fig. 2), with the exception of the $x = 1.8$ composition. The origin of the peak in Q_f at $x = 1.0$ is unknown, although Cava et al.²¹ have reported a phase change in the $\text{Ca}_2\text{Ta}_x\text{Nb}_{2-x}\text{O}_7$ system near $x = 1.62$ which may also occur in this system.

Mg-doping is even more effective in reducing τ_f , with a 38% reduction shown with just 12% of the B-sites occupied by Mg. Unfortunately, the effects on ϵ_r and Q_f are not as good, both plummeting by about 40%. This deleterious effect is almost certainly related to the introduction of additional oxygen vacancies required for charge compensation, according to $\text{Pb}_{1.5}(\text{Mg}_y\text{Nb}_{2-y})\text{O}_{6.5-1.5y}$.

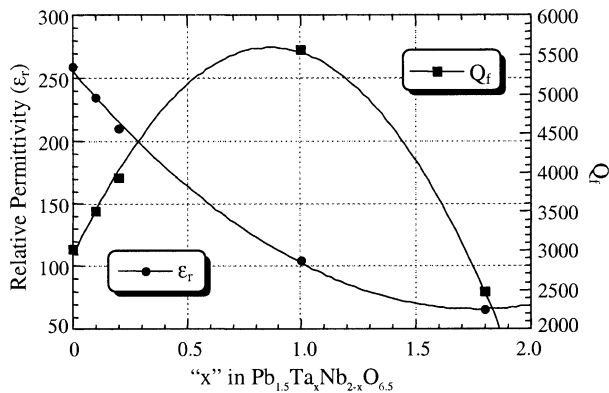


Fig. 2. The effect of Ta^{+5} -doping on the ϵ_r and Q of $\text{Pb}_{1.5}\text{Nb}_2\text{O}_{6.5}$.

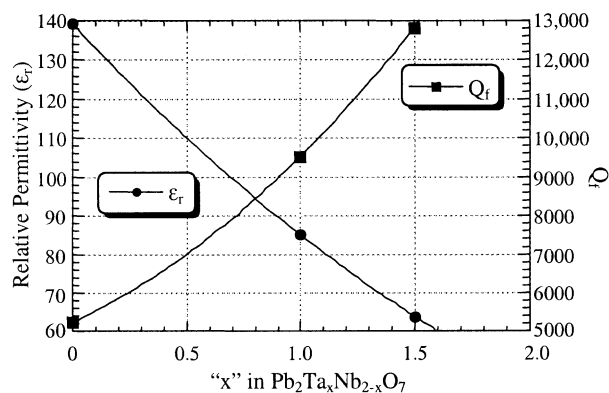


Fig. 3. The effect of Ta^{+5} -doping on the ϵ_r and Q of $\text{Pb}_2\text{Nb}_2\text{O}_7$.

3.2. $\text{Pb}_2\text{Nb}_2\text{O}_7$

Along with the significant decrease in τ_f shown in Fig. 1, Ta-doping in the $n = 2$ composition increases Q_f and lowers ϵ_r (Fig. 3). The composition which showed the best combination of properties was $n = 2$ and $x = 1.5$ ($\text{Pb}_2\text{Ta}_{1.5}\text{Nb}_{0.5}\text{O}_7$), for which $\tau_f = 223$ ppm/ $^\circ\text{C}$, $\epsilon_r = 64$, and $Q_{2.5\text{GHz}} = 5200$ ($Q_f = 12,800$).

3.3. Pb-rich phases

Fig. 4 shows the effect of Pb content on τ_f for the entire $\text{Pb}_n\text{Nb}_2\text{O}_{5+n}$ ($1.5 \leq n \leq 3.0$) series. The origin of the minimum at $n = 2$ is unknown, although it may be due to the relative stability of this phase or the spacing of the crystallographic layers, which is approximately 18.3 Å for $n = 2$. A phase change occurs at $n = 3.0$, where $\text{Pb}_3\text{Nb}_2\text{O}_8$ is stable. This phase has a very high τ_f (2161 ppm/ $^\circ\text{C}$), and the proximity of this phase boundary may also account for the increase in τ_f as n increases from 2 to 3.

The effect of Pb content on ϵ_r and Q is shown in Fig. 5. As the amount of Pb increases, ϵ_r is suppressed and Q increases, with Q at a maximum at about $n = 2.2$.

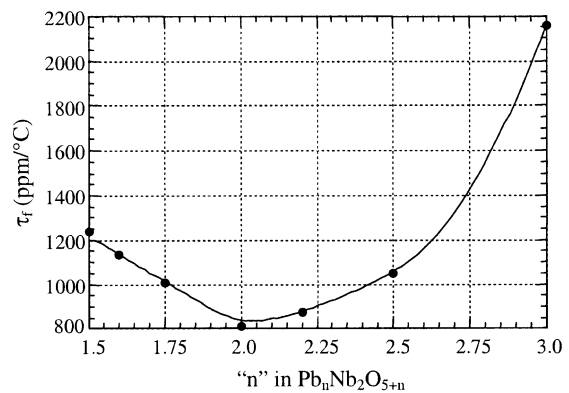


Fig. 4. The effect of Pb concentration (n) on the τ_f of $\text{Pb}_n\text{Nb}_2\text{O}_{5+n}$.

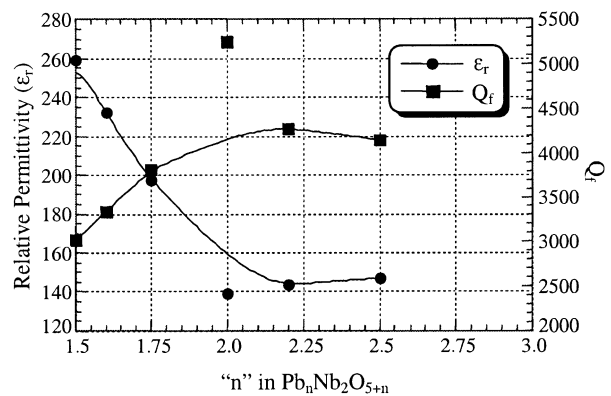


Fig. 5. The effect of Pb concentration (n) on the ϵ_r and Q of $\text{Pb}_n\text{Nb}_2\text{O}_{5+n}$.

The anomalous data at $n = 2$ are due to inadequately densified test pieces. Data on Q and, therefore, ε_r , were unobtainable for $n = 3$ due to a very poor resonance response.

4. Conclusions

Substitution of either Mg^{+2} or Ta^{+2} in place of Nb^{+5} in $Pb_{1.5}Nb_2O_{6.5}$ or $Pb_2Nb_2O_7$ can drastically reduce τ_f . In general, for $Pb_nTa_xNb_{2-x}O_{5+n}$, ε_r decreases and Q increases with increasing x . In the case of Mg^{+2} doping, both ε_r and Q decrease with increasing x , with low values of Q making this route especially unsuitable for microwave resonator production.

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