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Journal of the European Ceramic Society 24 (2004) 3739–3745

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Permittivity and temperature response of complex niobate perovskite dielectrics

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Received 23 May 2003; received in revised form 25 February 2004; accepted 6 March 2004

Abstract

Dielectric materials in the barium strontium zinc cobalt niobate system have been prepared to explore the consequences of independent variation of the population of the A and B sites in the perovskite structure. Results for the temperature coefficient of the resonant frequency follow the empirical relationship with the "*t*" factor established by Reaney. Permittivity results show deviation from linear behaviour with composition as previously observed by Kim. By comparing ionic polarisibilities calculated from the measured permittivities using the Clausius–Mossotti equation and from the ion additivity rule we show that the anomalous results are those for the high barium compositions. We demonstrate that these can be explained by compression of the A site ions and propose a simple calculation to estimate the extent of this effect which agrees well with the experimental results.

Keywords: Dielectric properties; Niobates; Microwave dielectrics

1. Introduction

Dielectric materials designed for use as resonators in the microwave frequency region and with a dielectric constant (ε_r) of around 30 are conventionally made from tantalum-containing materials. However, use of these materials is limited by the cost of tantalum. It is also possible to manufacture niobate analogues of these dielectric materials. Onoda et al.,[1] Kim et al.[2] and Colla et al.[3] explored solid solutions of BZN and SZN, i.e. compositions of the form:

$$(\mathrm{Ba(Zn_{1/3}Nb_{2/3})O_3})_x(\mathrm{Sr(Zn_{1/3}Nb_{2/3})O_3})_{(1-x)}$$

and found that the composition with $x = 0.3$ gave a dielectric constant (ε_r) of 40 and a temperature coefficient of resonant frequency (τ_f) of -5 ppm/°C. Endo et al.[4] made solid solutions of barium cobalt niobate and barium zinc niobate, i.e. compositions of the form:

$$(\mathrm{Ba(Co_{1/3}Nb_{2/3})O_3})_x(\mathrm{Ba(Zn_{1/3}Nb_{2/3})O_3})_{(1-x)}$$

and with $x = 0.7$ obtained a high Q_0 value and τ_f of 0 ppm/°C. A slightly more complex system was explored by OKI Industries.[5] This was a solid solution of barium cobalt niobate and strontium zinc niobate giving compositions of the form:

$$(\mathrm{Ba(Co_{1/3}Nb_{2/3})O_3})_x(\mathrm{Sr(Zn_{1/3}Nb_{2/3})O_3})_{(1-x)}$$

τ_f values of ~0 ppm/°C were obtained for $x \sim 0.35$.

Each of these systems has only one degree of freedom when altering the composition, and therefore composition changes designed to control one property (for example τ_f) produce variation in other properties such as permittivity. In this work we have explored independent variation of the population of the A and B sites in the perovskite structure with the aim of obtaining independent control of the material properties. These compositions cannot be expressed as the sum of two end members and are best described in terms of two independent variables:

$$(\mathrm{Ba}_x\mathrm{Sr}_{(1-x)})(\mathrm{Zn}_y\mathrm{Co}_{(1-y)})_{0.333}\mathrm{Nb}_{0.667}\mathrm{O}_3$$

Varying these two parameters enables us to explore the whole of the compositional space between the four "end members" defined by $(x, y) = (0, 0)$, $(0, 1)$, $(1, 0)$ and $(1, 1)$.

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doi:10.1016/j.jeurceramsoc.2004.03.007

As well as presenting our experimental results, we have compared them to previous work and to the empirical relationship established by Reaney et al.[6] between the tolerance "t" factor (the tolerance of a perovskite structure to fit ions of varying sizes) and τ_f.

$$t = \frac{(r_a + r_o)}{\sqrt{2}(r_b + r_o)}$$

where t is tolerance factor, r_a is the average radius of the a site ions, r_b is the average radius of the b site ions and r_o the average radius of the oxygen ions.

We have also compared ionic polarisibilities calculated from the measured permittivities using the Clausius–Mossotti equation and from the ionic polarisibilities of Shannon.[7]

2. Experimental

High purity (>99.5% purity) starting materials ($BaCO_3$, $SrCO_3$, $Co(OH)_2$, ZnO and Nb_2O_3) were weighed out, together with de-ionised water. The starting materials were mixed to form a slip and homogenised in a ball mill containing 15 mm spherical zirconia media for approximately 15 h, until the average particle size was below 1 μm. The resulting slip was freeze dried to <1% moisture content, and calcined at 1200 °C for 6 h. The calcined material was mixed with de-ionised water and re-milled for 15–24 h until the average particle size was below 2 μm. PEG-based binders (3 wt.%) were added, and the mixture freeze dried to <0.5% moisture content. The resulting powder was compacted into shape using a hydraulic press (o.d. 10 mm, t 20 mm) and subsequently had the binders removed in a static kiln 700 °C for 2 h. The resultant rods were sintered in air on a variety of profiles using an experimental matrix to gain the optimum sintering conditions. The maximum and minimum matrix conditions were 1375–1550 °C and 4–24 h. Firing cycles were chosen on the basis of the optimum density of the parts and varied according to the composition. The fired parts were centreless ground to reduce the outer diameter to approximately 6.5 mm and then sliced to obtain discs 3.0 mm thick.

These machined discs were then electrically tested in transmission using a sliver plated cavity (i.d. 20 mm, Ht 30 mm) connected to a Anritsu 37247B vector network analyser. Permittivity was calculated from the resonant frequency of the discs using the formula:

$$\varepsilon = \left(\frac{250}{\sqrt[3]{V} f_r} \right)^2$$

where V is the volume of the sample in mm^3 and f_r is the resonant frequency in GHz.

The parts were subsequently measured for frequency in a temperature controlled cabinet to calculate the τ_f value, according to the formula below.

$$\tau_f = \frac{1}{f_r} \left(\frac{d f_r}{dT} \right)$$

where f_r is the resonant frequency and T is the temperature in °C.

τ_f was determined from measurements of resonant frequency made over the range −30 to +70 °C.

3. Results and discussion

Table 1 summarises the compositions made and the results obtained.

The behaviour of the temperature coefficient of resonant frequency τ_f has been compared with the data produced by Reaney et al.[6] Their values of τ_ε, the temperature coefficient of permittivity, have been converted to τ_f values using the formula

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

where α is the thermal expansion coefficient and is taken to be 10 ppm/°C.[3]

The data follows the pattern of Reaney's results quite closely, as shown in Fig. 1. The compositional variation in this system allows us to access two regions of near zero τ_f value, around $t = 0.98$ and $t = 1.03$ with permittivities

Table 1
Compositions and electrical properties

Composition	Ba	Sr	Zn	Co	Permittivity	τ_f (ppm/°C)
1	0.95	0.05	0.315	0.018	38	+34
2	0.95	0.05	0.060	0.273	33	+5.9
3	0.95	0.05	0.003	0.330	30	+1.0
4	0.15	0.85	0.315	0.018	38	−11
5	0.05	0.95	0.300	0.033	36	−31
6	0.05	0.95	0.003	0.330	31	−56
7	0.35	0.65	0.200	0.133	38	−14
8	0.31	0.69	0.315	0.018	40	−6.3
9	0.33	0.67	0.260	0.073	39	−11
10	0.64	0.36	0.166	0.167	38	+80
11	0.60	0.40	0.233	0.100	40	+95
12	0.40	0.60	0.183	0.150	44	+110
13	0.40	0.60	0.133	0.200	42	−1.1
14	0.25	0.75	0.083	0.250	39	−29
15	0.15	0.85	0.133	0.200	39	−28
16	0.15	0.85	0.183	0.150	33	−35
17	0.15	0.85	0.033	0.300	35	−46
18	0.25	0.75	0.003	0.330	37	−45
19	0.50	0.50	0.003	0.330	40	+80
20	0.50	0.50	0.033	0.300	40	+80
21	0.75	0.25	0.003	0.330	39	+45
22	0.75	0.25	0.033	0.300	35	+44
23	0.35	0.65	0.233	0.100	44	+6.0
24	0.40	0.60	0.233	0.100	47	+41
25	0.35	0.65	0.283	0.050	41	+6.6

In every case the niobium level was 0.667 and the materials were stoichiometric ABO_3 perovskites, accurate to three decimal places.

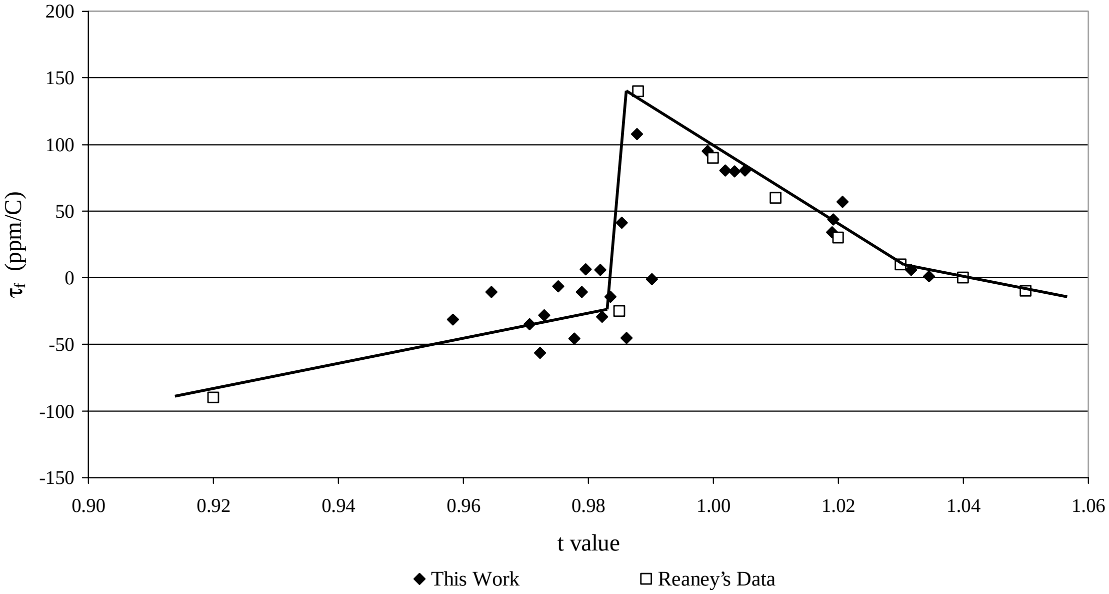

Fig. 1. Temperature coefficient of resonant frequency and "*t*" factor.

between 32 and 40. The *t*-value is primarily controlled by the A site occupancy, i.e. by the strontium content of the material.

The permittivities show the unusual non-linear variation with strontium content (Fig. 2) reported by Kim et al.[2] Kim's work was confined to a zinc-based system and his permittivities are therefore higher than ours but the maximum occurs at a similar composition.

The drop in permittivity when replacing zinc by cobalt, reported in previous work, is less easy to see in this data since it is masked by the greater effect of the change of A site occupancy.

In order to try to understand the changes in permittivity we have calculated the ionic polarisibility α for each composition using the Clausius–Mossotti equation.

$$\alpha = \frac{3V_{\rm m}(\varepsilon - 1)}{4\pi(\varepsilon + 2)}$$

Similar calculations for other dielectric materials have been made by Vineis et al.[8] and Borisevish and Davies[9]. The molar volumes $V_{\rm m}$ (Å^3) were obtained from X-ray data for the "end member" compounds corresponding to $x = 0$, 1; $y = 0$, 1. Using linear interpolation

$$V_{\rm m} = 68.518 - 4.562 \times \mathrm{Sr} - 0.445 \times \mathrm{Co}$$

where Sr is the mole fraction of strontium and Co is the mole fraction of cobalt.

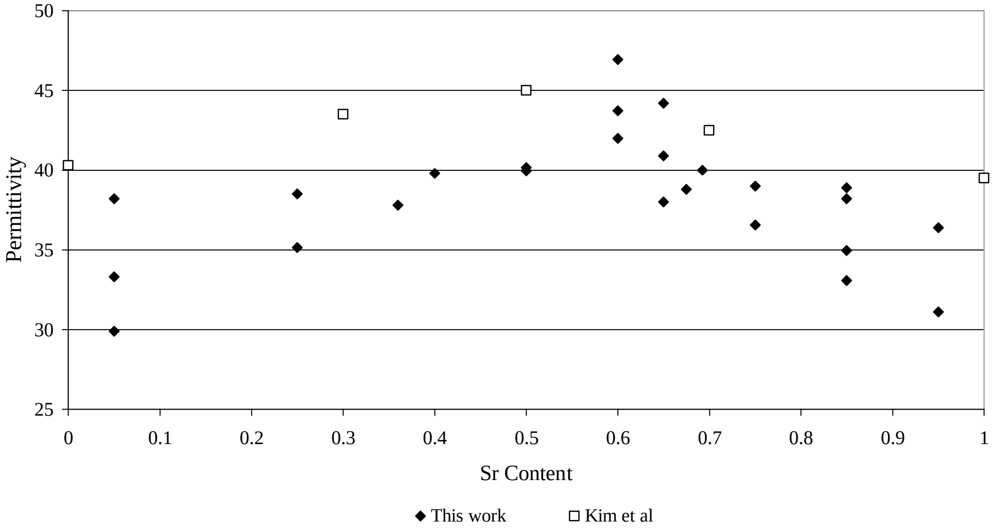

Fig. 2. Strontium content and permittivity.

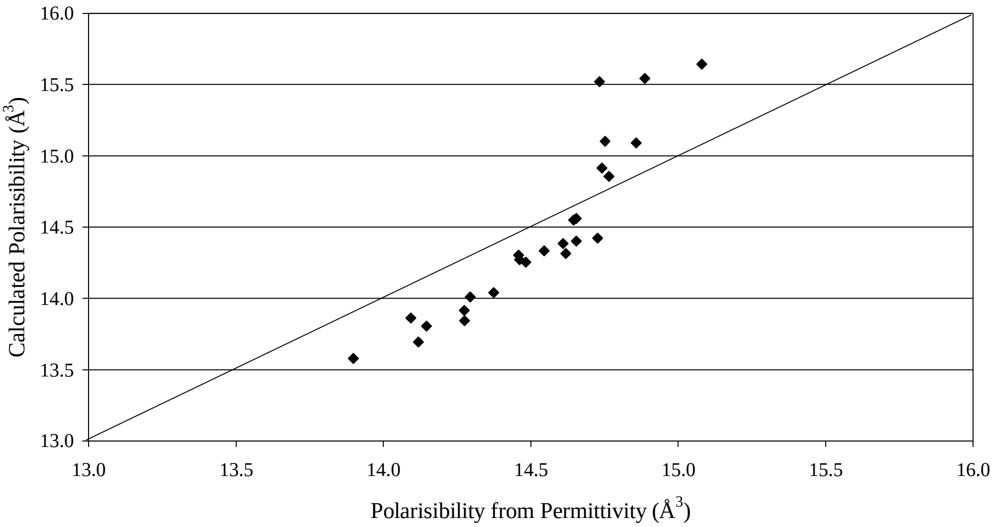

Fig. 3. Comparison of polarisibility calculated from permittivity and from ion additivity rule.

These results have been compared with the polarisibilities calculated using the ion additivity rule and ionic polarisibility values from Shannon[7]

Examination of Fig. 3 shows that the two sets of data agree quite well at lower polarisibilities and that it is the materials with the high (>14.7 Å^3) calculated polarisibilities which deviate from the expected line. In order to identify the materials showing the large deviations from predicted behaviour, the two polarisibility values are plotted as a function of strontium content in Fig. 4.

This clearly shows that the deviation occurs for the low (<0.6) and high (>0.4) strontium content samples.

In order to demonstrate that this was not due to an incorrect estimate of the molar volume, a selection of samples were subjected to X-ray diffraction analysis and the molar volumes were determined by indexing the diffraction patterns assuming a simple cubic cell. This assumption appears to be justified as there is no sign of splitting of the high angle lines in the X-ray diffraction traces. In Fig. 5 this data is compared with the values calculated from the "end member" densities and cell sizes back calculated by re-arranging the Clausius–Mossotti formula and using the measured permittivity and the polarisibility calculated from the material composition using the ion additivity rule.

It is clear that the linear interpolation of the end member values corresponds very closely to the experimental X-ray diffraction data and that the non-linear permittivity variation comes from the behaviour of the ions rather than from the cell sizes.

Combining the data presented in Figs. 1 and 4 we see that the change in the slope of the polarisibility versus strontium content curve coincides with the transition from a tilted to

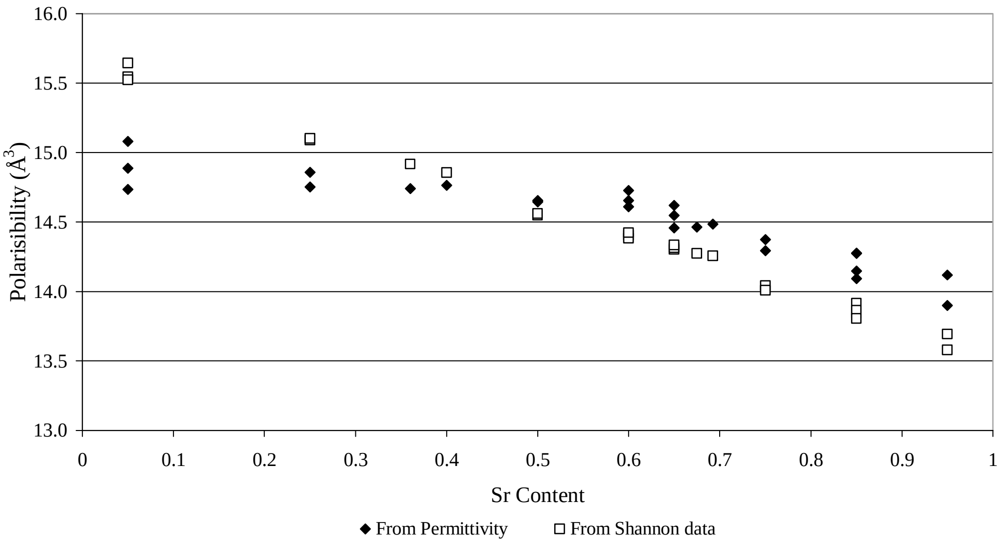

Fig. 4. Polarisibility and strontium content.

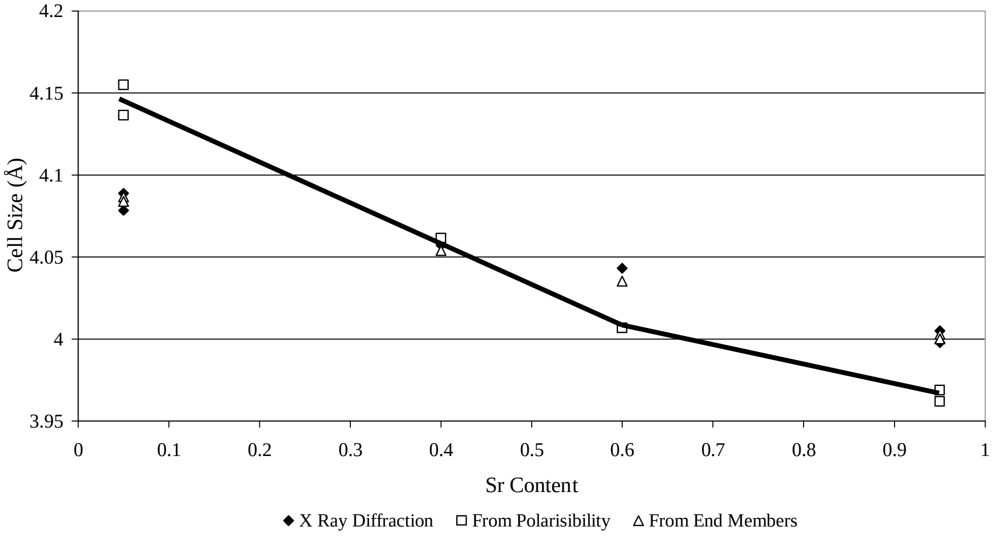

Fig. 5. Cell size calculated by various routes.

an un-tilted structure. This is illustrated in Fig. 6 where the data of Fig. 3 is re-plotted versus the t factor and combined with Reaney's line.[6]

The deviation from the expected polarisibilities occurs for $t > 0.99$, i.e. in the region where the octahedra are not tilted. A similar effect was noted by Fratello and Brandle[10] and attributed to cation compression. Our results fit with this concept since for $t < 1$ the structure can adjust for the size of the A site cations by octahedral tilting but it cannot do so for $t > 1$ and it is in this region that the deviation from the expected polarisibilities is observed.

In order to explore this concept further we first estimated the size of the compressed Ba ions from the observed cell sizes, assuming the oxygen ions to be rigid with a radius of 1.26 Å. We then scaled the polarisibility of the barium ion in proportion to the compression of the barium ion and recalculated the polarisibility of the material. We further used this recalculated polarisibility to predict the permittivity. This calculation was applied to all the materials which had t-values >0.995. This crude model predicted a large drop in permittivity at $t = 1$ and a rise in permittivity as t decreased further. Neither feature agrees with the experimental data.

We therefore revised our model and assumed that both the Ba^{2+} and the associated O^{2-} ions are compressed when $t < 1$. (The O^{2-} ions associated with strontium on the A site are assumed not to be compressed.) To calculate the compression factor we used the interpolated cell sizes ($a_{\text{X-ray}}$) and ionic size (a_{ionic}) given by

$$a_{\text{ionic}} = r_A + r_O$$

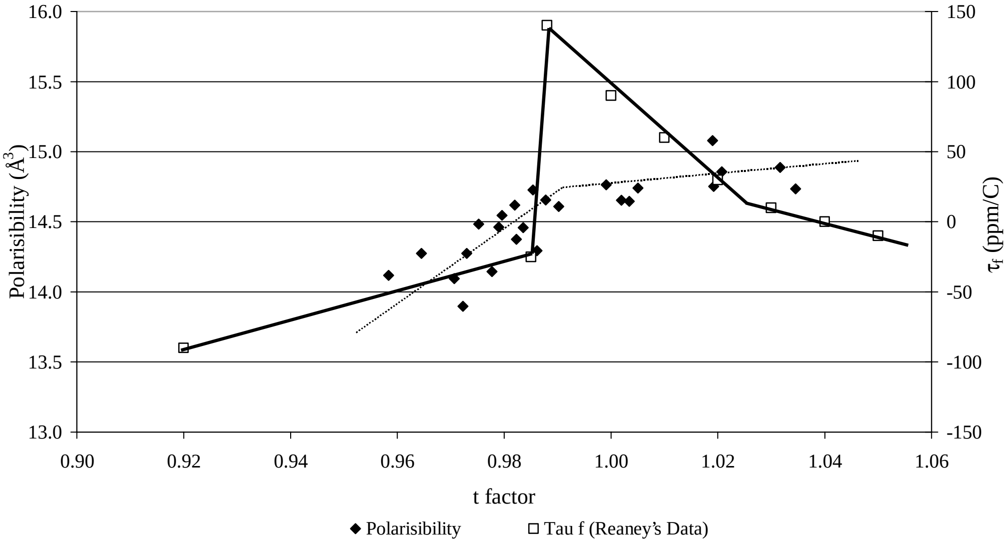

Fig. 6. Polarisibility and t factor.

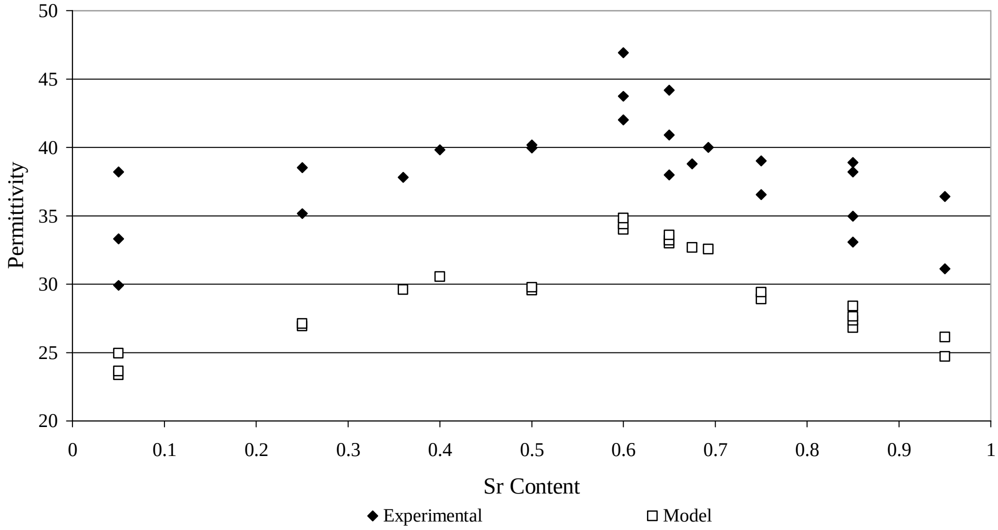

Fig. 7. Comparison of measured permittivity and calculation using ion compression model for materials with “*t*” >0.995.

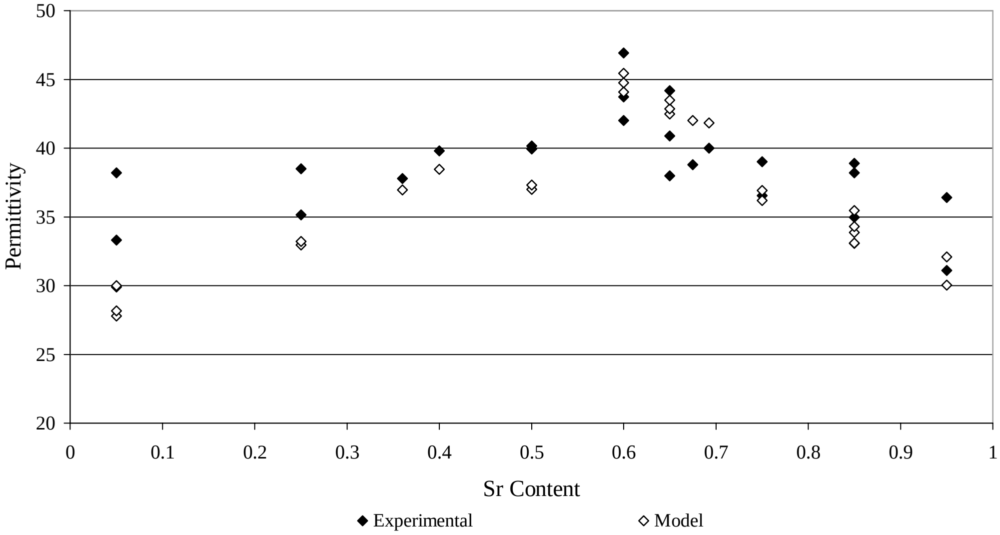

Fig. 8. As Fig. 7 but with polarisibility of Nb^{5+} increased to 4.4 $Å^3$.

where r_A is the average size of the A site ions and r_O is the ionic radius of the O^{2-} ions.

The compression factor C is then given by

$$C = \left(\frac{a_{\text{X-ray}}}{a_{\text{ionic}}}\right)^3$$

and the polarisibilities of the compressed ions are given by

$$\alpha'_X = \alpha_X \times C$$

for X = Ba^{2+} or O^{2-}.

These values were then used to calculate the total polarisibility and thus, using the Clausius–Mossotti equation, the permittivity. The calculated values are compared with the experimental data in Fig. 7.

This model predicts the drop in permittivity for compositions with strontium contents of <0.6 ($t < 0.99$) and gives a much better fit to the experimental data than the unmodified Clausius–Mossotti formula. However all the calculated permittivities are approximately 10 less than the measured values. This suggests a systematic error in the polarisibility values for an ion which is present at a constant level in the samples, i.e. Nb^{5+} or O^{2-}. Since much more data was available for oxygen than for niobium in the calculation of the polarisibilities, we suspect that the value for Nb^{5+} may have been underestimated. If the polarisibility value for Nb^{5+} is increased from Shannon’s value of 3.97–4.4 $Å^3$ then the fit to the data is much improved (Fig. 8).

4. Conclusions

The variation of resonant frequency with temperature (τ_f) for this set of solid solution compositions follows the relationship with *t*-value demonstrated by Reaney for “end member” compositions of similar permittivity.

This work demonstrates that the anomalous permittivity values occur at the high Ba end of the composition range examined and correspond to *t*-values >0.99, i.e. structures in which octahedral tilting does not occur.

To a first approximation these permittivity values can be explained by a simple model based on the compression of the barium ions on the A site and the associated oxygen ions.

An improved fit of the model to the experimental permittivities can be obtained by increasing the polarisibility value for Nb^{5+} to $4.4\,\text{Å}^3$.

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