Dielectric materials for applications in microwave communications†

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Dielectric ceramic materials have been studied for decades due to both their application in important technologies and the fundamentally interesting relationships among their crystal chemistry, crystal structures, and physical properties. Recent dramatic changes in microelectronics and in particular wireless communications technologies have made the importance of materials with the unusual combination of high dielectric constant, low dielectric loss and low temperature dependence of dielectric constant of great interest. In this review, the present state of knowledge of the chemistry, structure, and dielectric properties of these materials, as well as examples of our own work, are described.

Introduction

The revolution in wireless communications and information access is one of the most dramatic changes in technology in the past decade. This revolution is apparent on a daily basis in the ever increasing number of cellular telephone users. As in all technological systems, at the basis of the revolutionary changes in wireless communication technology are advances in materials. These materials are in use in the circuitry which wireless devices have in common with other microelectronics based technologies, but are also in use in parts of the technology which are distinctly different from those found in other systems. These unique technologies demand materials which have their own specialized requirements and functions. The importance of miniaturization cannot be overemphasized in any hand-held communications application, and can be seen in the dramatic decrease in the size and weight of devices such as cellular telephones in recent years. This constant need for miniaturization provides a continuing driving force for the discovery and the development of increasingly sophisticated materials to perform the same or improved function with decreased size and weight.

Of particular interest to materials chemists are the dielectric materials used as the basis for resonators and filters for the microwaves carrying the desired information. These materials are presently employed as bulk ceramics in microwave communication devices; they are not integrated into the microelectronics but are found as discrete components. The ceramic pieces are designed to be dielectric resonators, resonating at the frequency of the carrier signal to allow that signal to be efficiently separated from other signals in the microwave band.[1] The resonant frequency of the dielectric component depends on the dielectric constant of the dielectric and the size of the resonator. Looked at from another point of view, the size of the resonator at any particular resonant

frequency depends on the inverse of the square root of the dielectric constant of the dielectric, and thus the larger the dielectric constant the smaller the ceramic component needed. Compared to a vacuum cavity, for example ($K=1$) a dielectric with $K=36$ will have the same resonant frequency at 1/6 the size.[2] Thus materials with the highest possible dielectric constant would seem to be optimal for the task.

Unfortunately, there are other requirements for the resonator which make almost all materials with high dielectric constant such as ferroelectrics impossible to use for these applications. To be useful, the resonant frequency of the filters must not depend strongly on temperature. If that frequency were to be temperature dependent, then the carrier signal would drift in and out of resonance on hot and cold days. The practical requirement is that for a temperature range from approximately -40 to $100\,°C$, the change in resonant frequency as a function of temperature (TCF) should be less than $10\,\mathrm{ppm}\,°C^{-1}$. The TCF is related to the temperature coefficient of the dielectric constant, TCK, by: $TCF=-1/2\,TCK-\alpha$, where α is the thermal expansion coefficient.[3] Thus TCF is dominated by TCK, which can typically occur in the range of -2000 to $+2000\,\mathrm{ppm}\,°C^{-1}$ in common dielectric materials. This is an extremely stringent restriction, especially on materials with dielectric constants larger than about 30, resulting in the fact that very few materials are potentially usable in such applications.

Further, to optimize the signal intensity and the number of channels possible within a given frequency range, the loss of the resonator must be low. This in turn requires that the dielectric loss in the microwave frequency range (about 500 MHz to 20 GHz) of the dielectric material should be very low, with quality factor (Q), [defined as 1/(dielectric loss tangent)], better than 1000, preferably an order of magnitude higher. This requirement eliminates the use of many conventional high dielectric constant materials such as ferroelectrics.

These requirements: high dielectric constant, low temperature coefficient of dielectric constant, and low dielectric loss, are almost always mutually exclusive in dielectric materials. Further, the demands of mass production of the devices require reliable, reproducible processing of the ceramics, with tolerances of only a fraction of a ppm $°C^{-1}$ in TCK and 1% in dielectric constant from one component to the next. These stringent requirements make the development of advanced materials for microwave communications a challenging area of research, especially since many of these attributes are only poorly understood from a first principles viewpoint. In fact only a few such materials are known. Some of these are described briefly in this report. Due to the lack of detailed understanding of the fundamental physics which give rise to losses in bulk polycrystalline ceramics and the temperature coefficient of the dielectric constant in the microwave frequency range (described briefly below), the discovery of such materials is virtually completely empirical. There are other brief reviews,[3] and a modest book available[4] on this topic, and some authors

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(*e.g.* P.K. Davies at the University of Pennsylvania) have many publications in this area. In spite of its importance, it is not widely described in non-proprietary literature, and not broadly funded outside corporate research laboratories. In the following sections, some aspects of the most well known high K, high Q, low TCK dielectric materials are described, along with some of our own exploratory work in this area. This article concentrates almost exclusively on the materials chemistry of low TCK dielectric ceramics. Equally essential to understanding their observed properties are the effects of microstructure and processing, which are described here for some cases, but not extensively. A comprehensive review of that aspect of the field, by an expert in ceramic processing, would be of great interest.

$(Zr_{1-x}Sn_x)TiO_4$—zirconium tin titanate

This material, on the surface appearing relatively simple, but in fact very complex, is widely employed in microwave devices. Many of the issues faced in the understanding of the relationship between the dielectric properties and the detailed crystal structure of this compound are in fact surprisingly common to many of the other compounds in this small family of materials, even when they are based on entirely different structure types. The basic compound, $ZrTiO_4$, has long been known to have a relatively low temperature coefficient of the dielectric constant,[3] but has been found to have optimal properties, $K \approx 38$, TCF < 10 ppm $°C^{-1}$, and $Q \approx 5000$–$10,000$ at microwave frequencies, for solid solutions involving partial substitution of Sn^{4+} for Zr^{4+} at the 20% level.[5]

The crystal structure is of the α-PbO_2 type, shown in Fig. 1, based on columns of zigzag chains of edge shared metal–oxygen octahedra, two octahedra wide. These columns share corner oxygens with columns in the next metal plane in a close-packed oxygen lattice.[6] For materials heated at 1200 °C and higher, the entropic contribution to the total energy of the crystal is dominant, and Zr and Ti are fully disordered, randomly mixed on the octahedral metal sites. At low temperatures, however, the differences in coordination environments expected from Pauling's rules—that Ti should have octahedral coordination to oxygen and Zr cubic coordination—overcome entropy, and an ordered crystal structure is formed. In the ordered structure, the columns of edge shared metal–oxygen polyhedra are either exclusively TiO_6 octahedra or distorted ZrO_8 cubes formed by slight local shifts of the close-packed oxygens.[6] The Ti and Zr edge shared columns
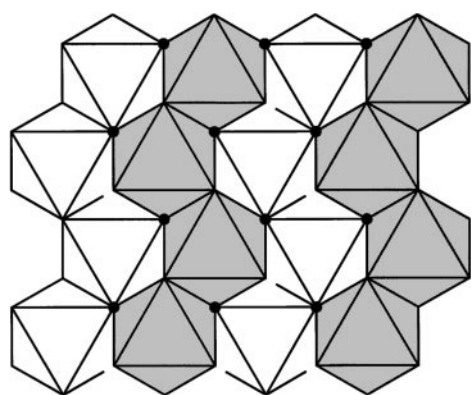
$\alpha - PbO_2$

Fig. 1 The crystal structure of $ZrTiO_4$, the α-PbO_2 type. The shaded and unshaded metal–oxygen octahedra are above and below the close packed plane of oxygen atoms in the plane of the paper. In the disordered variant, Zr and Ti are mixed on all metal sites. In the ordered variant, columns of octahedra are occupied by either Zr or Ti, with an accompanying distortion of the oxygen array.

alternate. The distortion of the close-packed oxygen lattice which occurs during the cation ordering results in the shortening of one of the crystallographic axes, an easily observable change often taken as the primary indicator that such ordering has occurred. The ordering transition is sluggish, occurring on the time scale of typical ceramic processing procedures (hours) and therefore processing parameters such as the cooling rate can have an important influence on the exact nature of the phase obtained. Further, it has been shown that there are more complex partially ordered states between the fully ordered and disordered variants involving different TiO_6–ZrO_8 column sequences in materials dependent on cooling rate and exact Zr/Ti ratio.[6]

The crystallographic form of $ZrTiO_4$ influences the dielectric properties to a small but significant degree. In one controlled experiment,[6] for pure $ZrTiO_4$ prepared at high temperature, where the Zr and Ti are fully disordered, the dielectric properties at microwave frequencies were found to be: $K = 43$, TCK $= 58$ ppm $°C^{-1}$, and $Q = 3100$, and for samples annealed for a long time at 1050 °C, showing a well ordered Zr/Ti array, the properties were found to be $K \approx 38$, TCK $= 76$ ppm $°C^{-1}$, and $Q \approx 2100$. Contrary to the generally negative influence of disorder[3,5] the Q value is larger in the disordered material, indicating the influence of other factors, not yet understood. Changes in K, Q, and TCK are observed in other dielectric systems as well as a function of cation disorder, an apparently generic characteristic of this class of materials. The influence of disorder on the properties of pure $ZrTiO_4$, however, is less pronounced than what is generally observed.

Though the effect of Zr/Ti disorder is significant, it is not as dramatic as partial Sn substitution for Zr. This substitution results in a sufficient decrease in TCK to allow the practical use of this material. As all the elements are tetravalent, it is possible over a small composition range to have mixed substitution of Sn for both Ti and Zr, resulting in a general formula $Zr_{1-x}Ti_{1-y}Sn_{x+y}O_4$. However the best properties are obtained for materials with pure Zr substitution $Zr_{1-x}Sn_xTiO_4$, where the solid solution range is approximately $0.0 < x < 0.4$. At compositions between $x = 0.2$ and $x = 0.3$, both the lowest TCF (1–5 ppm $°C^{-1}$) and highest microwave frequency Q values (7000–$10,000$) are obtained.[5] It is certainly surprising that both these important qualities are optimized near the same composition, as no microscopic connection between Q and TCF has thus far been established.

The effect of the Sn substitution on the crystal structure has been studied in an attempt to correlate the structure and the dielectric properties.[6] In general, the addition of a third metal element to a material like $ZrTiO_4$ would be expected to facilitate the occurrence of the disordered state, as partial mixing increases entropy and should therefore stabilize the more disordered phase. This is true for this system on averaging over many unit cells, but the true microscopic structure is much more complex. The Sn substitution, at temperatures which usually result in the ordered structure, actually causes a mixing of ordered chain fragments of TiO_6 octahedra with ordered chain fragments of double ZrO_8 cubes along single columns which in the fully ordered structure would contain only octahedra or cubes. It has been proposed that the Sn substitutions occur at the exact locations of the switching from TiO_6 octahedra to ZrO_8 cubes along the chains, thus resulting in more switching in the columns (and shorter chain fragments) with increasing Sn content. Thus, the size of the regions of ordered octahedra and cubes decreases with increasing Sn content. This decrease in the correlation lengths of the ordered regions occurs with the increasing Sn content, as does the increase in Q and decrease in TCF. It has also been shown that for a fixed Sn content, increased annealing time at low temperatures increases the Q value.[3] Since annealing is expected to decrease disorder, it is possible that its actual affect is to make the lengths of the ordered chain fragments in the

mixed columns more uniform within the overall average structure, through more uniformly distributing the substituted Sn at the interfaces between Ti rich and Zr rich regions. It has been proposed (though not proven) that this short-range ordering of the Sn is what improves the Q values.[6] Why such a complex local structure should decrease the TCK at the same time for this material has not been established. Due to the commercial significance of this material and its interesting crystal chemistry many other studies have been performed which test the effects of chemical additions and substitutions on the processing and properties of bulk dielectrics. Examples of these types of studies can be found in references 7 and 8. Though of interest, none of these chemical additions appear to greatly improve either the processing or properties of the basic $(Zr,Sn)TiO_4$ solid solution.

Ba$(Zn_{1/3}Ta_{2/3})O_3$ and related perovskites

These perovskites are of particular interest for microwave applications because they can be fabricated with exceptionally high Q values at microwave frequencies (see, for instance, refs. 9–14). Although the K values (25–30) are lower than those obtained for the $(Zr,Sn)TiO_4$ dielectrics, they do have low TCF values (<5 ppm $°C^{-1}$) and remarkably high Q values, in the range of 10,000–40,000. The high Q values in the pure materials are obtained after annealing at high temperatures for very long times, of the order of 100 hours at 1400 °C, conditions incompatible with reasonable commercial manufacturing practices. The long annealing times necessary to obtain high Q value materials indicates, as for $(Zr,Sn)TiO_4$, that order/ disorder on the transition metal sublattice has an important effect on the dielectric properties. Essential to the eventual commercialization of these materials was the discovery that for small changes in composition in the $(1-x)Ba(Zn_{1/3}Ta_{2/3})O_3$–$(x)BaZrO_3$ perovskite solid solution, for $x<0.05$, the heating time necessary at high temperatures to obtain the high Q state was reduced by a factor of 10. As in the case of $(Zr,Sn)TiO_4$, a complex relationship between local crystal structure and dielectric properties may be inferred. For the perovskites, however, the phenomenology seems more straightforward, making these materials of particular interest for detailed study.

The crystal structure of $Ba(Zn_{1/3}Ta_{2/3})O_3$ is that of a classic ordered perovskite with two transition metals (B and B') on the octahedral site. The most common B-site ordered perovskite
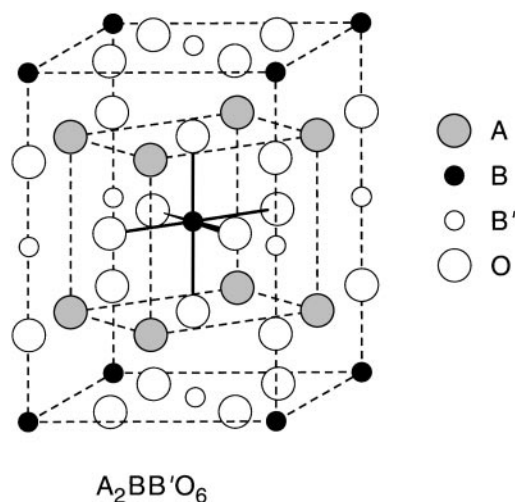

$A_2BB'O_6$

Fig. 2 The crystal structure of one of the ordered B-site perovskite structure types found for dielectric materials. This illustrates the ordered perovskite of stoichiometry $A_2BB'O_6$, with B and B' planes alternating in a 1 : 1 ratio along the perovskite subcell (111) direction. In the ordered $A_3BB'_2O_9$ variant found for $Ba(Zn_{1/3}Ta_{2/3})O_3$ the Zn and Ta occur in (111) planes alternating in a 1 : 2 ratio. These two structure types compete energetically in $Ba(Zn,Ta,Zr)O_3$ low TCK dielectrics.

structure type occurs for a stoichiometry $A_2BB'O_6$, shown in Fig. 2. The B and B' ions occur on alternating (111) planes in a 1 : 1 ratio. The ordered $A_3BB'_2O_9$ structure type, where the B and B' atoms occur in a 1 : 2 ratio, which occurs for $Ba(Zn_{1/3}Ta_{2/3})O_3$, is common to other related dielectric perovskites, with, for example, Mg or Ni in place of Zn, or Nb in place of Ta.[10] In the ordered form of this perovskite, as in the 1 : 1 variant, the Zn and Ta octahedra are ordered in the (111) perovskite planes. Each (111) plane contains only one type of small ion–oxygen octahedron, and the planes are ordered in the 1 : 2 stoichiometric proportion, in the sequence – Zn–Ta–Ta–Zn–Ta–Ta–.... The resulting symmetry, due to the (111) type plane stacking and accompanying small oxygen displacements, is trigonal. The attainment of perfect B-site ordering for the stoichiometric compounds is very sluggish. Partial disorder, which mixes the different B-site ions within single (111) planes, is very common under normal synthetic conditions, and all materials are highly disordered as initially synthesized.[9] The correlation between long annealing time, improved ordering of the B-site ions, and the highest Q dielectric properties has been clearly experimentally established in these materials.[9–14] The improved Q with decreased disorder is consistent with the idea that good atomic ordering decreases the frequency widths of phonon vibrations at infrared frequencies whose tails extend into the microwave region and are major contributors to the microwave frequency dielectric loss.[1,3,5]

So in this system everything seems to make sense until one considers what effect the solid solution with the $BaZrO_3$ perovskite might have on the dielectric properties. The addition of an additional B-site element is expected to encourage disorder on that sublattice, and such disorder has been deduced to occur based on the disappearance of the superlattice ordering reflections in conventional X-ray diffraction experiments. This disorder would have the effect of decreasing rather than increasing the Q values according to the picture of disorder broadened phonon frequency resonances. The opposite effect in fact occurs, with only 10 hours annealing time needed to attain the high Q state. As was found to be the case in $(Zr,Sn)TiO_4$, the full story involves local atomic ordering and is quite complex.

Because trigonal $Ba(Zn_{1/3}Ta_{2/3})O_3$ is based on small distortions of a cubic perovskite cell, there are eight possible unique (111) directions which can become the unique trigonal axis when the low symmetry phase forms out of the disordered cubic phase during ordering. Thus in crystals of $Ba(Zn_{1/3}Ta_{2/3})O_3$ there are twin domains with eight different orientations. The dimensions of these domains can be seen with an electron microscope, and are on the order of 2000 angstroms in the well ordered non-Zr doped material.[10] The domains are separated by domain boundaries. The ordering involves the growth of these ordered domains from the disordered B-site arrangement. For small levels of Zr doping, on the 1–3% doping level, these domains can still be seen, but decrease radically in dimension, becoming on the order of 25– 50 angstroms in size. Thus the apparent disorder deduced to occur on Zr doping of $Ba(Zn_{1/3}Ta_{2/3})O_3$ from conventional X-ray diffraction experiments is an incorrect conclusion—the extra peaks due to Zn/Ta ordering become weak and broad because the domain sizes get very small.[10] The possible explanation of the increased kinetics in the formation of the high Q state can then be explained as being due to the fact that the ordering times for forming these small domains of ordered material are much shorter than for forming the larger domains in the undoped material. However such small domains result in a larger relative volume of material in domain boundaries, which are expected to be dielectrically lossy. It has been speculated that the doped Zr in fact segregates to the domain boundaries, "stabilizing" them against lossy resonances. Further, when the doping level reaches 5%, the nature of the

short-range ordering changes, from one of a tripled perovskite: B–B′–B′–B–B′–B′, to one of a doubled perovskite: B–B′–B–B′– (Fig. 2). For the doubled perovskite, the B-site layers are no longer expected to be purely one atom type or another, but rather involve some mixture. This change in ordering type near 5% substitution has been suggested to be the origin of the discontinuous change in Q at low doping levels.[10]

Due to the commercial importance of these materials, there have been a variety of studies of the effects of doping on the observed properties. Complex structure–property relationships have been observed.[11–14] The related solid solution system $CaTiO_3$–$Ca(Al_{1/2}Ta_{1/2})O_3$ has been reported to have a high dielectric constant ($K \approx 46$) low TCF (0 ppm $°C^{-1}$ for some compositions and annealing conditions) and reasonable microwave frequency Q values (1000–4000).[15] The relatively high K value makes this material of particular interest. The dielectric properties for this system are again significantly affected by annealing time and temperature, suggesting that order/disorder on the B-site is important. A more complex perovskite system, $(Pb,Ca)(Fe,Nb,Sn)O_3$, has been reported to have a very high dielectric constant ($K \approx 85$–90), low TCF (near 0 ppm $°C^{-1}$) and moderate microwave frequency Q value (between 500–1500),[16] which is also worthy of further consideration for practical applications. It is of interest to note that for this system as well, the highest microwave Q and lowest TCF are reported to occur at the same composition and annealing conditions. No microscopic investigation of structure–property relations has been reported in either of these two cases.

As can be surmised from the preceding discussion, the detailed relationships among the temperature coefficient of the dielectric constant, chemistry, and crystal structure in complex perovskites are themselves very subtle and complex. However, from a global point of view, an overall empirical correlation between the temperature coefficient of the dielectric constant and the crystal structure, through the perovskite tolerance factor, has been established (Fig. 3).[17] Recall that the tolerance factor is a measure of the relative sizes of the AO and BO$_2$ layers, $t = (R_A + R_O)/\sqrt{2}(R_B + R_O)$. $t = 1$ indicates a perfect size match, with t less than 1 accommodated by rotation of the

metal–oxygen octahedra to create cavities of the correct size for the A cations, with accompanying structural distortions to lower symmetry. For low tolerance factor perovskites, ($t < 0.97$) positive TCKs of 50 ppm $°C^{-1}$ or larger are observed. There is a sharp crossover to large (-200 ppm $°C^{-1}$ or larger) negative TCKs in the very small t interval of $0.97 < t < 0.99$ associated with an accompanying change in the type of structural distortion. The TCK then gradually becomes less negative with increasing t, approaching 0 for the largest AO layer sizes near $t = 1.05$. Though such an empirical correlation is not expected to explain the detailed influence of complex order/disorder phenomena on TCK or dielectric loss, nor has it yet been interpreted in terms of the underlying lattice physics, it does present an important starting point for discussion of TCK–structure correlations in these materials.

As in the other dielectric family we have discussed in detail, $Zr_{1-x}Sn_xTiO_4$, the relationships between structure and properties of the $Ba(Zn_{1/3}Ta_{2/3})O_3$ perovskite dielectrics have been well established due to careful structural analysis on the microscopic scale. However, for these cases, as well as for all others in the family of microwave frequency dielectric materials, the next step in understanding: establishing a link between the *physics* of the system and the observed properties and structures through experimental study, is missing. In particular, the underlying physical reason why some atomic configurations favor a low TCF and others do not has not been experimentally established. In addition, clear experimental confirmation of the proposed effect of disorder on the phonon spectra is apparently lacking. The high degree of structure–property knowledge already extant on the perovskite systems suggests that they may be excellent candidates for detailed physical study and modeling.

Barium titanates: $Ba_2Ti_9O_{20}$, $BaTi_4O_9$, and Ba–Ln–Ti–O

The binary barium titanates were the first dielectric materials described as having practical application in modern microwave frequency resonators,[18,19] and remain in commercial use. Two binary materials have good dielectric properties:[2] $BaTi_4O_9$,
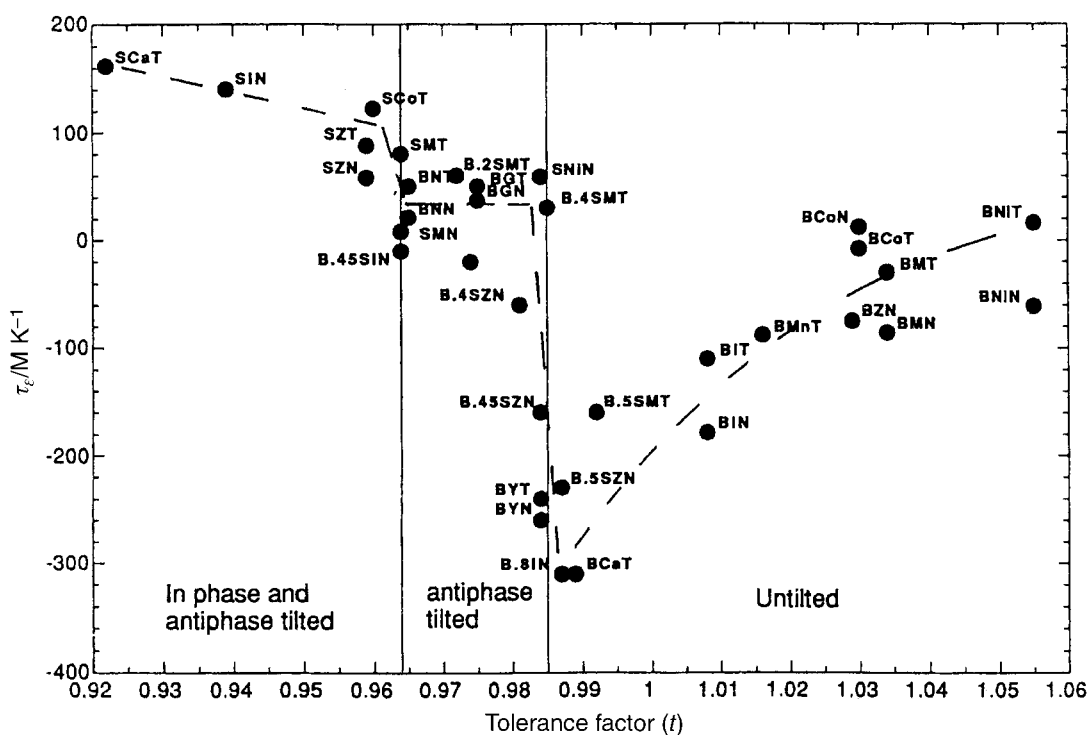

Fig. 3 Relationship between the temperature coefficient of the dielectric constant (τ_ε) and the tolerance factor (t) for perovskite dielectrics.[17] Abbreviations employed are: B = Ba, S = Sr, T = Ta, Z = Zn, N = Nb, M = Mg, I = In, G = Gd. For details see ref. 17.

$K = 38$, TCF $= 14$ ppm $°C^{-1}$, $Q > 10,000$, and $Ba_2Ti_9O_{20}$, $K = 39$, TCF $= 4$ ppm $°C^{-1}$, and $Q > 10,000$. As in the systems described above, extensive work has been performed to test the effects of different chemical additives on the dielectric properties (see *e.g.* refs. 2, 20 and 21). It has been found that SnO_2, ZnO or Ta_2O_5 additions in particular have a favorable influence in reducing the TCF for some applications. An excellent description of the many considerations involved in developing materials such as this for commercialization can be found in reference 2.

The issues surrounding the chemistry/structure/property relations in this family are considerably different from those encountered in the two materials families described above. In particular, due to the simpler crystal chemistry, there are no apparent issues involving order/disorder on the Ti sublattice. The basic materials themselves as synthesized display good basic properties. Improved or altered properties on atomic substitution or change in the Ba/Ti ratio primarily appear to involve the appearance of additional phases in the ceramics. These phases in some instances may have TCFs opposing those of the majority titanates, improving the overall TCF of the ceramic. Thus multiple phase mixtures may sometimes be desirable, unlike the case for the first two systems described.

The crystal structures of these materials are more "bronze-like" than perovskite-like, and they are relatively high in Ti content. Due to the relatively lower proportion of valence-stabilizing electropositive elements such as Ba or Zr, the Q values of this family of materials are quite sensitive to firing conditions and defect chemistry. This is a result of the fact that as a consequence of this kind of crystal chemistry Ti^{4+} is easily partially reduced to Ti^{3+} under normal ceramic processing conditions in these materials, as at high temperatures oxygen vacancies may be formed. The introduction of Ti^{3+} decreases Q through the introduction of electrical conductivity due to electrons by the defect reaction:

$$O_o \rightarrow \frac{1}{2}O_2(g) + Ti^{3+} + e^-$$
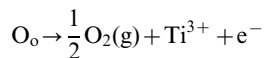
The variability of Q due to partial reduction in bulk ceramics was a hindrance to widespread acceptance of these dielectrics in microwave devices. Recently, however, more detailed understanding of the processing conditions necessary for suppression of Ti reduction has been obtained. The suppression of Ti reduction by aliovalent cation substitution (*i.e.* Mn for Ti) in small proportion has also been reported.[2] Thus these materials are in use in resonators at the present time.

Important members of this family of dielectrics are related complex ternary materials in $BaO–Ln_2O_3–TiO_2$ chemical systems with a bronze-like crystal structure. The compound forms for the large through intermediate size rare earths. These materials are important as they have the highest K (80–100) of all the low TCF dielectrics (TCF < 10 ppm $°C^{-1}$ for some compositions) presently known. The high K comes at the cost of relatively lower Q values, in the 1000–4000 range,[22] but the overall properties are acceptable for many applications. The dielectrics with the best properties consist almost exclusively of one phase, but that phase has a complex crystal structure, and until recently its exact composition was not even known. By the best current understanding, the compound is a solid solution, with formula $Ba_{6-3x}Ln_{8+2x}Ti_{18}O_{54}$. The limits of the solid solution are generally $0 < x < 0.8$, and depend on lanthanide size, with optimal properties near $x = 0.5$.[22] Nd and Sm based materials have been the most frequently studied. The solid solution involves the mixing of some of the Ba and Ln with vacancies on one crystallographic large atom site, in the appropriate ratio to maintain charge neutrality. TCF and Q are very strong functions of the composition.[22] Additives such as Pb and Bi have been found to be very helpful in stabilizing the low TCK behavior,[22,23] but do not have favorable effects on Q. Bi, at least, appears to substitute for the lanthanide, but the details of the crystal chemistry of Pb substitution are not yet known.

Processing of the ceramics is also an important issue.[22,24] Aside from the complex crystal chemistry of this phase, the crystal structure and therefore the dielectric properties display significant anisotropy. This adds a complexity in ceramic processing not encountered in the other materials discussed thus far. The preferred crystallite orientation normally present in standard ceramic forming procedures for non equi-axial crystallites results in a bulk ceramic body whose properties are not isotropic. In particular, when fine-tuning factors such as the TCF of the ceramic sample, careful consideration of the orientation of the crystallites is necessary.[22] This suggests that this material is at least partially "self-compensating" from the TCF point of view: the intrinsic TCF is likely to be different in different crystallographic directions, yielding the best TCFs for particular mixtures of orientations of the crystallites in a bulk sample.

It might be fair to say that the complexities of applying this dielectric material in as demanding an application as microwave device fabrication are a materials scientist's worst nightmare. Unfortunately, it is important to understand all the aspects of the structure/chemistry/property relationships in this material, as it represents a unique case of a material with high K with acceptable TCF and Q. It would be discouraging if it were representative of the complexities that such materials would always have to display to be useful. For the time being, at least, it comprises a class of one and has to be taken as the best example of its kind.

$Ca_5TiNb_2O_{12}$ perovskites, $Ca_2Ta_2O_7–Ca_2Nb_2O_7$ pyrochlores, BST–BSN, and $Ta_2O_5–Al_2O_3$

The materials described thus far are the most well studied microwave ceramic materials. A variety of others have been studied as well, such as those based on $MgTiO_3$ (for example ref. 25) and the bismuthate pyrochlores (for example ref. 26). Some aspects of our own work in this family of materials are now described. We have concentrated on attempting to find single-phase high Q systems such as the perovskites described above, multiple phase systems in which TCK is balanced by mixtures of different dielectrics, and systems related to materials already in use or considered for use in the near future in thin-film based devices.

We recently reported[27] a new single phase dielectric perovskite to be considered for such applications. The Nb based compound, $Ca_5Nb_2TiO_{12}$, displays a dielectric constant near 35, high quality factor ($Q > 5000$), and TCK < 5 ppm $°C^{-1}$. The TCK is highly dependent on processing conditions, indicating that order–disorder transitions on the B-site sublattice have a great effect on the dielectric properties. Unlike previously studied low TCK dielectric materials, these perovskites involve *three* cations in major proportion on the perovskite B-site. The chemical formula is better written as $Ca_4(CaNb_2Ti)O_{12}$. Ca, Ti and Nb are mixed on the perovskite octahedral site in the ratio $1:2:1$. The detailed crystal structure has not yet been determined, but the unit cell has orthorhombic symmetry with a cell volume involving multiple simple perovskite subcells. At low temperatures, the different B-site atoms may be fully or partially ordered in crystallographically inequivalent B-sites, and at high temperatures there may be more extensive disorder of atoms among the possible sites due to the influence of entropy.

The behavior of the temperature coefficient of the dielectric constant as a function of processing temperature and time is highly unusual. There is a double-crossing of zero TCK with processing temperature, summarized in Figs. 4 and 5. They present the TCK and K for both $Ca_5Nb_2TiO_{12}$ and the related compound $Ca_5Ta_2TiO_{12}$ for ceramics fired for 3 hours at a set
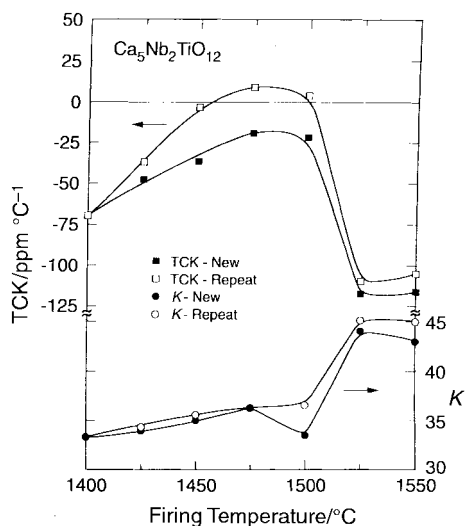
Fig. 4 K and TCK for $Ca_5TiNb_2O_{12}$ as a function of firing temperature and processing time for polycrystalline ceramics fired for 3 hours ("new") or multiple 3 hour firings in 25 °C increments ("repeat").

Fig. 5 K and TCK for $Ca_5TiTa_2O_{12}$ as a function of firing temperature and processing time for polycrystalline ceramics fired for 3 hours ("new") or multiple 3 hour firings in 25 °C increments ("repeat").

temperature, and those fired for 3 hours at low temperatures and then for 3 hours in 25 °C increments at each temperature up to the limit shown (labeled "repeat" in the figures). At low firing temperatures, the TCK is negative, at intermediate temperatures positive, and at high temperatures negative again. The double zero crossing of TCK is maintained under most experimental conditions, but it is seen that the positive TCK is not attained in the single firing run for the niobate, although small negative values are obtained. Further it is seen that the temperature at which the positive TCK region is reached on heating is shifted to lower firing temperature for the repeat firing pellets. Thus the atomic configuration which gives rise to the positive TCK state in these materials requires a time on the scale of hours to form. This strongly suggests that the positive TCK state is due to the formation of an ordered state of the cations on the B-sites. This ordered state appears to be short-range in nature, as the conventional powder X-ray diffraction patterns do not show the appearance of new diffraction peaks in the corresponding temperature interval. At the highest firing temperatures, the negative TCK behavior returns. The transition temperature to this state is between 1500 and 1525 for the niobate and 1575–1600 °C for the tantalate. For both materials, this transition occurs abruptly and is independent of firing time, suggesting the presence of a high temperature transition from an ordered B-site structure to a disordered B-site structure with good kinetics. Conventional powder X-ray diffraction analysis reveals that the materials remain single-phase perovskites, and that there has been no long-range structural rearrangement or discontinuity in lattice parameter. As for other materials in this family, small substitutions of another ion on the B-site, in this case Zr for Ti, greatly influence the ordering time and temperature.[28] The introduction of Zr increases greatly the temperature and time processing windows for which a zero TCK state may be attained (Fig. 6), enabling the eventual commercialization of this dielectric. It is expected to display competitive properties with materials currently in use. Nothing is yet known from a microscopic viewpoint about the short-range ordering of the three ions on the B-site as a function of processing time and temperature. The dramatic change from a low positive TCK state to a large negative TCK state as a function of cation disorder in these materials suggests that they may be excellent candidates for physical study to determine which underlying factors determine TCK in ceramic dielectrics.

Interesting low loss low TCK materials may also be found among chemically related materials based on the pyrochlore
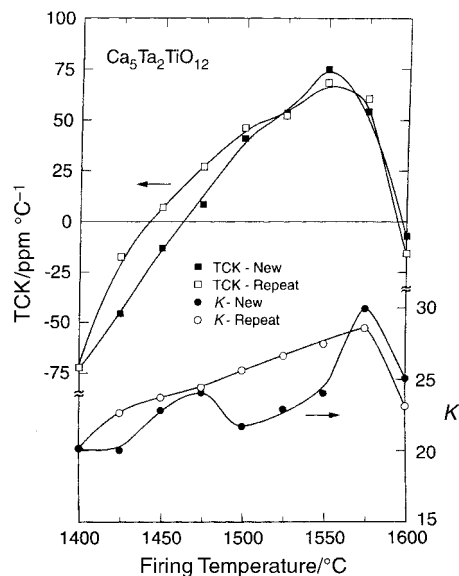
structure type, $Ca_2Ta_2O_7$ and $Ca_2Nb_2O_7$. The dielectric data for $Ca_2Ta_2O_7$: $K \cong 25$, $TCK \cong -450$ ppm $°C^{-1}$, and for $Ca_2Nb_2O_7$: $K \cong 25$, $TCK \cong 250$ ppm $°C^{-1}$, suggest that a low TCK material can be obtained in mixtures of the two phases.[29] The variation of TCK with composition across the $Ca_2Ta_{2-x}Nb_xO_7$ series is presented in Fig. 7. It is characteristic of that expected for a series in which a two-phase composition region is crossed between $x=0.2$ and $x=0.4$: mixing two compounds with TCK values of opposite sign. Fig. 8 depicts the sensitive dependence of TCK on composition near the balance point. The optimal material, $Ca_2Ta_{1.64}Nb_{0.36}O_7$, has a K of 30, TCK <2 ppm $°C^{-1}$, and $Q>5000$.

Both $Ca_2Ta_2O_7$ and $Ca_2Nb_2O_7$ have pyrochlore related structure types, though they are sufficiently different that a solid solution is not formed across the $Ca_2Ta_{2-x}Nb_xO_7$ series. For x up to 0.2, the materials are a solid solution of the high temperature polymorph of $Ca_2Ta_2O_7$. For x from 0.4 to 2, the
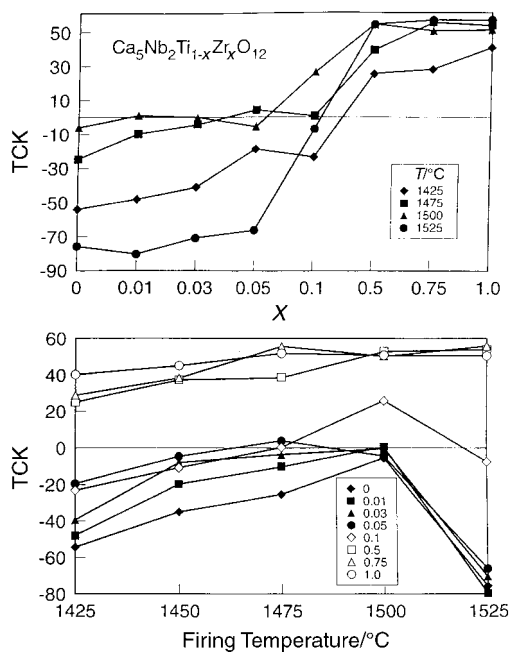
Fig. 6 TCK for $Ca_5Ti_{1-x}Zr_xNb_2O_{12}$ as a function of firing temperature and Zr substitution for polycrystalline ceramics fired for 3 hours, showing the improved stabilization of the low TCK phase.
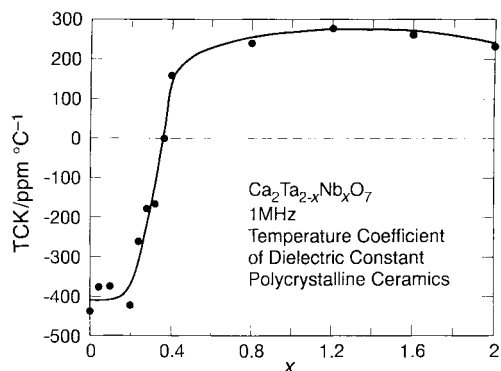
Fig. 7 The temperature coefficient of the dielectric constant (TCK) for bulk polycrystalline ceramics of $Ca_2Ta_{2-x}Nb_xO_7$.

Fig. 8 The relative change in dielectric constant in the vicinity of ambient temperature for compositions near the zero TCK value in the $Ca_2Ta_{2-x}Nb_xO_7$ system.

materials are a solid solution of the $Ca_2Nb_2O_7$ structure type. The samples in the composition region between $x = 0.2$ and 0.4 span the region where TCK is changing rapidly with composition, reaching a balance point near $x = 0.36$. At $x = 0.36$ a third pyrochlore related phase is dominant. It is the balance of the (small positive) TCK of that phase with the negative TCK of the $Ca_2Ta_2O_7$ type solid solution phase which yields the good dielectric materials in this chemical system. Though such mixed phase systems are not as interesting from a fundamental scientific viewpoint, they do illustrate the principle that it is possible to obtain high K, low TCK, low loss microwave dielectrics in multiple phase ceramics.

The final two systems that will be described briefly were studied in attempts to change the TCKs of high K dielectric systems presently being considered as the basis of advanced capacitance components in microelectronic memory and other applications in thin film rather than bulk form. It is widely realized that further miniaturization of capacitance components in microelectronic devices requires either the fabrication of three-dimensional capacitor geometries with a high effective two-dimensional area, a complex processing issue, or the development of new dielectrics to replace SiO_2. SiO_2, due to its relatively low dielectric constant and limitations on the minimum thickness for which reliable layers can be fabricated, has limits for the capacitance per unit area attainable. The latter alternative requires that the new dielectric not be poisonous to the other materials in the microelectronics circuitry, and that the processing necessary to make the dielectric is compatible with microelectronics processing, two very strong restrictions.

The ferroelectric perovskite barium strontium titanate $Ba_{1-x}Sr_xTiO_3$ (BST) has been very widely studied for use in high capacitance memory elements in microelectronics applications. Although fundamentally chemically incompatible with microelectronics, no other very high K materials ($K > 300$) have emerged as real alternatives. Equivalent compatibility issues also exist for other high K materials. The use of this dielectric would in fact require considerable alteration of microelectronics fabrication procedures, and it will be interesting to see whether its properties are ultimately sufficient motivation to try to work out all the processing issues its use raises.

The composition being considered for such applications, $Ba_{0.5}Sr_{0.5}TiO_3$, has a peak in the temperature dependence of its dielectric constant just below room temperature. Thus the capacitance of any device based on such a material will be highly temperature dependent, making its use difficult to accommodate in circuit design. It would therefore be important to compensate for its temperature coefficient of dielectric constant without decreasing its high dielectric constant. To do so, we employed a mixed phase approach,[30] as trying to alter the intrinsic properties of a dielectric to reduce its TCK would not be expected to work in ferroelectrics because very high K and low TCK are inherently exclusive. By mixing with a second
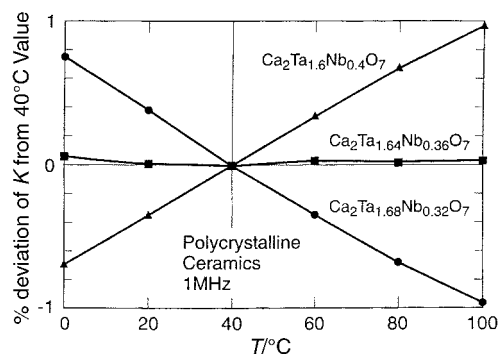
ferroelectric phase in thermodynamic equilibrium with BST at this composition, with an opposite temperature dependence, it should be possible to have the two temperature dependencies partially cancel each other out. We found this to be possible in thermodynamically stable mixtures of $Ba_{1-x}Sr_xTiO_3$ (BST) with another ferroelectric $Ba_{1-x}Sr_xNb_2O_6$ (BSN), which are in equilibrium at equal Ba:Sr ratios. The temperature dependence of the change in dielectric constant for two-phase mixtures for bulk ceramics of this kind is shown in Fig. 9. The figure shows that the temperature dependence of the dielectric constant of BST near room temperature is largely suppressed when mixed with a large proportion of BSN. High dielectric constants are maintained in the mixture, making such materials highly preferable in applications where the capacitance of a device should be only weakly dependent on temperature.

When consideration of the chemical and processing compatibility of dielectric materials with microelectronics is the primary issue, Ta_2O_5 emerges as the most likely near-term replacement for SiO_2 in a variety of significant microelectronics applications. The dielectric constant for Ta_2O_5 is approximately 25 compared to 4 for SiO_2. Additional important characteristics for practical application such as low leakage current, good breakdown field, and reproducible fabrication in large scale microelectronics facilities are also acceptable, and so Ta_2O_5 has progressed beyond the exploratory stage and into real technological development at this time.

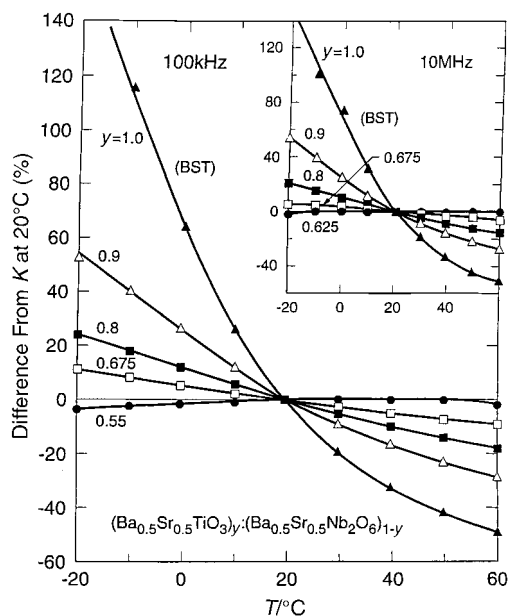The importance of this material for near-term application

Fig. 9 The temperature dependence of the dielectric constant relative to its value at 20 °C for multiple phase mixtures of $Ba_{0.5}Sr_{0.5}TiO_3$ and $Ba_{0.5}Sr_{0.5}Nb_2O_6$ in bulk ceramics.

suggests that determination of the effects of processing and chemical additives on its dielectric properties is of significant interest. In that regard, we systematically explored the effects on dielectric properties of bulk ceramics of chemical additives selected from the list of elements considered fully acceptable in microelectronics processing environments. The list of such elements is highly restricted, *e.g.* Si, Al, Ti, N, and B and a few others.

The solid state chemistry of Ta_2O_5 is very interesting due to the surprising complexity of its crystal structure. The structure contains Ta in many coordination environments, suggesting that many other metals may show solubility in significant proportion. This turns out to be true for all the metals on the "allowed" microelectronics element list. Although the partial substitution of SiO_2 in Ta_2O_5 only changes the dielectric properties as expected from an extrapolation between the end members and is therefore uninteresting, other substitutions have more dramatic effects. The partial substitution of Ti for Ta in bulk materials results in a surprising increase in K to 150 at the 8% substitution level.[31] This would be an important new high K material due to its compatibility with Si processing, but attempts to fabricate thin films of partially substituted high K material by microelectronics compatible processing have so far failed to yield high dielectric constants. This may be attributable to the fact that the thin films for microelectronics are fabricated under low temperature conditions and are either microcrystalline or amorphous. The phase of Ta_2O_5 present in the Ti substituted bulk ceramics is the "high temperature" form, which is apparently not accessible in low temperature syntheses, even for thin films where kinetics of diffusion are expected to be very good. The possibility remains, however, that with appropriate processing the high K material may be obtained.

Of particular relevance to the topic of this review is the unexpected effect of Al_2O_3 partial substitutions in Ta_2O_5.[32] Fig. 10 shows the temperature dependence of the dielectric constants of $(Ta_2O_5)_{1-x}(Al_2O_3)_x$ solid solutions for $0.0 < x < 0.2$. Two effects can be noted. Firstly the magnitude of the dielectric constant is not degraded on Al_2O_3 substitutions in this composition range, for example being approximately 42 at $x = 0.1$, even though the K of Al_2O_3 itself is only 8. Secondly it can be seen from the figure that the temperature coefficient of the dielectric constant, normally 440 ppm $°C^{-1}$, has decreased significantly in the Al_2O_3 substituted materials. This is shown in more detail in Fig. 11, where the difference from the $20 °C$ dielectric constant as a function of temperature is plotted for materials with different compositions. The figure shows that the TCK for $x = 0.15$ becomes very low indeed, less than a few ppm $°C^{-1}$. There apparently have been no attempts published to date to see whether this dramatic improvement in TCK can be seen in thin films processed under microelec-
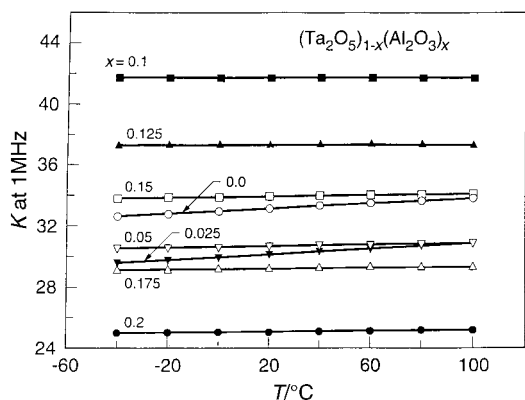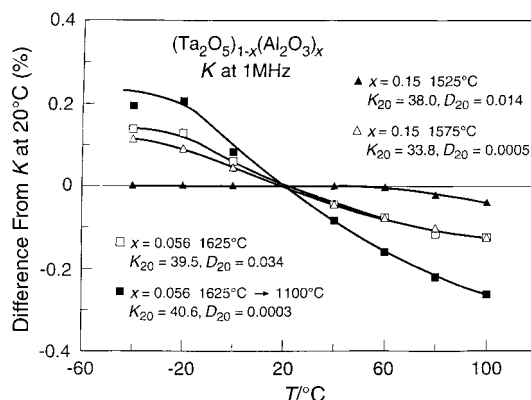
Fig. 11 Detail of the relative change in dielectric constant for Al_2O_3 doped polycrystalline bulk ceramics of Ta_2O_5.

tronics compatible conditions. However, because the Al_2O_3 substitutions stabilize the "low temperature" form of Ta_2O_5, the chances that these properties may be obtained in thin film form appear promising. In any case, Ta_2O_5 is widely employed as a bulk dielectric in other applications and the use of materials with Al_2O_3 addition and temperature stabilized dielectric constant may be of interest for other applications. The relationships between the structure and crystal chemistry of Ta_2O_5 and its dielectric constant and TCK are not presently understood, nor is it apparently under study. It would be of significant interest to characterize this material in further detail, as the microscopic mechanisms for these effects may be of use in designing new materials with similar properties.

Conclusions

Ceramic dielectrics with the particular combination of physical properties making them suitable for applications in microwave frequency resonators have been studied since the 1970s. For applications which require dielectric constants of 40 or less, good materials are known, though no one material at this point in time appears to have properties which are sufficiently superior to all others to dominate the commercial market. For materials with higher dielectric constants, a fundamental conflict exists at the level of the fundamental physics of materials—the atomic polarization processes necessary to achieve high dielectric constant also invariably give rise to dielectric loss and temperature dependence of the dielectric constant. Thus the development of microwave dielectric materials with dielectric constants of 75 or larger with suitable properties is in its early stages. There remains the real possibility that an exceptional material may be found on further exploration. In addition, development of specific new materials with good properties but with microelectronics compatibility will be an important step in the development of more integrated microwave/microelectronics systems. The importance of the communications and information industries to modern society certainly indicates that continued investment in the development of new materials for these applications is warranted.

An added bonus in the development of these materials is the complex relationship among their chemistry, crystal structure, and dielectric properties. Several excellent studies have been done in this area, but much more remains to be learned. With the motivation of understanding materials with significant technological importance, the study of the phenomena associated with atomic order and disorder on the local scale in complex solid solution chemical systems, a topic at the forefront of current materials research, becomes of even greater interest. Further, the real details of the microscopic mechanism for the connection between the

Fig. 10 The temperature and composition dependence of the dielectric constants for Al_2O_3 substituted solid solutions in Ta_2O_5 bulk ceramics.

structure and properties of these materials and their physical properties have not yet been established. Collaborative efforts between materials scientists interested in dielectrics and condensed matter physicists interested in lattice dynamics and defects in solids would be very productive in helping to understand the materials now known, and would be essential in helping to find new materials with superior properties in the future.

Acknowledgements

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