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Preparation and properties of $KNbO_3$ via the sol–gel method

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Sol–gel processing of a solution of niobium and potassium ethoxides in methanol was used to prepare polycrystalline potassium niobate ceramic discs. Gel powders completely crystallized after only 2 h at 600° C. Crystallized powders were hot-pressed at pressures less than half of that required in conventional methods. Densities of up to 99% were achieved without encountering the common problem associated with the evaporation of the potassium oxide and subsequent formation of a stable second phase. The variation of dielectric constant with temperature was measured up to several degrees above the Curie temperature ($\sim 420°$ C). Dielectric constants of dense samples were found to be more than one and one-half times greater than that of their single crystal counterparts.

1. Introduction

In the past few years the sol–gel method has been widely studied as a new route for the preparation of glasses and ceramics [1–3]. Some of the advantages of the sol–gel method are: the mixing of reactants on a molecular level, better control of stoichiometry because of the lower reaction temperatures, finer distribution of dopants, higher purity raw materials, and the ease of formation of ultrafine powders. In the sol–gel method the relevant constituents are intimately mixed in liquid solutions. Depending on the experimental conditions, either ultrafine particles can be precipitated, or an amorphous bulk gel can be formed. The ultrafine powders or the bulk gel are then crystallized and densified to yield ceramics at relatively low temperatures. In contrast to the sol–gel route, conventional processing of polycrystalline ceramics involves the mixing of much coarser powders which requires higher firing temperatures. A direct comparison of the preparation and properties of some ferroelectrics produced by these two different routes has been recently published [4]. The results show that some ferroelectrics with excellent properties can be prepared from organic solutions. Ultrafine powders precipitated from such organic precursors have been successfully sintered into ferroelectrics at relatively low temperatures [5–7]. Alternatively, the bulk gels have been crystallized and then converted into dense ferroelectrics [8, 9].

$KNbO_3$ was prepared in the form of single crystals as well as polycrystalline ceramics. The conventional way of obtaining high-grade polycrystalline ceramics is by solid-state reaction of K_2CO_3 and Nb_2O_5. However, one of the difficulties encountered in the preparation of both single crystal as well as polycrystalline potassium niobate, has been the loss of K_2O at elevated firing temperatures [10, 11], resulting in the formation of a second phase, $2K_2O \cdot 3Nb_2O_5$ which was undesirable. Oxygen deficiency has been another problem in the preparation of this material which results from high-temperature processing and gives rise to electronic conductivity.

In the present work, the processing and properties of ferroelectric $KNbO_3$, from decomposition of metal alkoxides, will be presented and compared to those of conventionally made ceramics.

2. Experimental procedure

Solutions were prepared from metal alkoxides in methanol without catalyst. Potassium ethoxide, > 95% purity (solid), and niobium ethoxide, 99.999% (liquid), were obtained from Alfa Chemicals (a semiquantitative chemical analysis of the potassium ethoxide is given in Table I). Solutions were prepared by dissolving potassium ethoxide in anhydrous methanol at a concentration of 0.5 mol potassium ethoxide in 1 litre methanol. This solution was stirred for 0.5 h. A stoichiometric ratio of niobium ethoxide was then added to the solution and stirred for 3 h to ensure the formation of the complex $KNb[OC_2H_5]_x[OCH_3]_y$ [12]. Hydrolysis and gelation were then performed by exposing the solution to the ambient atmosphere in open dishes. Gelation was observed after 4 h. Gel pieces dried for 100 h at room temperature were ground and sieved. Powders of less than 50 μm were

TABLE I Semiquantitative analysis of potassium ethoxide*

K	50.6%
Na	0.18
Mg	0.000 15
Si	0.003 9
Cu	0.0001 15
Al	0.001 5
Ca	0.001 5
Other elements	Nil
Gain on ignition	13.78

*Analysis performed by Pacific Spectrochemical Laboratory Inc., Los Angeles, California.

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cold-pressed into 1 cm diameter discs, 2 mm high at 5000 p.s.i. ($\sim 34.45\,\mathrm{N\,mm^{-2}}$) in stainless steel dies. The discs were then embedded in alumina powder and hot-pressed in alumina dies. The hot-pressing temperature ranged from 900 to 1000° C at a pressure of 3000 p.s.i. ($\sim 20.67\,\mathrm{N\,mm^{-2}}$). Samples were pressed for either 30 or 60 min. The density of the samples was measured by the Archimedean method in water. Capacitance at 1 kHz was measured by an impedance bridge (General Radio, Type 1608-A). The dielectric constant (e) was then calculated from capacitance (c) using the following equation:

$$e = \frac{ct}{Ae_0}$$

where t is the thickness, A is the effective area of the electrode and e_0 is the vacuum permittivity ($8.85 \times 10^{-12}\,\mathrm{F\,m^{-1}}$). For dielectric constants and dielectric losses at frequencies higher than 1 kHz, a Hewlett-Packard 4275-A, Multi-Frequency LCR Meter was used. Conductivity was measured by the ASTM D257 method. X-ray diffraction and scanning electron microscopy on fractured surfaces were also performed.

3. Results and discussion

3.1. Organic solution

Infrared studies and conductometric titrations of niobium ethoxide with potassium ethoxide in ethanol and/or methanol were performed to investigate the formation of a complex or double alkoxide of potassium and niobium [13]. Results of conductometric titrations along with the findings in the infrared study strongly indicate the formation of a complex in the solution, probably of the form $KNb[OC_2H_5]_6$. Fig. 1 is a schematic drawing of the suggested double-alkoxide formed in the solution. Complex formation permits homogeneity on the molecular level of the potassium and niobium compounds. The high level of homogeneity leads to controllable stoichiometry and superior electrical properties of sol–gel processed ceramics when compared to conventionally processed ceramics. At the moment, nuclear magnetic resonance (NMR) measurements are in progress to investigate further the structure of the double alkoxide formed and the chemistry of these types of concentrated solutions.

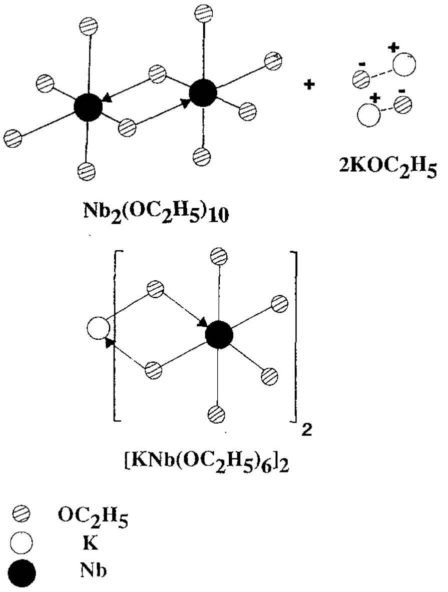

Figure 1 A proposed model for potassium niobium ethoxide complex.

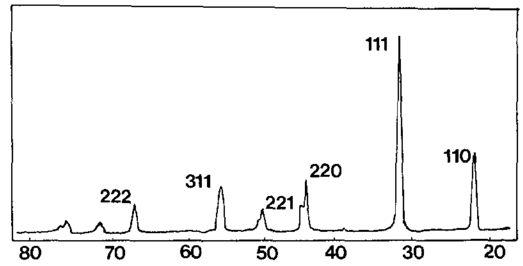

Figure 2 X-ray diffraction pattern of potassium niobate powder prepared by sol–gel processing.

3.2. Potassium niobate gel

After 4 h exposure to the ambient atmosphere at 25° C, the solution of potassium and niobium ethoxide in methanol began to gel. During this period the solution lost about 40% of its weight. After 100 h the weight stabilized but was still 25% more than the theoretical value for $KNbO_3$. This indicated that some organics and water were still trapped in the gel. Differential thermal analysis showed an endothermic peak around 134° C which is probably related to the evaporation of organics and water. At this stage the gel was amorphous by X-ray diffraction analysis. Conversion of the amorphous gel to the single phase of crystalline potassium niobate was complete after firing at 600° C for 2 h. An X-ray diffraction pattern of the crystallized $KNbO_3$, that agrees with the ASTM pattern of the 32-822, is presented in Fig. 2.

It is known that many factors, such as porosity, residual OH, residual stresses and microstructure which are governed by the raw materials used [14], catalysts [15], and temperature gellation [16], can influence the transformation of gel-derived amorphous solids at high temperatures. Starting from the solution, a wet gel is evolved which upon drying and further heat-treatment can turn into different solids, as shown in Fig. 3. However, currently there is insufficient

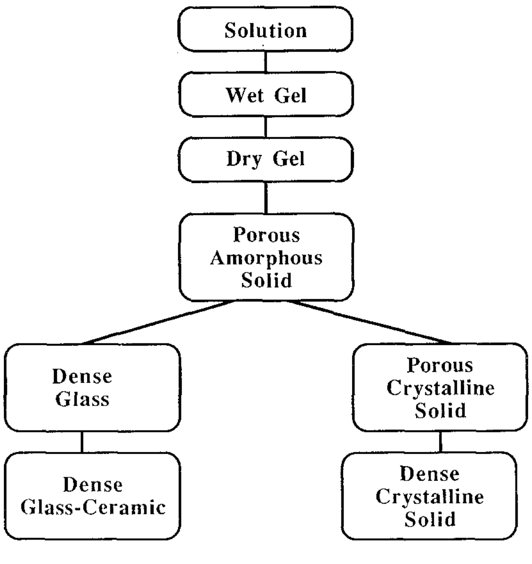

Figure 3 Possible routes of the evolution of a gel to dense solid.

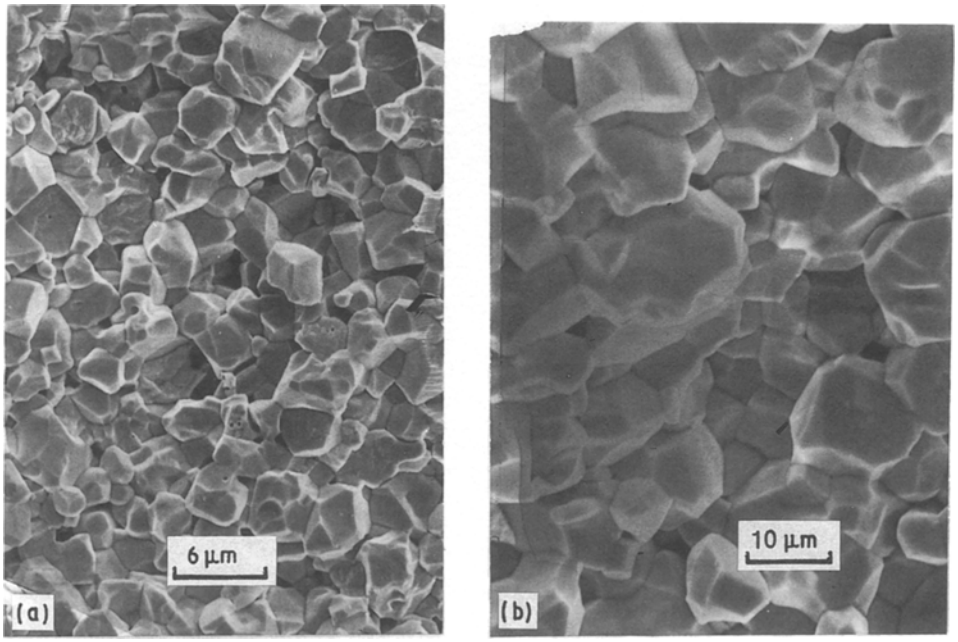

Figure 4 Scanning electron microscopy of the fractured surfaces of hot-pressed potassium niobate, (a) at 950° C, (b) at 1000° C.

knowledge to correlate the transformation of these noncrystalline porous oxides from gels with their structure and composition. Recently, based on experimental results and topological considerations, it was concluded that gel-derived amorphous oxides can be divided into two types according to their oxygen polyhedra [17]. Type A systems, which are primarily made up of networks of oxygen triangles and tetrahedra, densify relatively easily and transform into glass-like solids upon heat treatment. Type B systems, which are primarily made up of networks of oxygen octahedra, are likely to crystallize at relatively low temperatures ($< T_m/2\,K$) where T_m is the liquidus temperature.

Potassium niobate with a perovskite structure and a network of oxygen octahedra certainly falls into the second category. The driving forces for crystallization of type B gel-derived powders and perovskite materials was discussed for $BaTiO_3$ [17]. $KNbO_3$ with a similar structure and the network of oxygen is expected to behave similarly to $BaTiO_3$ and crystallize at temperatures lower than $T_m/2\,K$ (660° C). X-ray examination of heat-treated potassium niobate gel powders showed that crystallization indeed started as low as 400° C.

3.3. Potassium niobate ceramics

The single-phase $KNbO_3$ powder was pressed into 1 cm diameter discs by hot-pressing at different temperatures and pressures for 30 or 60 min. Samples at 950° C gave lower values of density and an average grain size of 4 to 5 μm. Densities of up to 99% theoretical were achieved when discs were pressed at 1000° C and 3000 p.s.i. ($\sim 20.67\,N\,mm^{-2}$) for only 30 min. The increase in temperature resulted in excessive but uniform grain growth (10 to 15 μm). Fig. 4 shows the scanning electron micrographs of fractured surfaces of pressed samples fired at 950 and 1000° C. Ceramic discs obtained were white with no sign of oxygen deficiency which would be manifested by a blue colour. The reduction of niobium from pentavalent to tetravalent may be because of oxygen deficiency or divalent cations of impurities. As a result, blue discoloration, due to free carrier absorption and a marked increase in conductivity, will be observed [18, 19].

A summary of the processing and properties of potassium niobate ceramics prepared by the sol–gel and conventional powder methods is presented in Table II. While most of the raw materials used in the conventional processing of potassium niobate have to be fired at temperatures higher than 800° C (where potassium oxide is highly volatile) for several hours with repeated cycles, gel powders are crystallized completely at 600° C after only 2 h. As a result of complex formation in the solution and the lower temperatures of crystallization, a stoichiometric compound was obtained without encountering the problem of second-phase formation. Better sinterability of sol–gel powders as a result of ultrafine particle size and large surface area resulted in higher densities obtained at much lower hot-pressing pressures (Table II).

Fig. 5 shows the variation of dielectric constant as a function of temperature, for a sol–gel sample pressed at 1000° C and 3000 p.s.i. ($\sim 20.67\,N\,mm^{-3}$) for 0.5 h, a single crystal [20, 21] and a sintered ceramic prepared by conventional methods [22].

The dielectric measurement of the conventionally sintered ceramic versus temperature (the only one available in the literature) does not continue to the Curie temperature and the transition from orthorhombic to tetragonal is not sharp. The sol–gel samples, however, gave sharp and defined transition temperatures and the dielectric constant was successfully measured up to higher than the Curie temperature. The Curie temperature and orthorhombic–tetragonal transition temperatures of the gel specimens were several degrees lower than those of the single crystal reported previously [20]. However, this phenomenon has been observed by other researchers [23, 24] where transition temperatures of $KNbO_3$ ceramics decreased as the hot-pressing pressure increased. This effect has

TABLE II A summary of properties of potassium niobate polycrystalline ceramics prepared via sol–gel processing and conventional powder methods

	Sol–gel	Conventional
Raw materials	Metal alkoxides (liquid solution)	Nb_2O_5 and K_2CO_3 (solid solution)
Calcination temperature (° C)	600	650–1000
Calcination time (h)	2	16–24
Sintering or hot-pressing temperature (° C)	950–1000	940–1054
Hot-pressing pressure (p.s.i. ($N mm^{-2}$))	2500–3000 (17.23–20.67)	5000–7000 (34.45–48.23)
Density ($g cm^{-3}$)	4.4–4.6	4.1–4.5
Dielectric constant at Curie temperature, 1 kHz	6200	3900 single crystal [20] 5000 [21]
Dielectric loss at 25° C, 1 kHz	0.06–0.15	0.05–0.24
Conductivity (Ωcm^{-1}) at 25° C	1.0×10^{-9}–2.7×10^{-8}	2×10^{-8}

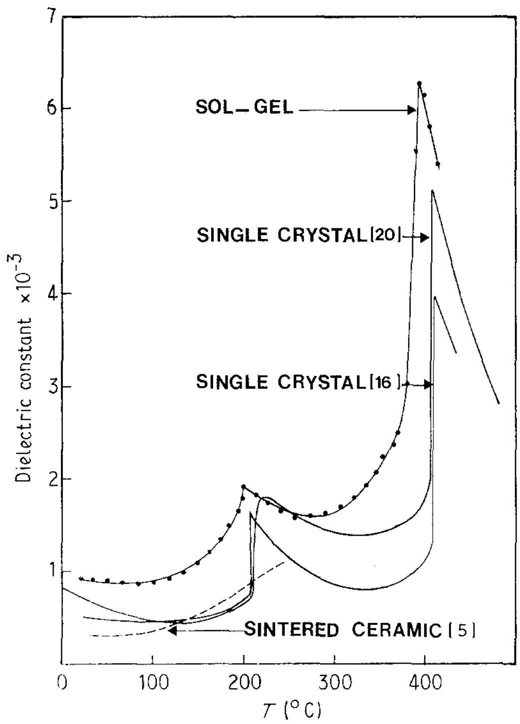

Figure 5 Variation of the dielectric constant with temperature.

been related to the internal mechanical stresses, which depend on the hot-pressing pressure and the temperature difference between optimum temperature of conventional sintering and hot-pressing temperature.

Sol–gel samples were found to have a very high dielectric constant in the whole temperature range measured, compared to two single crystals [20, 21] and a conventionally processed ceramic [22]. This abnormally high dielectric constant is not fully understood at this moment. However, similar observations in other ferroelectrics prepared from alkoxy derived, high-purity sub-micrometre powders were observed by other researchers [5–7]. This uncharacteristically high dielectric constant has been attributed to surface charge effects or the result of high-purity ultrafine particle sizes obtained from organic precursors.

Single crystals of ferroelectrics are usually difficult to grow and are far from perfect. They suffer from defects due to twinning, compositional inhomogeneities and impurities. These defects occur due to thermal fluctuations and impurities in the starting materials. Another problem specifically with $KNbO_3$ single crystals is the loss of potassium oxide at the high temperature of crystal growth and oxygen deficiency evident as the blue colour and the semiconducting effect in these crystals. Moreover, considering the fact that these crystals are seldom grown with a single domain, it is expected that complete polarization of the dipoles in an electrical field would not be possible. On the other hand, ceramic samples produced through a chemical route along with complex formation in the liquid stage which provides a high-degree of homogeneity through complex formation in the solution and hot-pressing which prevents the evaporation of volatile species and oxygen deficiency, have a better chance of a higher degree of polarization of their dipoles. This would result in higher dielectric constant in these ceramic samples when compared to their single-crystal counterparts.

Fig. 6 shows the frequency dependence of the dielectric loss tangent of a sol–gel sample hot-pressed at 1000° C and a conventionally hot-pressed ceramic [23]. The frequency dependence of the dielectric loss tangent of $KNbO_3$ ceramic prepared by sol–gel is fairly constant up to about 4×10^5 Hz and has much lower losses than the conventional ceramic at low frequencies.

The dielectric loss, ε'', is the sum of two contributions:

$$\varepsilon'' = \frac{1}{\omega c_0(R_1 + R_2)} + \frac{(\varepsilon_s - \varepsilon_\infty)\,\omega\tau}{1 + \omega^2\tau^2}$$

where τ is relaxation, ω is frequency and R is the resistance. The first term is inversely proportional to frequency and is relative to the electrical conductivity of the dielectric material ($\sigma \propto 1/(R_1 + R_2)$). At low frequencies the first term is larger and conductivity has the most contribution to the dielectric loss. As is seen in Fig. 6, dielectric loss of sol–gel derived sample is much lower than that of the conventional sample at low frequencies. Therefore, the high loss of the conventionally prepared ceramic at low frequencies, could be an indication of higher conductivity of this material compared to the sol–gel prepared sample. The second term in the above equation is Debye's relaxation term. It has been appreciated for many years that dipolar defects in dielectrics lead to relaxation effects which can be described by the Debye's

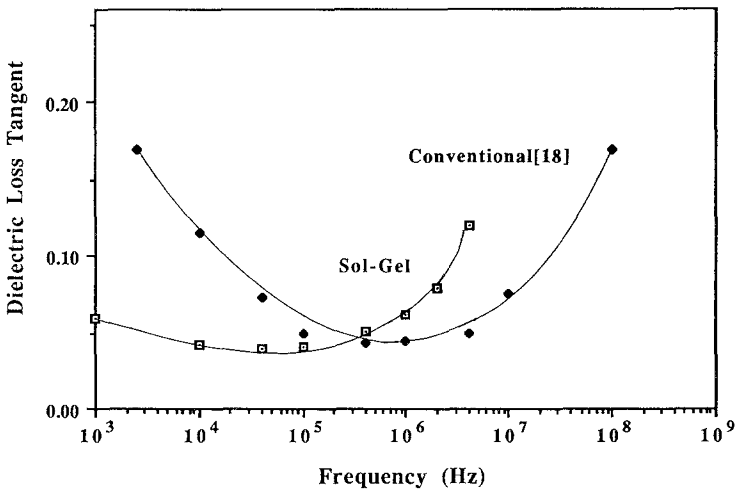

Figure 6 Frequency dependence of dielectric loss tangent.

equation. The more defects in the material, the shorter the relaxation time. Comparing sol–gel processing with the conventional powder method (as done in previous sections), it is expected that sol–gel samples will have higher purity and homogeneity than their conventional counterparts. It is therefore concluded that a higher concentration of defects in conventional samples results in space charge effects and a low relaxation time for these samples compared to sol–gel derived potassium niobate. A.c. conductivity of sol–gel samples at 1 kHz and 25° C were found to be low, while the conductivity of most single crystals is quite high (Table II). The semiconducting effect of single crystals resulted from oxygen deficiency and the reduction of Nb^{5+} to Nb^{4+}, could well be one of the reasons for lower dielectric constant, higher dielectric loss tangent and higher conductivity of $KNbO_3$ single crystals compared to polycrystalline ceramics prepared by sol–gel processing.

4. Conclusions

$KNbO_3$ was successfully prepared from metal alkoxides by the sol–gel process. The high degree of homogeneity achieved by the sol–gel process, through complex formation in the solution, presents an important advantage of this method over conventional ceramic processing, where solid-state reactions and diffusion govern the mixing process. Dielectric constant of a sol–gel sample, contrary to the sintered ceramic produced by conventional powders, was successfully measured from room temperature to the Curie temperature and was greater than that of the single crystals over the entire temperature range. The dielectric losses of sol–gel derived samples were mostly smaller and their electrical conductivities were an order of magnitude less than those of the conventional samples.

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