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# Sintering $LiTaO_3$ and $KTaO_3$ with the aid of manganese oxide

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The sintering of $LiTaO_3$ and $KTaO_3$ with the aid of manganese oxide was studied at 1080 to 1300° C by X-ray analysis, scanning electron microscopy (SEM) and X-ray microanalysis (XMA). The sintering of pure $LiTaO_3$ and $KTaO_3$ proceeds concurrently with grain growth, but only achieves a density of 83% at 1300° C and of 72% at 1280° C, respectively. The addition of 3 wt % of $MnO_2$ or $Mn_3O_4$ results in rapid densification of $LiTaO_3$ to 90 to 92% within 30 min at 1190° C. In the presence of manganese oxide, $KTaO_3$ densifies to 95% at 1280° C. The action of manganese oxide is attributed to the substitution of $Mn^{3+}$ for $Ta^{5+}$ in the $LiTaO_3$ or $KTaO_3$ lattice which enhances the diffusion of the rate-determining species, oxygen, in the oxide. In addition, a liquid phase formed at 1250° C in $KTaO_3$ may significantly contribute to the achievement of 95% densification.

## 1. Introduction

Alkali niobates and tantalates are useful ferroelectric materials and their single crystals are very important opto-electric materials. Although there are many reports on the growth and properties of alkali niobate and tantalate crystals, few studies have been made of their sintering behaviour. The preparation of dense sintered alkali niobate and tantalate ceramics is of great interest because of their potentially useful dielectric properties. From this viewpoint, we have already prepared 98% dense $LiNbO_3$ ceramics by the addition of CdO which promotes rapid densification and hinders exaggerated grain growth [1]. The sintering of $KTaO_3$ has been also studied, a 96% dense material having been produced in a dry air atmosphere [2].

As a continuation of this experimental programme, a study of the preparation and sintering of dense $LiTaO_3$ and $KTaO_3$ ceramics was undertaken. Since both $LiTaO_3$ and $KTaO_3$ are difficult to sinter to high density, an additive was sought which would enable high densification to be achieved. As a result, manganese oxide was found to be an efficient promoter, enabling $LiTaO_3$ and $KTaO_3$ to be sintered to densities of 90 to 95%. This paper describes the sintering of $LiTaO_3$ and $KTaO_3$ in the presence of manganese oxide and discusses the promoting mechanism.

## 2. Experimental details

The starting materials were tantalum pentoxide (99.9% pure, Mitsuwa Chem. Co.), lithium carbonate and potassium hydrogen carbonate (both were reagent grade, obtained from Kanto Chem. Co.).

An equimolecular mixture of $Ta_2O_5$ and $Li_2CO_3$ powder was blended in an agate mortar for 1 h and heated at 900° C for 2 h to obtain single phase $LiTaO_3$. The $LiTaO_3$ powder consisted of agglomerates predominantly 5 to 10 times the crystallite size of about 1.0 $\mu$m. Of the 24 different oxides which were tested as possible sintering additives for $LiTaO_3$, manganese oxide, $MnO_2$, was found to be the most effective. Mixtures of $LiTaO_3$ powder with varying amounts of $MnO_2$ were mechanically blended in a mortar for 3 h, then pressed at 70 MPa into pellets 2 to 3 mm in thickness and 16 mm in diameter. A pellet was packed in a powder of the same composition and heated at 1125 to 1300° C for 5 to 120 min in air. The relative densities ($R$) of the sintered compacts were determined by accurate weighing the

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dimensional measurement using a micrometer. The theoretical density was taken as 7.45 g cm$^{-3}$ of single crystal of $LiTaO_3$ [3].

Mixtures of $Ta_2O_5$ and $KHCO_3$ powders in a 1:2 molar ratio were heated at 900° C for 4 h in air and ground in an agate mortar. This procedure was repeated twice to complete the formation of polycrystalline $KTaO_3$, which consisted of agglomerates of 10 to 50 times the crystallite size of about 0.5 $\mu$m. Addition of 9 different oxides known to facilitate the sintering of $LiNbO_3$ and $LiTaO_3$ were tested for their effect on $KTaO_3$; magnanese oxide, $Mn_3O_4$, was agian found to be the most effective. A set of sintering experiments similar to those with $LiTaO_3$ were carried out with mixtures of $KTaO_3$ and $Mn_3O_4$ powders. Sintering was carried out at 1080 to 1280° C for 30 to 360 min in air. The theoretical density was determined to be 7.013 g cm$^{-3}$ from the lattice constant of this $KTaO_3$ powder.

Fractured surfaces of sintered $LiTaO_3$ and $KTaO_3$ compacts were used for SEM measurements of the average grain size by the standard stereological technique. Fractured surfaces were also polished with 0.25 $\mu$m diamond paste for analysis of Mn$K\alpha$ line. The dielectric constant ($\epsilon$) and the loss tangent ($\tan\delta$) of sintered compacts of $LiTaO_3$ and $KTaO_3$ at 600 kHz and 200 kHz, respectively, were determined at room temperature using a Q-meter.

## 3. Results

### 3.1. Sintering of $LiTaO_3$

Table I shows the densities of $LiTaO_3$ compacts sintered at 1125° C for 2 h in air with 3 wt % of various oxide additives. The addition of the transition metal oxides, $MnO_2$, CoO, $Fe_2O_3$ (or $Fe_3O_4$) and CuO promotes sintering while $Sb_2O_3$, $Cr_2O_3$ and $B_2O_3$ hinder it. $MnO_2$ is the most effective additive. Fig. 1 shows the effect of $MnO_2$ content on the sintering of $LiTaO_3$, from which it is seen that as the $MnO_2$ content varies from 3 to 5 wt %, the density increases to 85%, then decreases. The densities of sintered compacts of $LiTaO_3$, both pure and with 3 wt % of added $MnO_2$, are plotted against log(time) in Fig. 2. Although slight densification occurs in pure $LiTaO_3$ at 1190 to 1250° C, the density increases linearly with log time at 1300° C, reaching 83% after 2 h. The addition of $MnO_2$ causes rapid densification even at 1125 to 1190° C, leading to a density of 85 to 90% within 30 min and essentially ceasing after that. Iso-

TABLE I Relative density of sintered compacts of $LiTaO_3$ with 3 wt% oxide (sintering condition: 1125° C, 2 h, in air)

| Oxide | Density (%) |
|---|---|
| none | 60 |
| $MnO_2$ | 85 |
| CoO | 79 |
| $Fe_2O_3$ | 79 |
| $Fe_3O_4$ | 74 |
| CuO | 73 |
| $Bi_2O_3$ | 72 |
| $GeO_2$ | 70 |
| MgO | 69 |
| $V_2O_5$ | 69 |
| CdO | 68 |
| $SiO_2$ | 65 |
| ZnO | 63 |
| $TiO_2$ | 63 |
| $In_2O_3$ | 60 |
| PbO | 60 |
| CaO | 60 |
| NiO | 60 |
| $Al_2O_3$ | 56 |
| $SnO_2$ | 56 |
| $Nb_2O_5$ | 55 |
| $ThO_2$ | 55 |
| $Sb_2O_3$ | 54 |
| $Cr_2O_3$ | 54 |
| $B_2O_3$ | 52 |

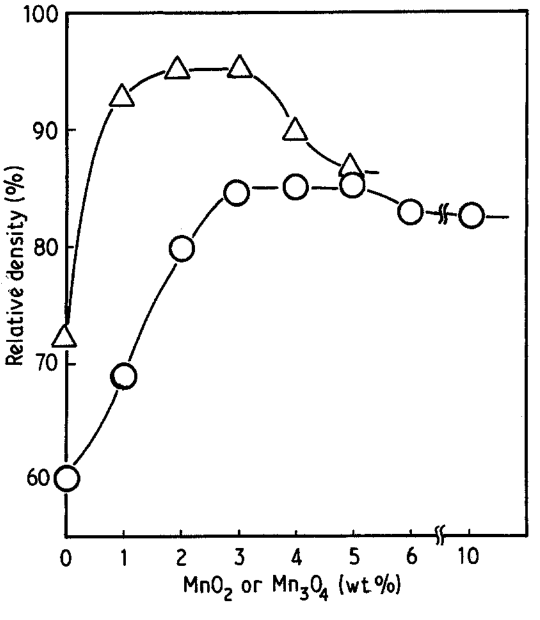

*Figure 1* Density dependence on $MnO_2$ or $Mn_3O_4$ concentration for $LiTaO_3$ sintered at 1125° C for 2 h or $KTaO_3$ sintered at 1280° C for 1.5 h, respectively. ○: $LiTaO_3$, △: $KTaO_3$.

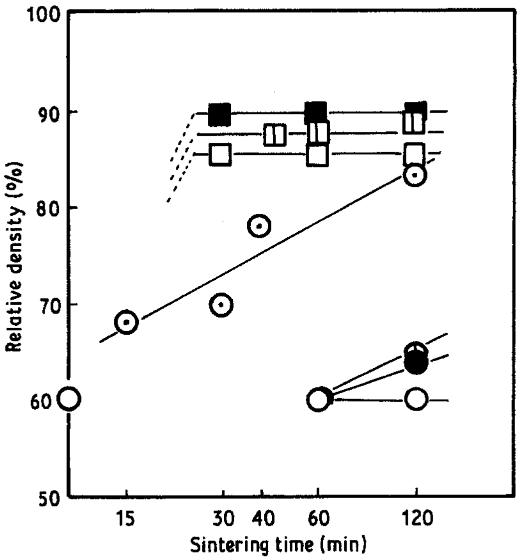

*Figure 2* Relationship between relative density and log time: pure LiTaO$_3$; ○: 1125° C, •: 1190° C, ⊕: 1250° C, ⊙: 1300° C MnO$_2$-containing LiTaO$_3$; □: 1125° C, ◫: 1175° C, ■: 1190° C.

TABLE II Relative density of sintered compacts of KTaO$_3$ with 3 wt % oxide (sintering condition: 1280° C, 1.5 h, in air)

| Oxide | Density (%) |
|---|---|
| none | 72 |
| Mn$_3$O$_4$ | 95 |
| Fe$_2$O$_3$ | 90 |
| MnO$_2$ | 90 |
| CoO (or Co$_3$O$_4$) | 88 |
| ZnO | 85 |
| Fe$_3$O$_4$ | 81 |
| CdO | 80 |
| GeO$_2$ | 79 |
| Y$_2$O$_3$ | 70 |

thermal grain growth data are plotted in Fig. 3. In pure LiTaO$_3$, grain growth proceeds in a similar way to that of densification (Fig. 2), approximately following the equation $G^3 = Kt$ at 1250 to 1300° C (where $G$ is the grain size, $K$ is a constant and $t$ is time). The addition of MnO$_2$ causes the grain size to increase rapidly to $> 10\,\mu$m within 30 min at 1125 to 1190° C. Further grain size increases are more gradual.

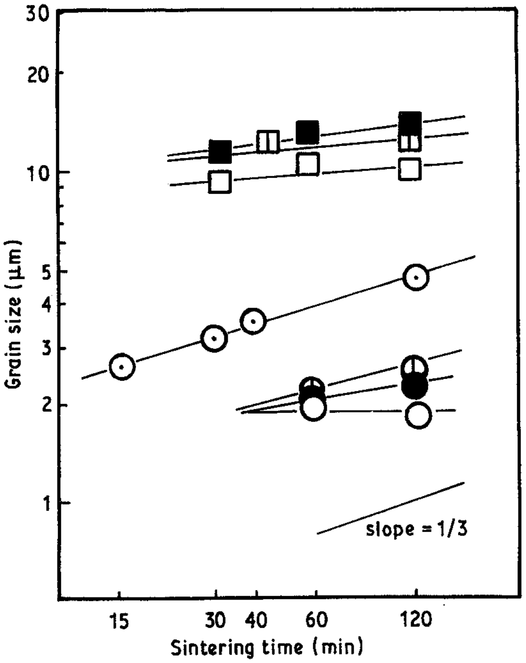

*Figure 3* Isothermal grain growth of sintered compacts of pure and MnO$_2$-containing LiTaO$_3$. The point identification is the same as in Fig. 2.

## 3.2. Sintering of KTaO$_3$

Table II shows the densities of sintered KTaO$_3$ compacts with 9 different oxides at 1280° C for 1.5 h in air. It is evident that Mn$_3$O$_4$ is the most effective in promoting KTaO$_3$ sintering. The influence of the Mn$_3$O$_4$ content on the density is shown in Fig. 1, indicating that 2 to 3 wt % is an optimum amount. Fig. 4 shows the densities of KTaO$_3$ compacts, both pure and containing 3 wt % Mn$_3$O$_4$, sintered at 1080 to 1280° C for 1.5 h in

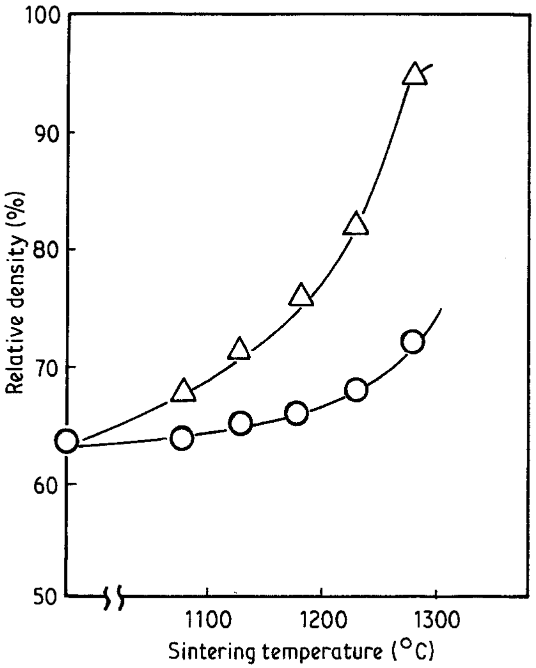

*Figure 4* Density dependence on temperature for KTaO$_3$ sintered for 1.5 h. ○: pure KTaO$_3$, △: Mn$_3$O$_4$-containing KTaO$_3$.

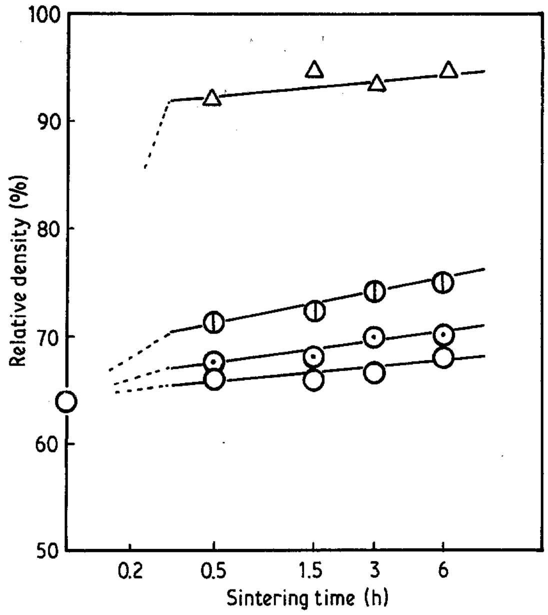

*Figure 5* Relationship between relative density and log time: pure $KTaO_3$; ○: 1180° C, ⊙: 1230° C, ⦶: 1280° C $Mn_3O_4$-containing $KTaO_3$; △: 1280° C.

air. In pure $KTaO_3$, the density increases with increasing temperature, but densities of only 72% are attained even at 1280° C. Thus, pure $KTaO_3$ is very difficult to sinter. The addition of $Mn_3O_4$ obviously assists the sintering of $KTaO_3$, resulting in a much greater density (95% at 1280° C). Fig. 5 shows the sintering rates for both pure and $Mn_3O_4$-containing $KTaO_3$. The pure $KTaO_3$ shows a gradual linear increase in density with log time. In th presence of $Mn_3O_4$, the density reaches 92% within 30 min at 1280° C.

## 3.3. Dielectric constants and tan δ of sintered compacts of $LiTaO_3$ and $KTaO_3$

Fig. 6 shows the relationship between the log dielectric constant ($\epsilon$) of the sintered compacts and their density. The $\epsilon$ value increases linearly with increasing density for both $LiTaO_3$ and $KTaO_3$. The values of $\epsilon$ for $LiTaO_3$ and $KTaO_3$ (50 and 440, respectively) determined by extrapolation of the straight line to the ordinate corresponding to $R = 100\%$, are typical of the values expected for fully dense ceramics. The value of $\epsilon$ for $KTaO_3$ (~ 440) is greater than that of single crystal specimens ($\epsilon = 243$). The tan δ values are in the range 0.002 to 0.03 for $LiTaO_3$ and 0.02 to 0.12 for $KTaO_3$.

# 4. Discussion

## 4.1. Sintering of $LiTaO_3$

Densification of pure $LiTaO_3$ occurs concurrently with grain growth at 1190 to 1300° C (Figs. 2 and 3): SEM photographs show that at 1125° C, grain growth occurs only within the agglomerates.

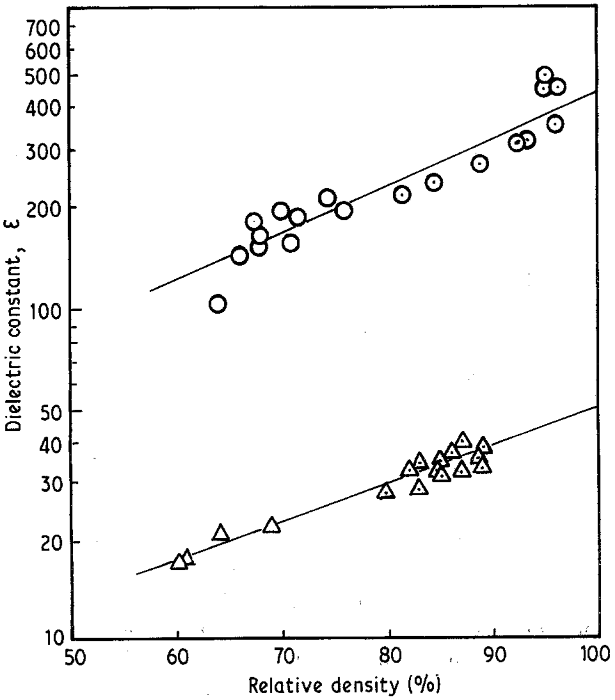

*Figure 6* Relationship between the dielectric constant of sintered compacts of $LiTaO_3$ and $KTaO_3$ and their density. △: pure $LiTaO_3$, ◬: $MnO_2$-containing $LiTaO_3$ ○: pure $KTaO_3$, ⊙: $Mn_3O_4$-containing $KTaO_3$.

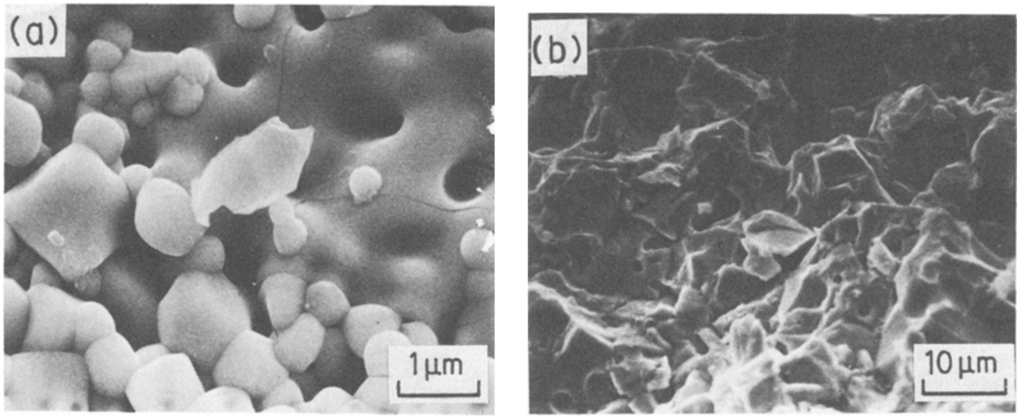

*Figure* 7 Scanning electron micrographs of fractured surface of sintered compacts of $LiTaO_3$: (a) pure $LiTaO_3$ sintered at 1300° C for 2 h; (b) $MnO_2$-containing $LiTaO_3$ sintered at 1195° C for 2 h.

Prolonged heat treatment for $\geqslant 120$ min at 1300° C results in the development of large grains, resulting from the onset of exaggerated grain growth, as shown in Fig. 7a. This prevents densification greater than 83%. The presence of $MnO_2$ promotes the sintering of $LiTaO_3$ such that a density of 85 to 90% is reached within 30 min, after that further density increases are not observed in spite of a slight increase in grain size with time. It is clear that this cessation of densification is due to very rapid grain growth resulting in the formation of residual cavities or pores on the grain boundaries (Fig. 7b).

$MnO_2$ was found to decompose to $Mn_3O_4$ at about 900° C by X-ray analysis, indicating all the manganese is present as $Mn_3O_4$ at the sintering temperatures of 1125 to 1190° C. It is this $Mn_3O_4$ which promotes the sintering of $LiTaO_3$. Since the ionic radius of $O^{2-}$ ($r = 0.140$ nm) is much larger than that of $Ta^{5+}$ ($r = 0.064$ nm) [4] or $Li^+$ ($r = 0.074$ nm) [4], it seems likely that the rate-controlling step in the sintering of $LiTaO_3$ is the diffusion of oxygen. The ionic radius of $Mn^{3+}$ ($r = 0.065$ nm) [4] is almost the same as that of $Ta^{5+}$, suggesting that $Mn^{3+}$ ions could substitute for $Ta^{5+}$ in the $LiTaO_3$ lattice, thereby producing oxygen vacancies which facilitate the diffusion of oxygen in $LiTaO_3$ and its rapid densification. Evidence for the dissolution of manganese ions in $LiTaO_3$ is provided by the XMA result that manganese is almost homogeneously distributed on the polished surfaces of the $LiTaO_3$ ceramic samples. Since the manganese is present as $Mn_3O_4$ under the sintering conditions, an attempt was made to achieve similarly high densification by the addition of $Mn_3O_4$, but exaggerated grain growth occurred again in this sample, which hindered densification of $> 92\%$.

## 4.2. Sintering of $KTaO_3$

The densification in pure $KTaO_3$ proceeds slowly with increasing temperature or with log time (Figs. 4 and 5). Grain growth was also found to occur slowly with increasing temperature: even at 1280° C the grain sizes were only 0.5 to 1.0 $\mu$m (Fig. 8a). These results suggest that densification in pure $KTaO_3$ occurs concurrently with grain growth. The addition of $Mn_3O_4$ causes rapid densification of $KTaO_3$ as was the case with $LiTaO_3$. A DTA experiment with $KTaO_3$ powder containing 3 wt% $Mn_3O_4$ showed a small broad endothermic peak at 1250° C, followed by a large peak at 1330° C. Since both peaks were reversible on cooling, the former is possible due to the formation of a liquid phase and the latter due to the melting of $KTaO_3$, its temperature lowered by the presence of $Mn_3O_4$ (the melting point of pure $KTaO_3$ is reported to be 1370° C). The formation of a liquid phase is confirmed by the SEM observation of a partially melted appearance of the fractured surface of a compact sintered at 1280° C (Fig. 8b). This liquid phase is probably a manganese-containing compound which results from reaction of $Mn_3O_4$ with $KTaO_3$, since the XMA result on the polished surface indicates that manganese is mainly concentrated on the grain boundaries. Therefore, $Mn_3O_4$ appears to promote the sintering of $KTaO_3$ by two processes: the formation of a liquid phase and partial substitution of $Mn^{3+}$ for $Ta^{5+}$ in $KTaO_3$ to produce

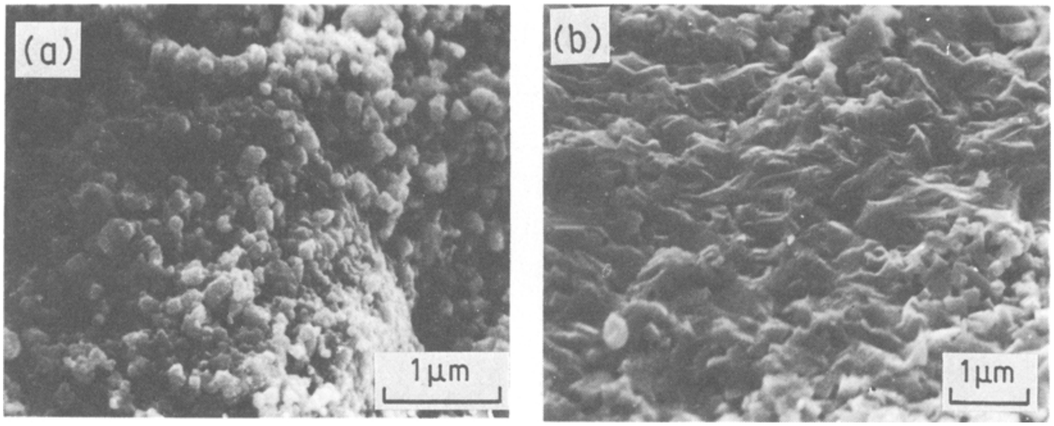

*Figure 8* Scanning electron micrographs of fractured surface of sintered compacts of $KTaO_3$: (a) pure $KTaO_3$ sintered at 1280° C for 1.5 h; (b) $Mn_3O_4$-containing $KTaO_3$ sintered at 1280° C for 1.5 h.

oxygen vacancies similar to those postulated in $LiTaO_3$. The contribution of the liquid phase is particularly significant at higher temperatures, and explains rapid densification of $KTaO_3$ above 1250° C.

## 5. Conclusion

The sintering of $LiTaO_3$ and $KTaO_3$ with the aid of $Mn_3O_4$ was studied at 1125 to 1300° C and at 1080 to 1280° C, respectively.

The sintering of the pure phases was found to proceed concurrently with grain growth. $LiTaO_3$ was not able to sinter to greater than 83% density at 1300° C, due to exaggerated grain growth. Pure $KTaO_3$ was difficult to sinter to densities greater than 72% at 1280° C.

Of the many oxides tested, addition of 3 wt % of $Mn_3O_4$ was found to the most effective in promoting densification in both $LiTaO_3$ and $KTaO_3$. In the presence of $Mn_3O_4$, $LiTaO_3$ could be densified to ~ 92% at 1190° C and $KTaO_3$ was densified to 95% at 1280° C. The effect of $Mn_3O_4$ can be explained in terms of the substitution of $Mn^{3+}$ for $Ta^{5+}$ in $LiTaO_3$ or $KTaO_3$ which enhances the diffusion of oxygen. Additionally the formation of a liquid phase at 1250° C in $KTaO_3$ makes a significant contribution to the achievement of 95% density.

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