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Effects of Fe_2O_3 Addition on the Sintering of $KTaO_3$

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SUMMARY

The sintering behavior of $KTaO_3$ was studied with an addition of Fe_2O_3 at 1200–1300°C for 0·5–180 h. By adding 0·5 wt% Fe_2O_3 a relative density of 94% was obtained at 1300°C after sintering for 24 h. The densification rate was very high at high temperatures. It is due to accelerated volume diffusion by the displacement of Fe^{3+} for Ta^{5+} in the $KTaO_3$ lattice at high temperatures. The dielectric constant was determined to be about 340 by extrapolation to 100% relative density.

1 INTRODUCTION

Potassium tantalate, having the cubic perovskite structure, is a ferro-electric material. Many studies have been made on the growth of single crystals of $KTaO_3$.[1,2] Low-temperature properties of the single crystal have been investigated by dielectric and thermal conductivity measurements.[3] However, there are only a few studies on the sintering of $KTaO_3$ because of the poor densification of alkali tantalates.[4] Dense compacts of $KTaO_3$ were required for dielectric measurements. The authors have already prepared dense compacts of alkali niobates and tantalates with the aid of additives such as CdO or Mn_2O_3.[5,6] This paper describes the sintering behavior of $KTaO_3$ with Fe_2O_3 as additive and the resulting properties.

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2 EXPERIMENTAL

Potassium hydrogen carbonate, $KHCO_3$ (reagent grade from Kanto Chem. Co., Tokyo, Japan) and tantalum pentoxide (99·9% pure from Mitsuwa Chem. Co., Osaka, Japan) were used as starting materials. Pellets of the mixture of $KHCO_3$ and Ta_2O_5 with the stoichiometric composition of $KTaO_3$ were calcined in a closed crucible at 850°C for 3 h to obtain the single phase of $KTaO_3$. The powder was completely reacted to $KTaO_3$ single phase. The calcined pellets were ground in an agate mortar for 1 h. Fe_2O_3 which was the most effective additive for densification of the tested oxides was added up to 2 wt% with the starting powder of $KTaO_3$. The starting powders, after well mixing, were compressed to a circular pellet with 16 × 3 mm under 110 MPa. Sintering was conducted at 1200–1300°C for 0·5–180 h in an electric furnace. To prevent the vaporization of potassium, the pressed pellets were covered with calcined powder of the same composition.

Relative densities of the compact were determined from both bulk density and theoretical density. The theoretical density was calculated as 7·013 gcm^{-3} from the lattice parameters of the $KTaO_3$ powders used in this experiment. Fractured surfaces of the compacts were observed by Scanning Electron Microscope. The dielectric constants (ε) and the tangent losses ($\tan\delta$) at 600 kHz were determined at room temperatures by using a Q-meter.

3 RESULTS AND DISCUSSION

Figure 1 shows the effect of adding Fe_2O_3 on the sintering of $KTaO_3$ at 1300°C for 2 h in air. Up to 0·5 wt% Fe_2O_3, the relative density increased to 93% of theoretical density, and then decreased with increasing addition of Fe_2O_3. Accordingly, 0·5 wt% Fe_2O_3 addition was the most effective for sintering of $KTaO_3$ powders. Relative densities of compacts without and with 0·5 wt% Fe_2O_3 are plotted against log time in Fig. 2. In the case of sintering without additives, poor densification was achieved at 1200–1300°C. The relative density was still only about 71% at 1300°C for 24 h. On the other hand, the addition of 0·5 wt% Fe_2O_3 caused rapid densification at 1200–1300°C. The densification rate increased very rapidly with increasing temperature. Especially, compacts with relative densities over 90% were obtained at 1250–1300°C within 0·5 h. The highest relative density was 94% at 1300°C for 24 h but ceased after that. In the $KTaO_3$–Fe_2O_3 system, densification at the initial stage of sintering occurred with a high rate within 0·5 h at high temperatures. Generally, high rate of

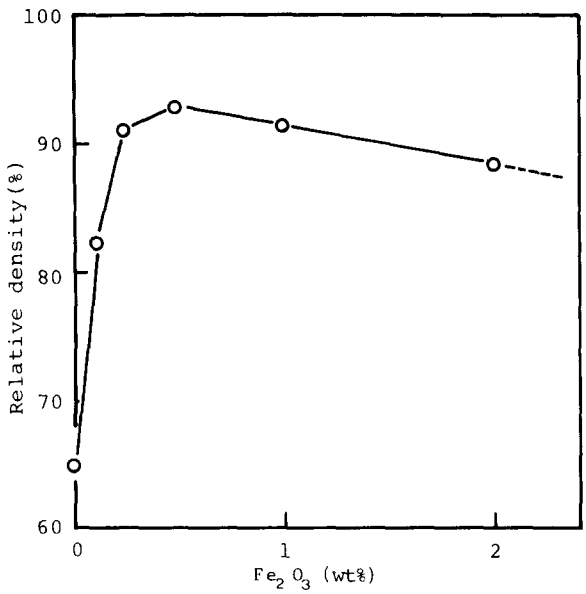

Fig. 1. Effects of Fe_2O_3 addition on sintering of $KTaO_3$ at 1300°C for 2 h.

densification is considered to be due to the presence of a liquid phase, whose contribution is very effective for particle rearrangements at the initial stage of sintering. But there was no evidence of the presence of a liquid phase by observation of the microstructure in the present system. However, the ionic radius of Ta^{5+} (0·068 nm) is very close to that of Fe^{3+} (0·064 nm), so that displacement of Ta^{5+} by Fe^{3+} in the $KTaO_3$-lattice takes place producing

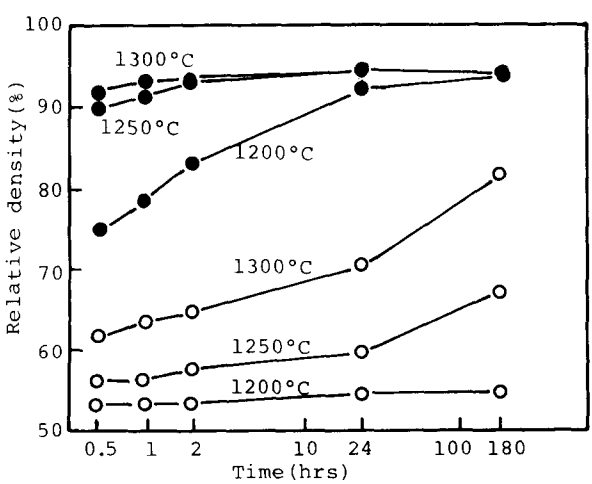

Fig. 2. Relationship between relative density and log time, ○, no additive; ●, 0·5 wt% Fe_2O_3 addition.

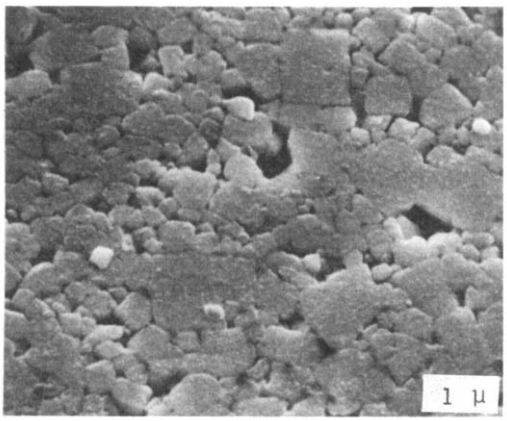

Fig. 3. SEM photograph of fractured surface of the compact sintered at 1250°C for 2 h.

oxygen vacancies. Moreover, the present sintering temperatures are very close to the melting point of $KTaO_3$ (1370°C). Accordingly, the high rate of densification can be explained by accelerated volume diffusion at high temperatures of oxygen vacancies.

Grain growth was not observed in the sintering of $KTaO_3$ without additives. There was no dependence of grain growth on both sintering temperatures and sintering times. On the contrary, a small amount of grain growth was observed for the sintering with addition of 0·5 wt% Fe_2O_3. The size was somewhat larger with increasing sintering temperatures. However, the grain size distribution was very uniform without abnormal grain growth, as shown in Fig. 3.

The plot of logarithmic dielectric constants against relative density indicates a straight line as shown in Fig. 4. The straight line is a good

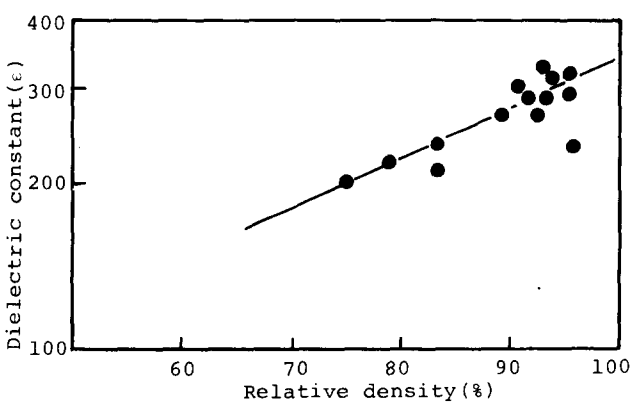

Fig. 4. Logarithmic dielectric constants against relative density.

confirmation of the logarithmic mixture rule. By extrapolation of the line to 100% relative density a value of about 340 was determined. This value is greater than that of single crystal ($\varepsilon = 243$). The dielectric losses ($\tan\delta$) decreased linearly with increasing relative density. The compacts with 90–96% relative density had a value of dielectric loss of about $0{\cdot}5 \times 10^{-2}$.

4 CONCLUSION

Sintering of $KTaO_3$ powder was conducted at 1200–1300°C under atmospheric pressure.

Increased densification was observed at 1250–1300°C with the addition of Fe_2O_3, while sintering without additive showed low relative density. The maximum relative density of 94% was attained at 1300°C for 24 h by adding 0·5 wt% Fe_2O_3. The high rate of densification is due to accelerated oxygen volume diffusion by displacement of Fe^{3+} for Ta^{5+}.

Almost no grain growth was observed and there was no correlation between sintering temperatures and grain size.

Logarithmic dielectric constants against relative density conformed well with the logarithmic mixture rule. The dielectric constant extrapolated to 100% relative density was about 340.

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