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SINTERING AND PROPERTIES OF BaTiO$_3$-BaB$_2$O$_4$ DIELECTRICS

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Résumé - La densification de BaTiO$_3$ en présence de l'eutectique liquide BaB$_2$O$_4$ a été analysée. L'aptitude au frittage a été modifiée par addition d'un excès de TiO$_2$ et il a été établi qu'un contrôle effectif de la croissance granulaire peut être réalisé. Les propriétés électriques des céramiques ferroélectriques sont discutées sur la base de l'analyse microstructurale et des données de densification.

Abstract - Densification of BaTiO$_3$ in the presence of BaB$_2$O$_4$ eutectic liquid was investigated. Sintering behaviour was varied with additions of excess TiO$_2$ and it was shown that effective grain growth control may be achieved. Electrical properties of ferroelectric ceramics are discussed on the basis of microstructural analysis and densification data.

I - INTRODUCTION

Commercial BaTiO$_3$ with a slight excess of TiO$_2$ usually requires a sintering temperature between 1350 - 1400°C. For manufacturing BaTiO$_3$-based electronic components this sintering temperature is too high, and various additives are thought to decrease the sintering temperature without undue worsening of the electrical characteristics.

Castelliz and Routil (1) investigated the influence of additions of B$_2$O$_3$ on the sintering and electrical properties of BaTiO$_3$. The authors reported a significant decrease in sintering temperature; however, they did not observe formation of ternary BaO.B$_2$O$_3$.TiO$_2$ phase, which was reported later (2).

Sintering in a reactive system is difficult to control. From this point of view, the system BaTiO$_3$-BaB$_2$O$_4$ is more appealing. The phase diagram BaTiO$_3$-BaB$_2$O$_4$, determined by Goto and Cross (3), shows an eutectic at 942°C and containing 32 m/o BaTiO$_3$. No solid solubility was detected and the authors succeeded in growing high purity BaTiO$_3$ crystals in this system.

II - EXPERIMENTAL METHODS

BaB$_2$O$_4$ was synthesized by reacting HBO$_3$ with BaCO$_3$ by heating in steps with a final firing at 1000°C. The structure of BaB$_2$O$_4$ was
in accordance with data reported in ASTM card No 15-862. Milled BaB$_2$O$_4$ powder was added to several commercial electronic grades of BaTiO$_3$, supplied by TRANSELCO and TAM. After mixing in acetone, dried samples were pressed into pellets and discs, and fired at various temperatures. Some samples were prepared with excess TiO$_2$. The microstructure of sintered specimens was examined by optical metallography and scanning electron microscopy. Sintering curves were drawn from photographs taken on a heating microscope. Capacitance and dielectric loss were determined at 1 kHz and 1 MHz.

III - RESULTS AND DISCUSSION

III.1. Sintering behaviour and microstructure development

Fig. 1 shows shrinkage-temperature curves of pressed pellets composed of BaTiO$_3$ and BaTiO$_3$ doped with TiO$_2$ and/or BaB$_2$O$_4$. The BaTiO$_3$ sample shows a sintering behaviour as expected, i.e. significant shrinkage in the narrow sintering interval of 1300-1350. Final porosity after sintering for 3 hours at 1350°C was 7%. Addition of 2 w/o BaB$_2$O$_4$ significantly lowered the starting sintering temperature to below 1000°C. The decrease in sintering temperature is ascribed to liquid phase formation in the BaTiO$_3$-BaB$_2$O$_4$ system (eutectic at 942°C). However, the degree of densification was much lower than that of BaTiO$_3$ without additive. After 2 hours at 1250°C, samples retained 12% - 15% porosity. Even after prolonged heating at 1400°C, porosity in sintered BaTiO$_3$-BaB$_2$O$_4$ samples did not decrease below 12%.

Samples composed of BaTiO$_3$, BaB$_2$O$_4$ (2 w/o) and TiO$_2$ (1 w/o) showed quite different sintering behaviour. The onset of sintering temperature remained low, below 1000°C; however, the extent of sintering was already significant at 1250°C. After 2 hours at 1250°C, the porosity decreased below 5%.

Fig. 2 shows SEM micrographs of BaTiO$_3$ - 2 w/o BaB$_2$O$_4$ and BaTiO$_3$ - 2 w/o BaB$_2$O$_4$ - 1 w/o TiO$_2$ samples after sintering at 1250°C for 3 hours. The large grain size microstructure of BaTiO$_3$ sintered in the presence of BaB$_2$O$_4$ at 1250°C is comparable with the microstructure of BaTiO$_3$ sintered with excess TiO$_2$ at 1400°C. The significant difference represents large pores within the grains in the BaTiO$_3$-BaB$_2$O$_4$ sample, which are not likely to be removed during subsequent sintering and which explains the low shrinkage noted in dilatometric experiment.

Fig. 3 demonstrates the influence of excess TiO$_2$ on the microstructure of a BaTiO$_3$ - 2 w/o BaB$_2$O$_4$ sample sintered for 3 h at 1250°C. The sample shows a dense, uniform microstructure with small grains. Pores are still located on grain boundaries, a prerequisite for a high final density.

It may be concluded that fine grain size and low porosity in the sample shown in Fig. 3 is a consequence of the combined effects of BaB$_2$O$_4$ and TiO$_2$.

A possible explanation of the observed phenomenon of slow grain growth of BaTiO$_3$ from a BaB$_2$O$_4$-BaTiO$_3$ eutectic melt in the presence of excess TiO$_2$ may be the decrease in solubility of BaTiO$_3$ in a eutectic melt saturated with TiO$_2$. Decreased solubility effects slow grain growth, which in turn prevents capture of pores within the grains, resulting in a high sintered density. More experiments are necessary to confirm this hypothesis.

III.2. Dielectric properties of sintered BaTiO$_3$-BaB$_2$O$_4$ and BaTiO$_3$-BaB$_2$O$_4$-TiO$_2$ compositions
The practical aim of the present research was to investigate the suitability of BaB$_2$O$_4$ for decreasing the sintering temperature of BaTiO$_3$ based disc capacitors. Fig. 4 shows the temperature dependence of the relative dielectric constant of BaB$_2$O$_4$-TiO$_2$ doped BaTiO$_3$ and pure BaTiO$_3$. The increase in dielectric constant of the doped sample is a consequence of the much finer grain size of the doped sample. Similar influence was already reported in other systems (4). Both samples had an acceptable dielectric loss factor of 200$x10^{-4}$ at 1 KHz.

Fig. 5 shows the influence of BaB$_2$O$_4$-TiO$_2$ dopants on DC/T curve of commercial "type 2" capacitor composition.

The decrease in relative DC is due to dilution of ferroelectric phase with low DC additive. It is important to note the significant reduction in sintering temperature offered by the additive. It may therefore be concluded that BaB$_2$O$_4$-TiO$_2$ additive is of potential value in the manufacture of BaTiO$_3$ based dielectric ceramics.

Addition of 2 wt % of BaB$_2$O$_4$ decreases the densification temperature of BaTiO$_3$ to 1250°C. Sintering in the presence of a liquid phase results in a coarse grained structure, which may be controlled by the addition of TiO$_2$. BaB$_2$O$_4$ does not react with BaTiO$_3$ as does B$_2$O$_3$, which forms the ternary compound, and does not shift the Curie temperature of BaTiO$_3$. Therefore it may be used to modify the firing characteristics of BaTiO$_3$-based dielectrics without adversely affecting the electrical characteristics.
Fig. 2 - BaTiO$_3$ +2 w/o BaB$_2$O$_4$
1250°C, 3 h

Fig. 3 - BaTiO$_3$ +2 w/o BaB$_2$O$_4$ + 1 w/o TiO$_2$
1250°C, 3 h

Fig. 5 - Temperature dependence of relative dielectric constant of commercial DC 6000 composition and commercial DC 6000 composition with additives, sintered under various conditions

REFERENCES

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