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Reaction During Sintering of Barium Titanate with Lithium Fluoride

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The reactions occurring during sintering of stoichiometric BaTiO₃ with small additions of LiF were studied at temperatures between 700° and 900°C. BaTiO₃ reacts with LiF to form a cubic solid solution and Li₂TiO₃. During sintering, the cubic solid solution coexists with Li₂TiO₃ and forms a liquid phase at 740°±5°C. The occurrence of a liquid phase at this temperature results in an enhancement of the sintering process and leads to the development of a highly dense microstructure.

SINTERING of BaTiO₃ using LiF as an additive has received much attention for several years. The primary interest in this area arises from the fact that a small addition of LiF allows the formation of a liquid phase significantly below the normal sintering temperature of BaTiO₃, causing a substantial reduction of the processing temperature for BaTiO₃-based electronic ceramics. The beneficial effect of LiF additions to the sintering of BaTiO₃ was first reported by Walker *et al.*,¹ who found that 0.5 to 3.0 wt% LiF aided densification of BaTiO₃ at a much lower temperature than could be achieved without additives. Amin *et al.*² and Anderson *et al.*³ have sintered BaTiO₃ with minor additions of LiF at temperatures below 900°C using long firing periods and obtained BaTiO₃ capacitors with improved dielectric properties. In a more comprehensive study, Haussonne *et al.*⁴ have reported the effect of 1 to 2 wt% LiF additions on the sintering characteristics and dielectric properties of BaTiO₃ with variable Ba/Ti ratio and observed that the densification behavior and dielectric properties of the ceramics depend largely on the presence of a pseudocubic perovskite phase, the formation of which requires an excess of Ba. A significant weight loss due mainly to the volatilization of large amounts of both Li and F was observed during sintering which caused a considerable shift of the Curie temperature of BaTiO₃. The densification of LiF-fluxed BaTiO₃ with variable Ba/Ti ratio has also been studied by Tolino and Blum,⁵ who pointed out that the initial Ba/Ti ratio and LiF addition are independently important in determining the densification of BaTiO₃. In a recent publication, Desgardin *et al.*⁶ have reported the use of BaLiF₃ as a sintering aid which was found to provide a better control of the overall

densification process because of the low weight loss during sintering.

From the foregoing literature data, it is apparent that the interaction between BaTiO₃ and LiF, and the nature of the liquid phase which forms during sintering, must be elucidated before the densification behavior and microstructure development of BaTiO₃ are clearly understood. The work described here is primarily concerned with the reaction involved between stoichiometric BaTiO₃ and LiF, and its significance to the formation of a liquid phase during sintering. To a lesser extent, the effect of the liquid phase on the densification behavior and microstructure development of BaTiO₃ is briefly discussed.

EXPERIMENTAL PROCEDURE

The stoichiometric BaTiO₃ powder used in this study was prepared by the liquid-mix process⁷ using BaCO₃ and tetraisopropyl titanate as the starting materials. In this process, BaTiO₃ powder of 99.9% purity and crystallite size of ≈0.1 μm was obtained. For the reaction

study, mixtures containing various proportions of LiF* and BaTiO₃ powders were ground in an agate mortar and then mixed in a shaker mill for 30 min using a plastic container. The powder thus obtained was pressed into pellets, placed on a Pt foil, and heated at 700°C for prolonged periods with intermittent cooling, crushing, and pressing to ensure homogeneity and to attain equilibrium. At the end of the heat treatment, the phases present in the fired samples were identified by X-ray powder diffraction (XRD) using CuKα radiation. Liquid formation in the system was studied by differential thermal analysis-thermogravimetric analysis (DTA-TGA)[†] of the original mixtures using a heating and cooling rate of 10°C/min. For the sintering study, stoichiometric BaTiO₃ powder containing 2 wt% LiF was ground in an agate mortar under alcohol, dried in an oven, and mixed in a shaker mill for 30 min with poly(vinyl alcohol) as a binder. The mixtures were pressed into pellets and sintered at temperatures between 700° and 900°C for periods ranging from 1 to 25 h. The bulk densities of the sintered pellets were determined by the liquid displacement method using xylene as a medium. Microstructural examination was performed on both the fractured and polished surfaces of the sintered samples using a scanning electron microscope (SEM).

RESULTS AND DISCUSSION

The XRD patterns of the fired samples containing 1 to 2 wt% LiF revealed only a single-phase cubic pattern which resembled that of the cubic perovskite-type solid solution reported earlier.⁶ However, the XRD pattern of the composition containing 5 wt% LiF showed a few additional lines which matched those of the compound Li₂TiO₃ (Fig. 1). The characteristic peaks with corresponding (*hkl*) values for Li₂TiO₃

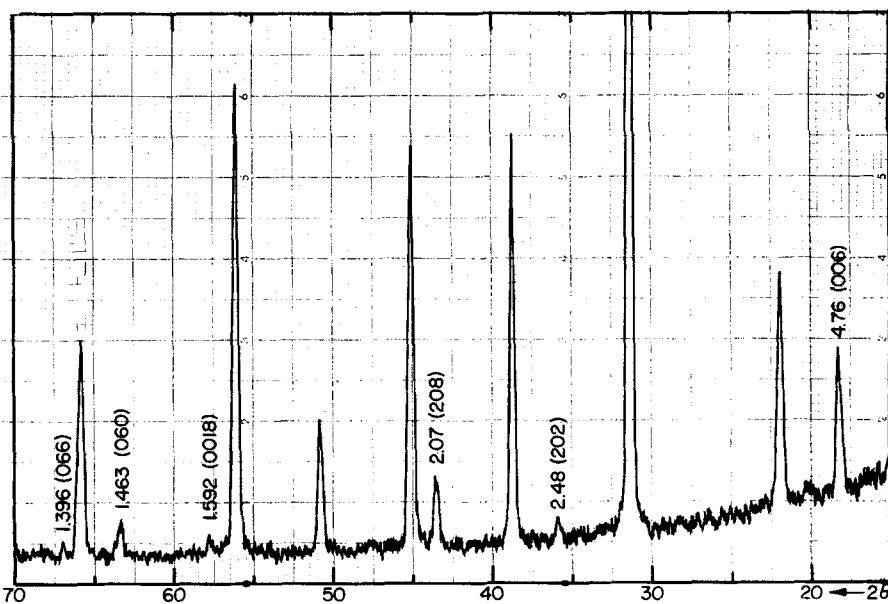


Fig. 1. X-ray powder diffraction pattern of BaTiO₃ containing 5 wt% LiF heated at 700°C for 5 h showing the presence of Li₂TiO₃ (represented as labeled peaks) as a reaction product.

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†Certified reagent grade, Fisher Scientific Co., Fair Lawn, NJ.

‡Mettler Instrument Corp., Princeton, NJ.

were identified by comparison with the ASTM index card.⁸ It was further observed that the intensity of the compound increased progressively as the LiF content in the mixtures was increased. Thus, it is apparent that BaTiO₃ reacts with LiF to form a cubic solid solution and Li₂TiO₃. It is further evident from the XRD patterns that the cubic solid solution and Li₂TiO₃ formed at the initial stage of sintering coexist with one another at elevated temperatures.

The DTA results obtained from several compositions showed the presence of an endothermic peak at 740°C. For all the compositions studied, this is the only peak that appeared during both the heating and cooling cycles. The appearance of an endothermic peak at 740°C is attributed to the formation of a liquid phase in the system. It is interesting to note that the corresponding TGA curves for the mixtures did not show any significant weight loss up to a temperature of 750°C. However, above this temperature, a steady and continuous weight loss was observed for all the samples. It seems likely that the rate of loss due to volatilization is a function of melt formation in the system.

The sintering characteristics of BaTiO₃ with 2 wt% LiF addition were found to vary with temperature and time. In general, a significant enhancement of densification was observed when samples were fired at temperatures above 740°C, which is the melt formation temperature in the system. This suggests that the sintering kinetics are probably controlled by the formation of a liquid phase. The SEM photomicrograph of the fracture surface of a sample sintered at 760°C for 10 h is shown in Fig. 2. The morphology reveals the presence of many interconnected and rounded grains with large annular regions free of pores. This is typical of the microstructure which is likely to be developed as a consequence of continuous grain growth in the presence of a small amount of liquid. The density of the sintered samples increased with increasing temperature, which again suggests the formation of more liquid as the

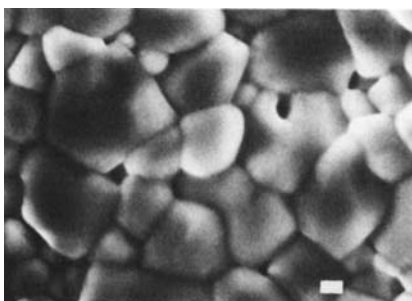


Fig. 2. Scanning electron micrograph of fracture surface of BaTiO₃ containing 2 wt% LiF sintered at 760°C for 10 h (bar=1 μm).

sintering temperature was raised. The maximum density achieved for a sample sintered at 900°C for 25 h was 97% of the theoretical. The SEM photomicrograph of the polished surface of this sample is shown in Fig. 3, which exhibits a dense microstructure with evidence of some grain growth occurring at this sintering temperature. As evident from the microstructure, a few pores present are located mainly at the grain boundaries and occasionally inside the grains. Prolonged sintering above 900°C resulted mostly in an excessive weight loss due to volatilization. The densification rate was found to be significantly reduced probably because of the loss of the liquid as the sintering proceeds. It is apparent that further work is needed to obtain a clear understanding of the simultaneous volatilization and densification processes involved in the sintering of LiF-fluxed BaTiO₃.

CONCLUSIONS

The sintering of BaTiO₃ with LiF as a densification aid results in the formation of a cubic solid solution and Li₂TiO₃. A liquid phase is formed at 740°C which essentially controls the overall sintering process. The amount of liquid formed increases with increasing sintering temperature and its presence even in a small quantity greatly enhances the densification process. Pro-

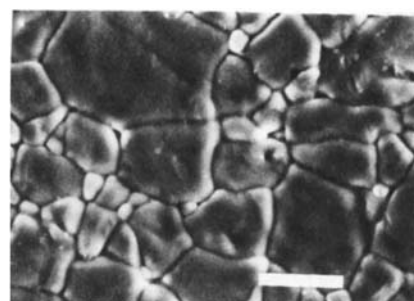


Fig. 3. Scanning electron micrograph of polished section of BaTiO₃ containing 2 wt% LiF sintered at 900°C for 25 h (bar=10 μm).

longed sintering above 900°C results in an extensive weight loss due to the volatilization of the samples which, in turn, affects the sintering rate and grain growth kinetics in the system.

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