

Microstructure vs. Dielectric Property Correlation in the Stoichiometric Sillenites

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Abstract

$\text{Bi}_{12}\text{SiO}_{20}$, $\text{Bi}_{12}\text{GeO}_{20}$ and $\text{Bi}_{12}\text{TiO}_{20}$ compounds with the sillenite crystal structure were synthesized and sintered into the dense ceramic bodies. An analyses of the microwave dielectric properties of the Si, Ge and Ti sillenites showed a permittivity (ϵ) of ~ 40 and a negative temperature coefficient of the resonant frequency for all analogues (from -20 to -40 ppm/K). The Qxf value of the Si and Ge sillenites was measured to be ~ 8.000 GHz. The Ti analogue shows a significantly lower Qxf value (~ 2.500 GHz) and is sensitive to the heat-treatment conditions. By increasing the sintering temperature the size of the grains increases, which correlates with an increase in the Qxf value.

1. Introduction

In contrast to conventional microwave ceramics, which are used for discrete passive elements, the new generation of microwave ceramics is designed for integration into microwave modules. Because of the specific architecture of the modules and the technology of production, the dielectric and chemical properties of these materials must be strictly controlled. The main problems in the development of materials for low-temperature co-fired ceramic (LTCC) integrated modules arise from the chemical incompatibility of the different materials within the module at the co-firing temperature. For the reliable functionality of the module the interaction between different ceramic tapes and the electrode material must be avoided completely.

Chemical compatibility. Due to the importance of the chemical compatibility between the ceramics and the metal electrode this issue must be carefully considered before initiating an experimental procedure of processing parameters and adjustment of the dielectric properties.

In the LTCC modules Ag or Cu is mainly used for electrode materials because of their high conductivity. The advantage of Ag is that it can be processed in the air while for Cu a slightly reducing

atmosphere is needed to prevent oxidation.

Theoretical studies of Bi_2O_3 -containing binaries¹⁾ have shown that the probability of chemical compatibility with Ag increases with the increase in a concentration of Bi_2O_3 . In addition, high concentrations of Bi_2O_3 assure a low enough sintering temperature and relatively high permittivity due to high ionic polarizability of Bi. As a result, different compounds with high Bi_2O_3 concentrations were tested in terms of their chemical compatibility with Ag. To identify the compounds chemically compatible with Ag a phase composition analyses of a mixture of ceramic and metal powder, fired for 3 h at 850°C (or lower when melting occurred), must reveal the appearance of no additional phases. With such an approach the family of compounds with the sillenite structure was recognized as being compatible with Ag.

Sillenites. Stoichiometric sillenites are compounds with the crystal structure of $g\text{-Bi}_2\text{O}_3$ ²⁾ (Fig. 1) and the general formula $\text{Bi}_{12}\text{MO}_{20}$ (e.g. $\text{M} = \text{Si}^{4+}$, Ge^{4+} , $1/2 \text{Al}^{3+} + 1/2 \text{P}^{5+}$, $4/5 \text{V}^{5+} + 1/5$ vacancies).^{3,4)} Nonstoichiometric sillenites are either oxygen deficient or have an excess of oxygen (e.g. $\text{Bi}_{12}(\text{Bi}_{0.5}^{3+}\text{Ga}_{0.5}^{3+})\text{O}_{20}$).³⁾ Preliminary results of our investigation showed that sillenites are low temperature sintering materials ($T_s < 850^\circ\text{C}$) with low losses and a modest negative

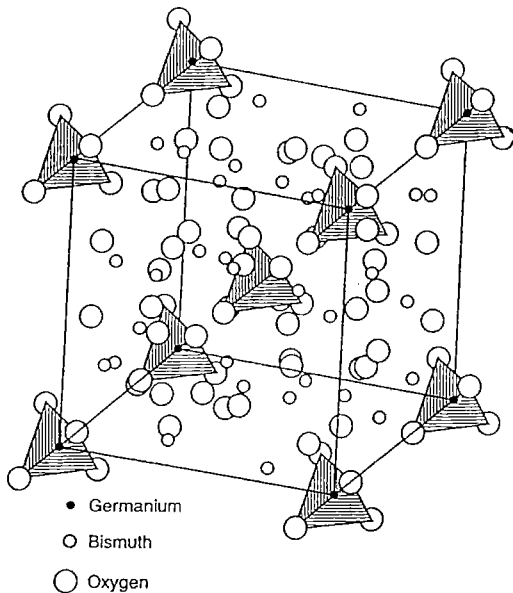


Fig. 1. Schematic presentation of the crystal structure of the stoichiometric sillenites²⁾.

temperature coefficient of resonant frequency. All this makes sillenites a potential dielectric material for advanced co-fired integrated modules used in telecommunications technology.

2. Experimental Procedure

The syntheses of the Si, Ge and Ti sillenites were conducted using solid-state reaction techniques. Stoichiometric mixtures of dried reagent-grade oxides were homogenized and fired at temperatures from 600°C to 750°C with an intermediate grinding step to achieve equilibrium. The progress of the reactions was monitored using a powder x-ray diffractometer with θ -2 θ Bragg-Brentano geometry (Philips PW1710). For the characterization of the dielectric properties ceramic pellets with diameter 10 mm and the height 4 mm were sintered at 750°C to 850°C for 10 hours to obtain > 97% of theoretical density. Density measurements on the sintered ceramics were performed by Hg and hexan pycnometry.

Analysis of the microwave dielectric properties was carried out by the cavity-reflection method using a Network Analyzer (HP 8719C).⁵⁾

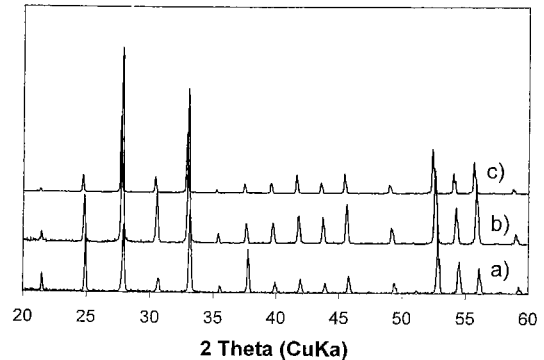


Fig. 2. Powder x-ray diffraction patterns of the $\text{Bi}_{12}\text{SiO}_{20}$ (a), $\text{Bi}_{12}\text{GeO}_{20}$ (b) and $\text{Bi}_{12}\text{TiO}_{20}$ (c) compounds.

3. Results and Discussion

The synthesis of the sillenite compounds resulted in single-phase ceramic powders with no secondary phase detected by the powder x-ray diffraction analyses (Fig. 2).

The synthesized powders were milled to a particle size of $\sim 1 \mu\text{m}$ and then used for investigations of the influence of sintering parameters on the microstructural characteristics and consequently on the dielectric properties. The experiments were conducted with changing various sintering parameter such as sintering temperature, dwell time, cooling rate and oxygen partial pressure.

As expected, before densification of the ceramics is complete the permittivity and dielectric losses are significantly influenced by the sintering temperature and dwell time due to variations in the porosity. However, experiments also showed that there is a wide range of sintering temperatures (740~820°C) for which sillenite ceramics with > 97% of theoretical density are obtained, and that the final dielectric properties again depend on the sintering conditions. Therefore, additional studies were undertaken to determine the influence of the sintering conditions within this window on the dielectric properties of sillenite ceramics.

Experiments revealed no influence of the cooling rate and oxygen partial pressure on the dielectric properties of sintered sillenites, only a moderate influ-

ence of the dwell time but a significant influence of the sintering temperature. The dielectric measurements on the Si, Ge and Ti sillenites showed permittivities of ~ 40 and a negative temperature coefficient of the resonant frequency for all analogues (from -20 to -40 ppm/K). The Qxf value of the Si and Ge sillenite was measured to be ~ 8000 GHz. The Ti analogue shows a significantly lower Qxf value (~ 2500 GHz), which can be explained by the increased contribution of the intrinsic dielectric losses resulting from the large ionic radius of the four-coordinated Ti^{4+} . In addition, the Ti analogue showed an increase in the Qxf value from 2.400 to 3.200 GHz related to an increase in the sintering temperature from $740\sim 820^\circ\text{C}$. To explain this phenomena, comprehensive microstructural analyses were performed.

The density measurements revealed that all the ceramic samples sintered from $740\sim 820^\circ\text{C}$ are equally dense ($>97\%$ of theoretical density). SEM analyses combined with EDS microanalyses showed no secondary phases present and the homogenous composition of the grains corresponding to the nominal

composition. All the samples were also thermally etched to reveal the microstructure. An important correlation between the grain size, sintering temperature and dielectric losses was revealed by this investigation. By increasing the sintering temperature the grain size increases which correlates with an increase in the Qxf value (Fig. 3).

The observed correlation can be explained by the grain-boundary influence on the dielectric properties. It is well known that grain boundaries are regions with a higher degree of chemical disorder, usually combined with a high surface energy (i.e. the existence of strains in the boundary crystal lattice layers). All these features of the grain boundaries contribute to extrinsic dielectric losses; however, in many cases the surface energy is low and the grains are large enough so that the contribution is almost negligible.⁶⁾ But in ceramics where a high grain surface energy is associated with small grains, the contribution to the extrinsic dielectric losses is so high that it significantly influences the total Q-value of the ceramics. In such cases, the increase in the grain size reduces the total surface energy and

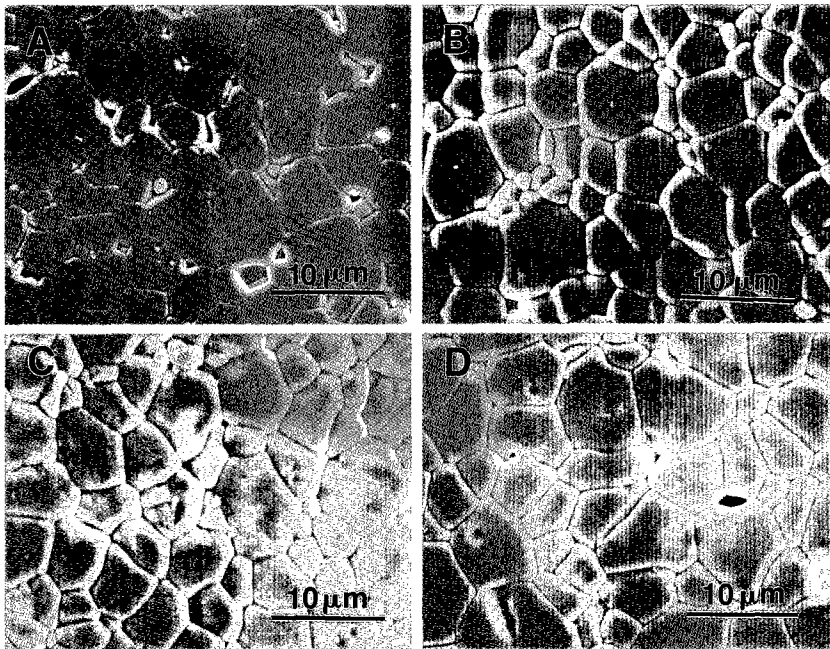


Fig. 3. SEM micrographs of thermally etched $\text{Bi}_{12}\text{Ti}_{20}$ sillenite ceramics sintered at 740°C (a), 760°C (b), 800°C (c) and 820°C (d) for 10 hours.

causes an increase in the Q-value; exactly the same effect was observed in this study of Si, Ge and Ti sillenites.

References

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