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Sintering Aids for LTCC Electronic Elements — Heating Microscope Studies and Microstructure Analysis

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The effect of a few low melting compounds, mixtures, and glasses on the sintering temperature of microwave and varistor ceramics, destined for multilayer LTCC elements, was analyzed in a heating microscope. It was found that 5 wt% of Li_2CO_3, LiF or $0.5AlF_3$–$0.5CaB_4O_7$ causes a significant decrease in the sintering temperature of willemite Zn_2SiO_4, enabling its co-sintering with commercial AgPd pastes. Addition of 5 wt% of Li_2CO_3 or 50 wt% of SiO_2–B_2O_3–Al_2O_3–CaO–MgO glass leads to the same effect in the case of another candidate for microwave substrates — diopside $CaMgSi_2O_6$. For two varistor ceramics, based on doped ZnO and $Cu_2Ta_4O_{12}$ perovskite, 0.5 and 4 wt% of AlF_3–CaB_4O_7 mixture was used as an efficient sintering aid. Good sinterability at low temperatures of the microwave and varistor ceramics with modified composition was confirmed by scanning electron microscope studies.

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PACS/topics: sintering aids, varistor, microwave ceramics, heating microscope studies, SEM studies

1. Introduction

Low temperature cofired ceramics (LTCC) is a relatively cheap and simple technique for manufacturing miniaturized discrete multilayer electronic components (like capacitors, varistors) advanced substrates, and modules with integrated conductive paths and passive components. A key problem for cost reduction is lowering of the sintering temperature of ceramic tapes which, after stacking, laminating, and cofiring with conductive layers are forming an LTCC structure. Such lowering without deterioration of the properties of a ceramic material desired for a given application is often a big challenge. Heating microscope studies are a useful tool for the quick choice of additives enabling realization of this goal.

This work was focused on adjustment of sintering aids for microwave ceramics — willemite [1] and diopside [2] and varistor ceramics — conventional one based on doped ZnO [3] and perovskite based on $Cu_2Ta_4O_{12}$ [4]. Aside from studies using a heating microscope for characterization of behavior during heating, scanning electron microscopy was utilized for confirmation of effective densification of the investigated materials during the sintering process.

2. Experimental procedure

Two low dielectric permittivity materials, willemite Zn_2SiO_4 and diopside $CaMgSi_2O_6$, and a varistor material, $Cu_2Ta_4O_{12}$, were synthesized by solid state reaction method. The products were milled in a Fritsch ball mill. The second ceramic varistor material, ZnO doped with Bi, Sb, Co, Mn, Cr, B, and Si oxides, was obtained by co-precipitation method. For lowering of the sintering temperature of these materials, four additives with low melting temperatures were chosen: Li_2CO_3, LiF, $0.5AlF_3$–$0.5CaB_4O_7$, and SiO_2–B_2O_3–Al_2O_3–CaO-MgO glass of E type. The powders of Zn_2SiO_4, $CaMgSi_2O_6$, $Cu_2Ta_4O_{12}$, and doped ZnO were mixed with appropriate amounts of the sintering aids, ball milled, pressed into pellets, and sintered in the temperature range 950–1000 °C. The behavior of the sintering aids, undoped ceramics, and the ceramics with addition of sintering aids was characterized during heating in the temperature range 20–1400 °C, using a Leitz heating microscope. The microstructure and densification degree of the modified ceramics and their cooperation with conductive layers were investigated using a FEI scanning electron microscopy (SEM).

3. Results and discussion

Based on the results of heating microscope studies of the sintering aids it was found that melting temperatures are 905, 849, 722, and 1059 °C for $0.5AlF_3$–$0.5CaB_4O_7$, LiF, Li_2CO_3, and glass E, respectively. The softening temperature of glass E is 870 °C. Figure 1 shows selected images illustrating the changes during heating of the shape and dimensions of $0.5AlF_3$–$0.5CaB_4O_7$, LiF, and Li_2CO_3 samples.

Three additives, AlF_3–CaB_4O_7, Li_2CO_3, and LiF were introduced in small amounts of 0.5–5%, and served as sintering aids which, due to formation of liquid phase, facilitated sintering process, and decreased the firing temperatures of the microwave and varistor ceramics under investigation. The glass E was utilized as a main component of a composite, in which glass and diopside were mixed in the equal proportion. Willemite doped with 5% of $0.5AlF_3$–$0.5CaB_4O_7$, Li_2CO_3 or LiF was found to be sinterable at low temperatures 960–980 °C, as illustrated in Fig. 2a.

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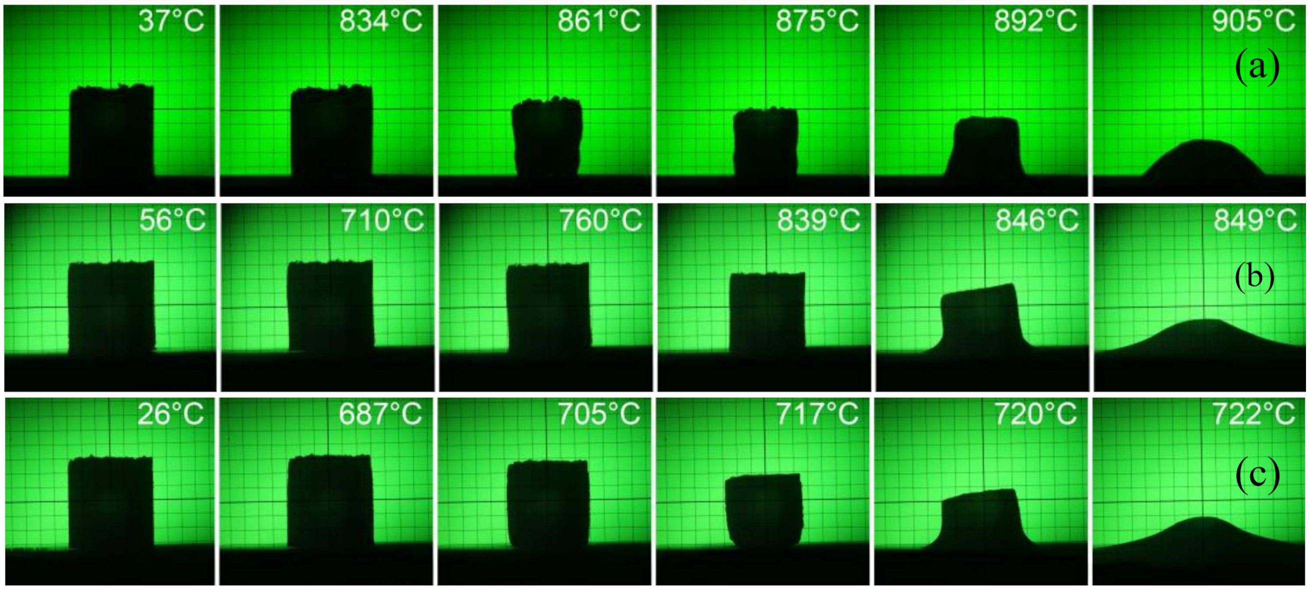

Fig. 1. Images from the heating microscope for the additives: (a) $0.5AlF_3$–$0.5CaB_4O_7$, (b) LiF, (c) Li_2CO_3.

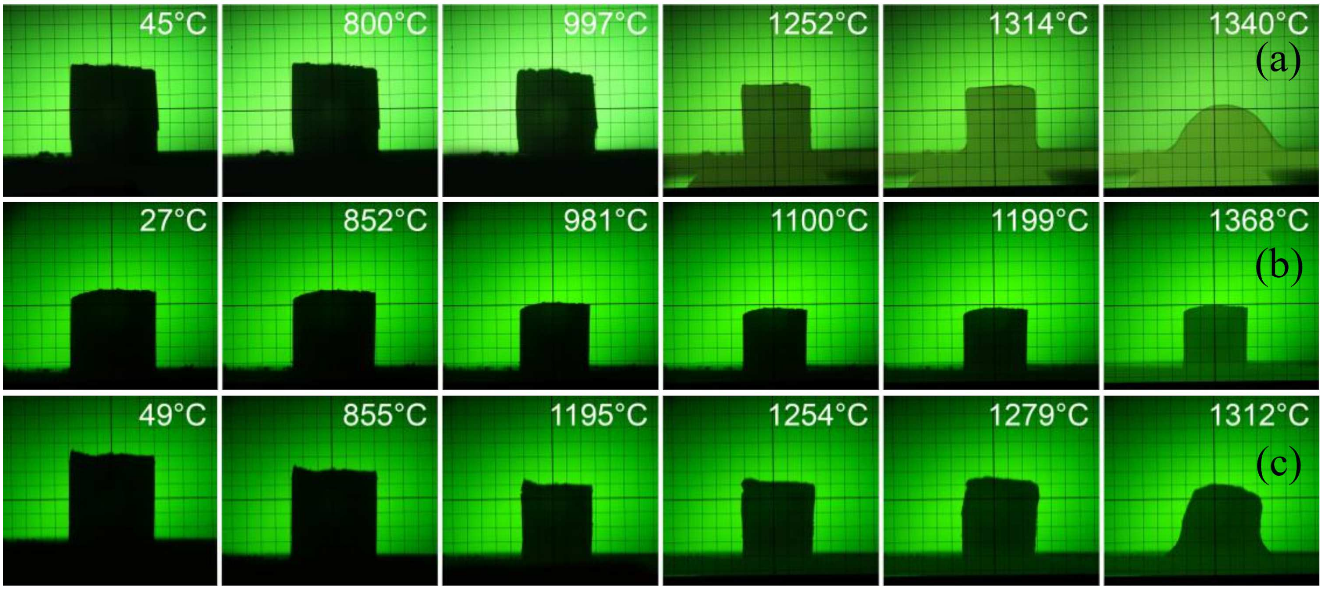

Fig. 2. Images from the heating microscope for: (a) willemite with 5% LiF, (b) $Cu_2Ta_4O_{12}$ with 4% of $0.5AlF_3$–$0.5CaB_4O_7$, (c) doped ZnO with 0.5% of $0.5AlF_3$–$0.5CaB_4O_7$.

It was confirmed that willemite ceramics with 5% of $0.5AlF_3$–$0.5CaB_4O_7$ addition can be cofired with Ag–Pd thick films at 980 °C, as shown in Fig. 3a for a test multilayer LTCC structure. Diopside–glass E composite exhibits low sintering temperature of 980 °C and a significant closed porosity (Fig. 3b) which results in a desired lowering of dielectric permittivity of the composite.

The AlF_3–CaB_4O_7 addition at a level of 4% and 0.5%, respectively, is an effective sintering aid for both varistor ceramics, based on $Cu_2Ta_4O_{12}$ and ZnO. Images from the heating microscope in Figs. 2b and c illustrate shrinkage of these ceramics. Figure 4 presents the fracture of a test multilayer LTCC structure built of AlF_3–CaB_4O_7 doped $Cu_2Ta_4O_{12}$ ceramic layers and AgPd conductive layers. Ceramic layers have a compact microstructure with a low porosity, despite a significant reduction of the sintering temperature (from 1220 °C for pure $Cu_2Ta_4O_{12}$ to 960 °C for doped ceramics). As in the case of the undoped copper tantalate, there is a significant variation in grain sizes, contributing to the Maxwell–Wagner type polarization effects which are the characteristics of the group of compounds with the $CaCu_3Ti_4O_{12}$ structure.

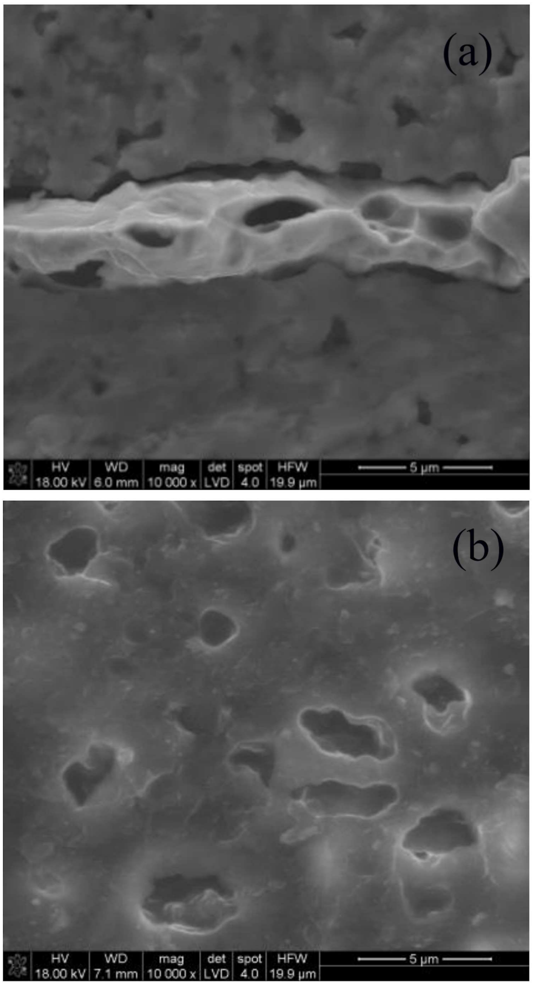

Fig. 3. SEM images: (a) willemite with 5% AlF_3–CaB_4O_7 with AgPd thick film, (b) diopside-glass E layer.

Due to the relatively low sintering temperature, grains are small in size (a few hundred nanometers to 2 μm). The cooperation between ceramic and conductive layers is good.

4. Conclusion

Additives that decrease sintering temperatures of willemite and diopside microwave ceramics, and ZnO and $Cu_2Ta_4O_{12}$ varistor ceramics were selected on the basis of heating microscope studies. SEM observations of test LTCC structures confirmed sinterability of the doped ceramics at temperatures below 1000 °C and their good compatibility with conductive layers made of commercial AgPd pastes.

Acknowledgments

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References

[1] Y. Guo, H. Ohsato, K.I. Kakimoto, *J. Eur. Ceram. Soc.* **26**, 1827 (2006).

[2] B.K. Choi, S.W. Jang, E.S. Kim, *Mater. Res. Bull.* **67**, 234 (2015).

[3] J. Kulawik, D. Szwagierczak, B. Synkiewicz, *Microelectron. Int.* **31**, 163 (2014).

[4] D. Szwagierczak, J. Kulawik, *J. Eur. Ceram. Soc.* **28**, 2075 (2008).

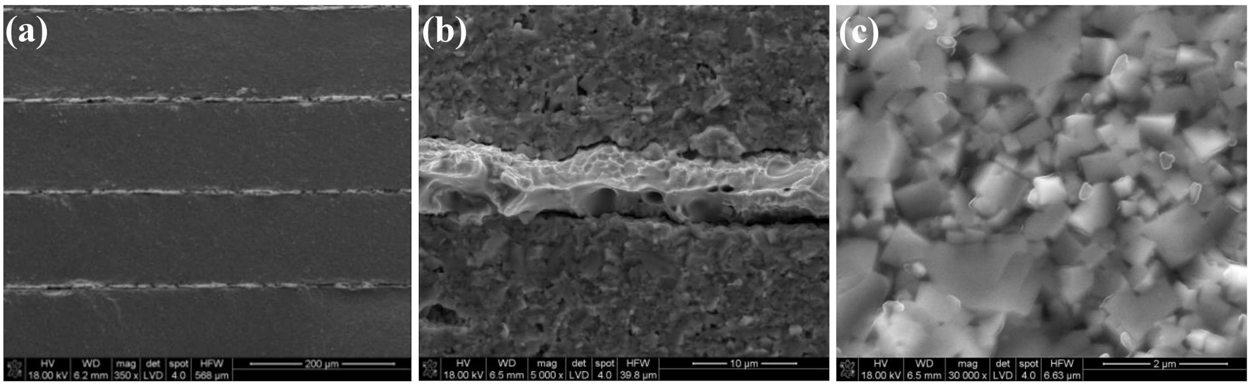

Fig. 4. SEM images of a multilayer structure with AlF_3–CaB_4O_7 doped $Cu_2Ta_4O_{12}$ layers and AgPd thick.