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Application News

Electron Probe Microanalyzer EPMA-8050G

Measurement of Elemental Distribution of Multi-Layer Ceramic Capacitor

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User Benefits

- It is possible to confirm the state of dispersion of trace amounts of dopant elements in the dielectric layer.
- It is possible to investigate the distribution of trace rare earth elements doped in the core-shell structure.
- The state of diffusion of component elements in the glass frit at the dielectric layer/external electrode interface can be confirmed.

■ Introduction

Multi-Layer Ceramic Capacitors (MLCC) are used in electronic devices in all industries, including mobile phones and automobiles, among others. In particular, demand for MLCC is expanding accompanying the electrification of automobiles and popularization of automated driving. In response to these trends, research on miniaturization of MLCC and high-capacity electrostatic capacitance is underway in order to meet demands for further miniaturization, weight reduction, and long life in electronic devices. Because capacitance is proportional to the dielectric constant of the dielectric substance and the total number of dielectrics, and is inversely proportional to the thickness of the dielectric layers, it is necessary to select dielectric materials with a high dielectric constant, reduce the thickness of the dielectric layers, and adopt a multi-layer structure. Evaluation of the fine multi-layer structure and the distribution of trace dopant elements is important for achieving these aims.

This Application News article introduces an example of an analysis of trace dopant elements of MLCC using an EPMA™ electron probe microanalyzer (EPMA-8050G).

■ MLCC

MLCC have a multi-layer construction consisting of an inner structure of alternately-stacked layers of metal inner electrodes and dielectric layers, enclosed on its outer side by an external electrode. Large-capacity electrostatic capacitance is achieved in MLCC by thinning the dielectric layers by using fine dielectric ceramic particles and controlling those particles to a uniform distribution and adopting a multi-layer structure with a larger number of stacked layers. To achieve a high dielectric constant at room temperature, the dielectric is doped with barium zirconate ($BaZrO_3$) or strontium titanate ($SrTiO_3$) as a "shifter" that reduces the peak of the Curie temperature to room temperature and increases the relative dielectric constant, while magnesium titanate ($MgTiO_3$) or calcium titanate ($CaTiO_3$) is doped as a "depressor" to smooth variations in the peak of the Curie temperature so as to reduce the temperature variation rate (temperature dependence) of the relative dielectric constant.

Fig. 1 shows the result of a cross-sectional analysis of an MLCC formed by a nickel (Ni) inner electrode and ceramic particles of barium titanate ($BaTiO_3$) as the dielectric substance. The analysis region is indicated by the red square in the OM-image, which is an EPMA optical micrograph. From the evenly-spaced alternating pattern of the $BaTiO_3$ dielectric layers and the partially-discontinuous Ni inner electrodes in Fig. 1, it can be understood that this MLCC has a multi-layer structure. The dispersion condition of the trace dopant elements magnesium (Mg), silicon (Si), manganese (Mn), and dysprosium (Dy) can also be understood, and the Overlay image shows that Mg is distributed in the Mn segregation region.

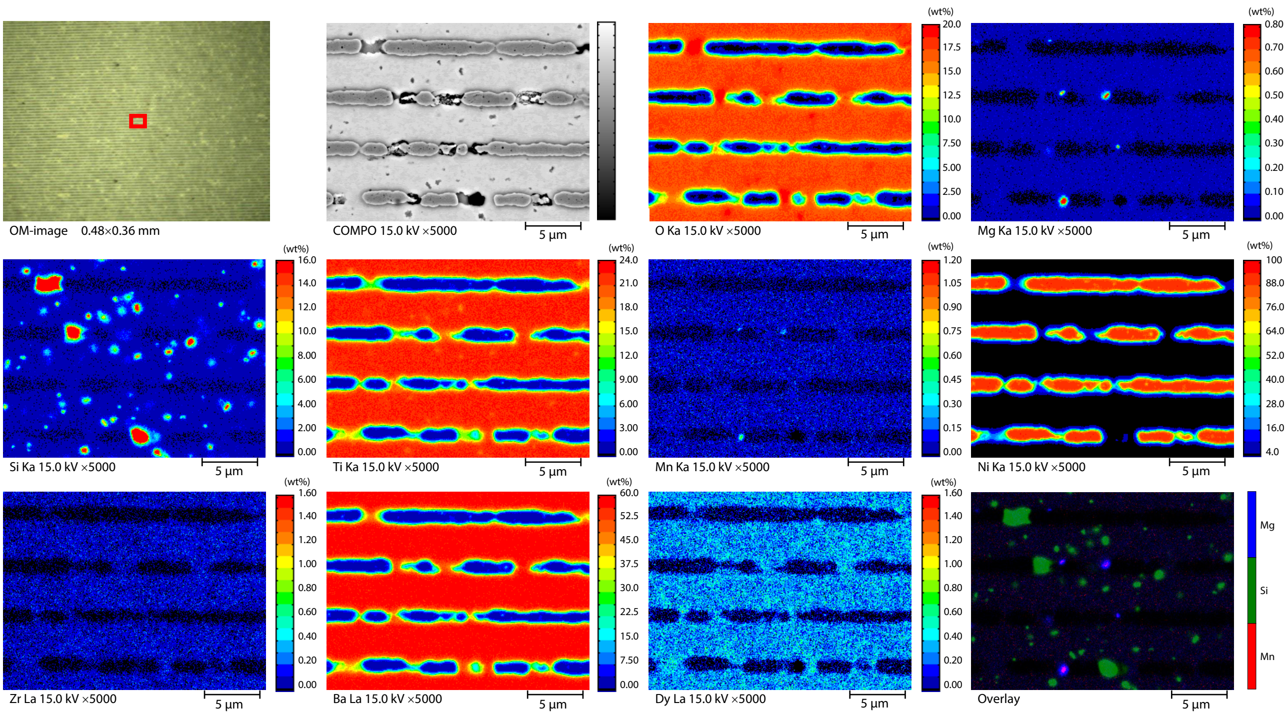

Fig. 1 Mapping of Inner Electrodes and Dielectric Layers

■ Trace Dopant Elements in Dielectric Layer

The ceramic particles of the dielectric have a core-shell structure comprising a core part and a surrounding shell part. Due to the low dielectric constant of the shell relative to the high dielectric constant of the core, segregation of the dopants to the shell will influence temperature characteristics. Therefore, the amount of trace dopants and the sintering conditions were studied. As a result, rare earth elements such as Dy and holmium (Ho) were dissolved in solid solution in the shell to lower the temperature dependence of the dielectric constant and improve temperature characteristics, with the aim of achieving longer device life.

Fig. 2 and Fig. 3 show the spectra of the elements Mg and Dy, which were doped in trace amounts in the dielectric layer, and the mapping images of the distributions of those elements, respectively. A concentration gradient can be observed in the distributions of Dy and Mg, which cause a low-temperature shift of the peak of the Curie temperature. [1] The concentration difference is about 0.02 wt% for Mg and about 0.2 wt% for Dy.

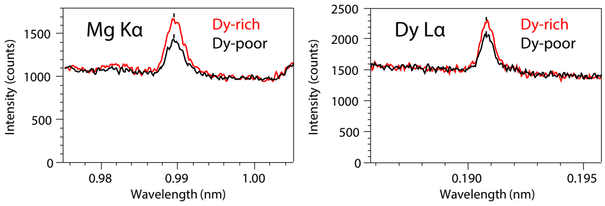

Fig. 2 Spectra of Trace Dopant Elements in Dielectric Layer

■ External Electrode

The external electrode of MLCC comprises a copper (Cu) terminal electrode and a nickel (Ni) plating to prevent solder dissolution, and a tin (Sn) plating which enhances wettability for solder.

Fig. 4 shows the result of a mapping analysis of the interface between the Cu terminal electrode and the dielectric layer, which is coated with a Cu paste consisting of glass frit, Cu powder particles, a solvent, and other additives. In zinc (Zn) based glass frit, which has high reduction resistance and displays crystallization, the component elements boron (B), Si, and Zn diffuse in the dielectric layer and bond by reaction with the dielectric layer. [1]

■ Conclusion

Use of EPMA enables visualization of the dispersion condition of trace dopant elements in thin-layer dielectric layers. Visualization of the concentration gradient of the rare earth elements in the core part and shell part of the core-shell structure is also possible. It is also possible to evaluate the optimum composition and sintering conditions of the glass frit by investigating its elemental distribution, which influences the bond strength between the dielectric layer and the external electrode.

<References>

1) Takeshi Nomura, Multi-Layer Ceramic Capacitors (MLCC): Materials, Manufacture, Packaging Technology and Recent Trends, R&D Support Center Co., Ltd., 66, 101, 184 (2020) (in Japanese)

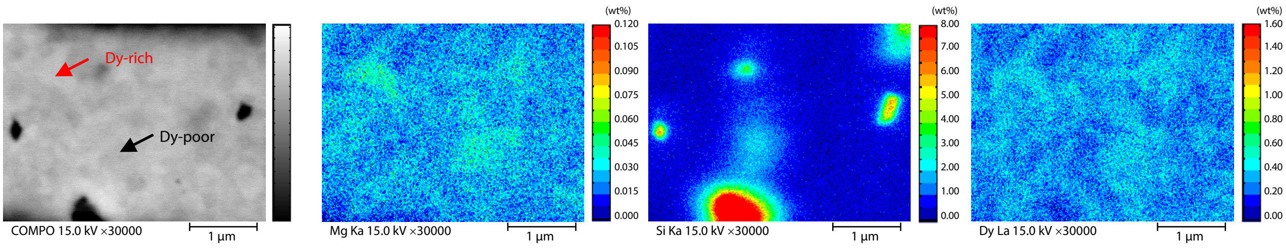

Fig. 3 Mapping of Trace Dopant Elements in Dielectric Layer

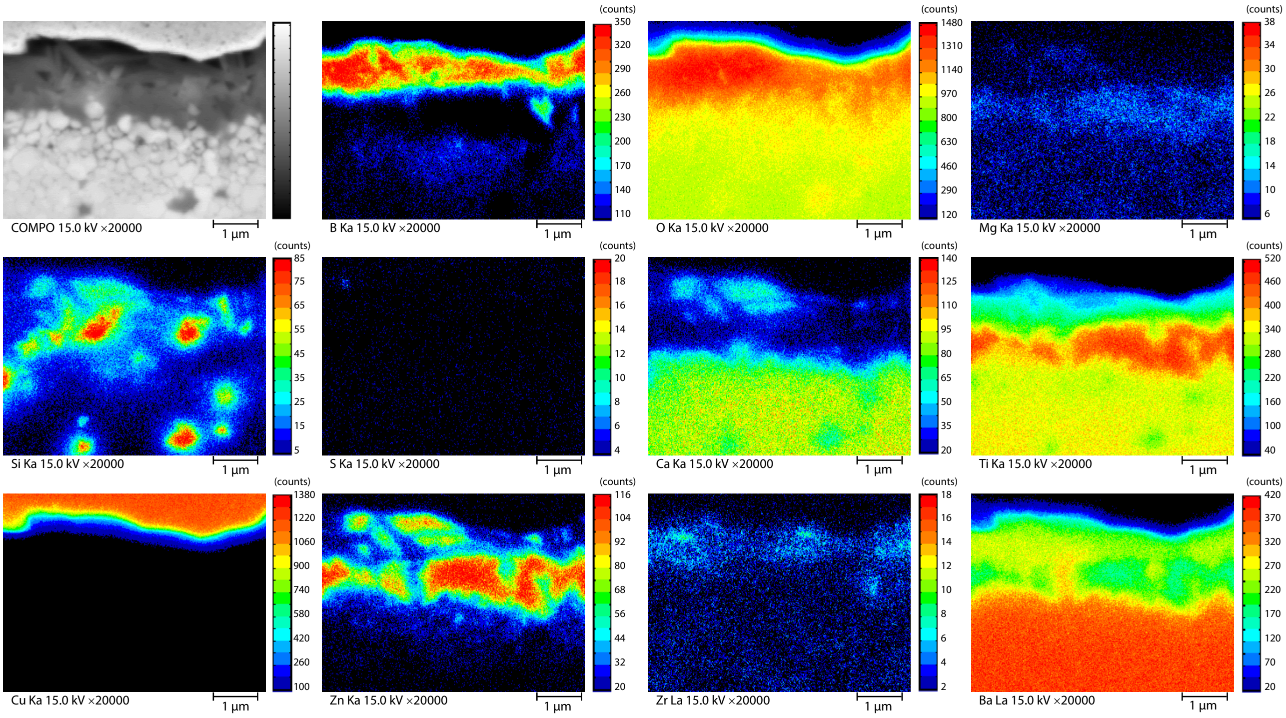

Fig. 4 Mapping of Dielectric Layer/Cu Terminal Electrode Interface

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