Multilayer ceramic capacitors (MLCCs) are composed of several hundreds of alternately stacked dielectric layers and internal electrode layers, as shown in Fig. 1. Conventional mass-production processes for MLCCs require a high-temperature sintering of about 1300°C to obtain a dense body, and those processes consume much energy. To preserve the earth’s environment, some investigations were proposed to decrease sintering temperature, but the extent to which the temperature has been decreased is still not enough. Densification properties during the sintering of dielectrics and electrodes are quite different, because dielectrics are made of ceramics and electrodes are made of metal. The analysis of the fluctuation of the local homogeneity of small-chip MLCCs after sintering is very important to obtain a high reliability. However, the sintering process and resultant local homogeneity fluctuation of low temperature sintered MLCCs were not sufficiently analyzed yet.

Absorption bands of some dielectric ceramics appear at the mid-infrared region [1,2], and some of their peaks change owing to changes in the homogeneity of ceramics. Therefore, it is possible to evaluate the homogeneity of ceramics by mid-infrared spectroscopy. A conventional infrared spectrometer cannot obtain a spectrum from a small sample with a satisfactory signal-to-noise ratio because of the low brilliance of a conventional light source. However, it is possible to obtain a satisfactory mid-infrared spectrum from small samples using a microfocus spectrometer combined with synchrotron radiation as a high brilliance light source at beamline BL43IR. The purpose of this study is to analyze the local homogeneity fluctuation of low temperature sintered MLCCs using BL43IR beamline of SPring-8 with a microfocus apparatus.

The MLCCs sample were prepared by the conventional green-sheet method. BaTiO3 powder was mixed with 3.08 wt% Li-B-O glass powder to prepare the low sintering temperature material. A green sheet was prepared by the conventional coating method from the mixture of mixed powder, an organic binder, and a solvent. The thickness of the prepared green sheet was about 13 µm. The Ni internal electrode was printed at one of the surfaces of the green sheet. One hundred green sheets were stacked and pressed, and then cut to a certain size to obtain individual green chips. The obtained green chips were sintered in the temperature range from 650°C to 750°C at a weak reduced atmosphere. The microstructure of the polished cross section of sintered samples was observed with FE-SEM (Hitachi, S-4000). Mid-infrared (MIR) spectra were observed in the range from 400 to 6000 cm⁻¹ with an infrared spectrometer (Bruker IFS120HRX).

The microstructure of the samples sintered at various temperatures was superimposed on Figs. 2-4. The number of pores decreased with increasing sintering temperature. However, no significant
difference between the cover-region (Fig. 2) and center-region (Fig. 3) of the samples sintered at the same temperatures was observed in the SEM images. The Ti-O vibration peaks on IR spectra obtained from the center-region and cover-region of the samples sintered at various temperatures are shown in Fig. 2 and Fig. 3, respectively. The vibrational structure of peaks can be observed in the range from 450 to 750 cm$^{-1}$ on the obtained spectra. The relative intensity of low-wave-number side of the peak was decreased with increasing sintering temperature. The physical meanings of these vibrational structures have not been sufficiently understood yet, but it was observed that the degree of the symmetry of the peak shape increased with increasing sintering temperature. Therefore, it is possible to evaluate the degree of sintering using the degree of symmetry of the Ti-O peak on IR spectra. The IR spectra obtained from center- and cover-regions of the 700°C sintered sample are shown in Fig. 4. The low degree of symmetry and low resolution of the vibrational structure in the spectrum obtained from the center-region shows a relatively low degree of sintering. In the sintering process, a grain growth process follows a densification process. The densification process contains the densification of powder compacts and homogenization of individual grains. The microstructure of compressed powder changes during the densification process, but barely changes during the homogenization of individual grains. Therefore, it may be understood by the lower symmetry of the Ti-O peak obtained from center-region than those of cover-region that the homogenization of center-region of the samples was delayed cover-region. The densification of the Ni internal electrode proceeds at a temperature lower than that of ceramics during sintering. And those dense internal electrodes retarded the densification of ceramics at the center-region since the dense electrodes could not shrink further.

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