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# Transmittance and cathodoluminescence of AlN ceramics sintered with $Ca_3Al_2O_6$ as sintering additive

Takayuki Honma [a], Yuichiro Kuroki [a], Tomoichiro Okamoto [a], Masasuke Takata [a,*], Yukihiro Kanechika [b], Masanobu Azuma [b], Hitofumi Taniguchi [c]

[a] Department of Electrical Engineering, Nagaoka University of Technology, 1603-1 Kamitomioka, Nagaoka, Niigata 940-2188, Japan
[b] Advanced Materials Development Department, Tokuyama Corporation, 1-1 Mikage, Shunan, Yamaguchi 745-8648, Japan
[c] Tsukuba Research Laboratory, Tokuyama Corporation, 40 Wadai, Tsukuba, Ibaraki 300-4247, Japan

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**Abstract**

Aluminum nitride ceramics were prepared by sintering with 0–4.8 mass% of $Ca_3Al_2O_6$ ($C_3A$) as a sintering additive. The transmittance in the range of 260–550 nm increased with increasing amount of $C_3A$. The cathodoluminescence intensity attributed to oxygen-induced defects decreased with increasing amount of $C_3A$. From the results, the increase of the transmittance in the range of 260–550 nm was considered to be related to the decrease of the oxygen-induced defect density.


*Keywords:* Transmittance; Cathodoluminescence; Aluminum nitride; $Ca_3Al_2O_6$

## 1. Introduction

Recently, the heat generated in semiconductor devices such as a LSI and a high-power laser is increasing. The radiation of the generated heat is an important issue to develop the devices with high performance. Since aluminum nitride (AlN) has a high thermal conductivity (320 W $m^{-1}$ $K^{-1}$ [1]) and a high-electrical resistivity, it is now used as a heat sink for a laser diode. Furthermore, AlN has been attracting attention as a translucent ceramics due to its wide band gap energy of 6.2 eV [2–4].

Several groups discussed the sinterability and the thermal conductivity of AlN ceramics sintered with Ca-based additives [5–7]. Kuramoto et al. [8,9] reported the fabrication of the transparent and translucent AlN ceramics sintered with CaO and $Ca_3Al_2O_6$ ($C_3A$), respectively. The other groups reported the translucent AlN ceramics fabricated by spark plasma sintering without additives [10] and with $CaF_2$ [11,12]. Previously, we have reported the relationship between the thermal conductivity and lattice defects for AlN ceramics sintered with various amounts of $C_3A$ [13]. However, there is no report concerning the effect of $C_3A$ amount on the transmittance of AlN ceramics. The purpose of this study is to investigate the relationship between the transmittance and lattice defects for AlN ceramics sintered with various amounts of $C_3A$.

## 2. Experimental procedure

The $C_3A$ powders (0.5–4.8 mass%) synthesized from $CaCO_3$ and $Al_2O_3$ powders were added to AlN powders (F-grade, Tokuyama Corp.), and mixed for 1.5 h in ethanol using a planetary ball mill. After drying, the mixtures were pressed into pellets (4 cm in diameter) and then cold-isostatic-pressed at 250 MPa. The pellets were sintered at 1880 °C for 50 h in $N_2$ atmosphere. The sintered bodies were ground to 0.3 mm thickness. Both sides of each sample were mirror-polished.

The densities of the samples were measured by the Archimedes method. The morphology of the fracture surface of the samples was observed using a scanning electron microscope (SEM; JEOL, JSM-5510). The samples were identified using an X-ray diffractometer (XRD; Rigaku, RINT-1400). The elemental analysis was carried out using an energy dispersive X-ray spectroscope (EDS; JEOL, JED-2201). The

* Corresponding author. Tel.: +81 258 47 9509; fax: +81 258 47 3604.
*E-mail address:* takata@vos.nagaokaut.ac.jp (M. Takata).

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total transmittances of the 0.3 mm-thick samples were measured at wavelengths in the range of 200–800 nm using a UV–vis-NIR spectrophotometer (Shimadzu, SolidSpec-3700DUV). The lattice defects in the samples were evaluated by cathodoluminescence (CL) using electron-beam accelerated by 20 kV at room temperature. The oxygen contents in the samples were measured using an oxygen–nitrogen analyzer (HORIBA, EMGA-550).

## 3. Results and discussion

Fig. 1 shows the relationship between the relative density of AlN ceramics and the amount of $C_3A$. The relative densities of all the samples were >99%.

The SEM images of fracture surfaces of AlN ceramics sintered without additive, and with 0.5 and 1.0 mass% $C_3A$ are shown in Fig. 2. The microstructure of the samples sintered without $C_3A$ contained pores <1 μm in diameter. On the other hand, no pore was observed in the samples sintered with $C_3A$. No secondary phase attributed to $C_3A$ was observed at the grain boundary or the triple point.

Analysis of XRD and EDS were carried out to investigate the secondary phase in the samples. For all samples, only single-phase of hexagonal AlN was found and Ca was not detected by XRD and EDS analysis, respectively. The eutectic structure [14] is produced between $C_3A$ and $Al_2O_3$ existing on the surface of AlN raw powder as the natural oxide layer. The eutectic temperature ~1400 °C is much lower than the sintering temperature of 1880 °C in this work. Therefore, the generated liquid phase might be gradually vaporized from the samples during the sintering.

Fig. 3 indicates the transparency of 0.3 mm-thick AlN ceramics sintered without additive, and with 0.5 and 1.0 mass% $C_3A$. The transparency of the sample sintered without $C_3A$ was low, while those of the samples sintered with $C_3A$ were very high.

Fig. 4 shows the transmission spectra of the samples sintered with various amounts of $C_3A$. The transmittance at 800 nm was 43% for the sample sintered without $C_3A$, and it increased dramatically to 77% for the samples sintered with 0.5–4.8 mass% $C_3A$. With increasing amount of $C_3A$, the transmittance in the range of 260–550 nm slightly increased. The transmittances of all the samples were almost 0% at ~260 nm.

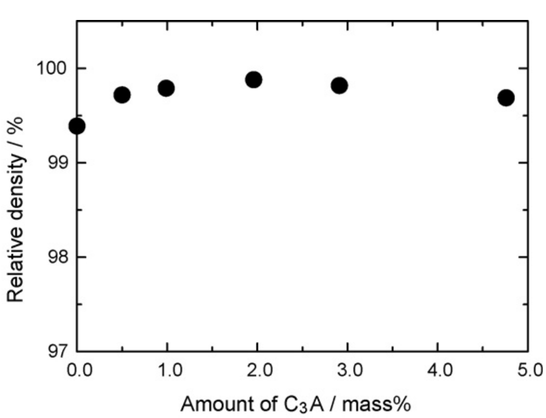


Fig. 1. Relationship between relative density of AlN ceramics and amount of $C_3A$.

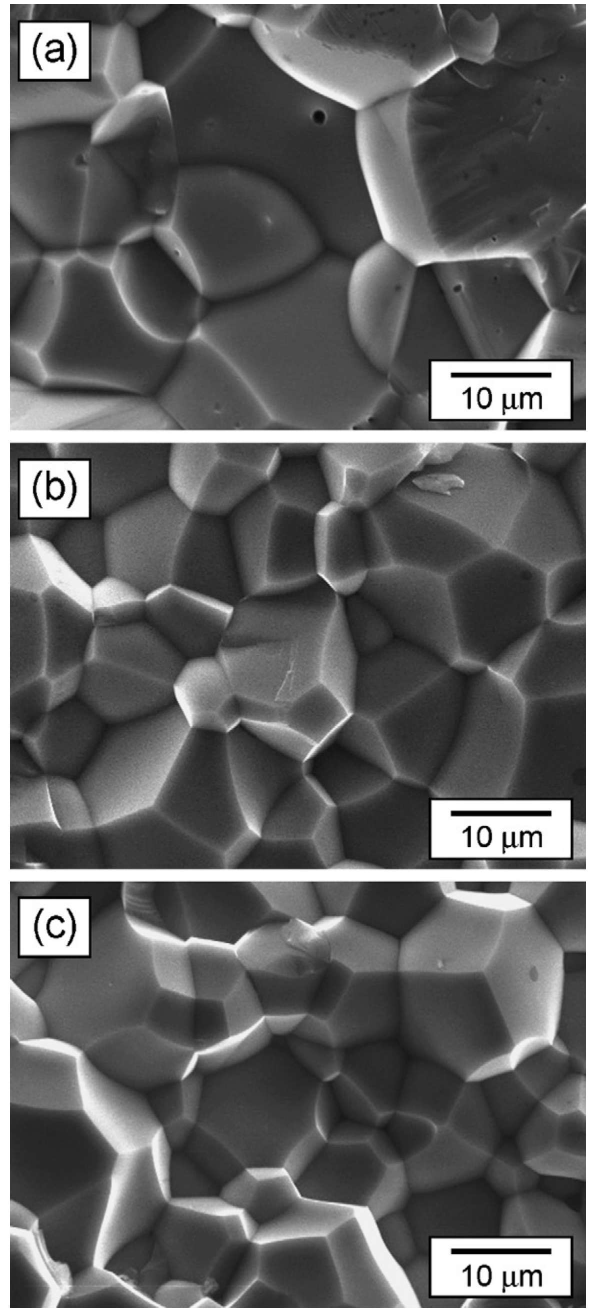


Fig. 2. SEM images of fracture surfaces of AlN ceramics sintered (a) without additive, (b) with 0.5 and (c) 1.0 mass% $C_3A$.

The CL spectra of AlN ceramics sintered with various amounts of $C_3A$ are shown in Fig. 5. The luminescence peaks at about 354 nm were observed. The intensity of the luminescence peak decreased with increasing amount of $C_3A$ (Fig. 5(b)), reflecting the decrease of the defect density. Some groups reported that the CL and photoluminescence peaks of AlN ceramics were observed at about 308–375 nm [15–17]. They discussed that the luminescence were attributed to the nitrogen vacancies or the oxygen-related defects.

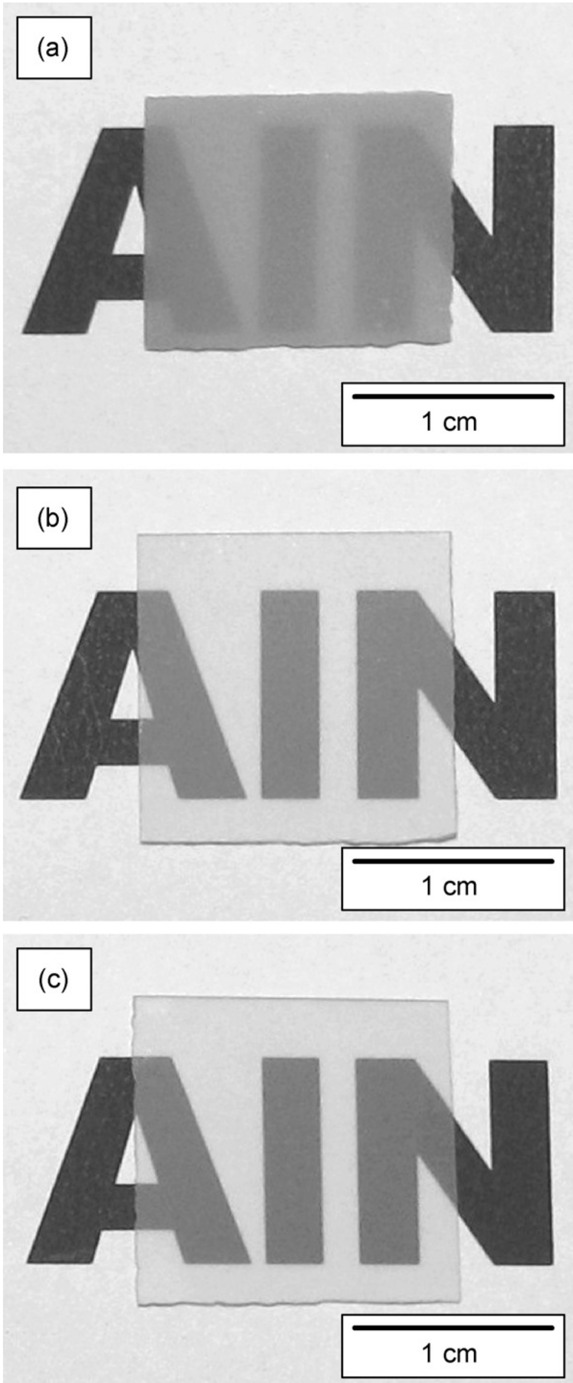


Fig. 3. Transparency of 0.3 mm-thick AlN ceramics sintered (a) without additive, (b) with 0.5 and (c) 1.0 mass% $C_3A$.

To investigate the cause of the defects in AlN ceramics sintered with $C_3A$, the oxygen contents in AlN ceramics were measured. Fig. 6 shows the relationship between the oxygen content and the amount of $C_3A$. The oxygen content was 0.27 mass% for the sample sintered without $C_3A$. The content decreased with increasing amount of $C_3A$ and became 0.03 mass% at 4.8 mass% $C_3A$. From the comparison between the oxygen content (Fig. 6) and the CL peak intensity (Fig. 5(b)), the CL was considered to be related to the oxygen-induced defects in AlN ceramics.

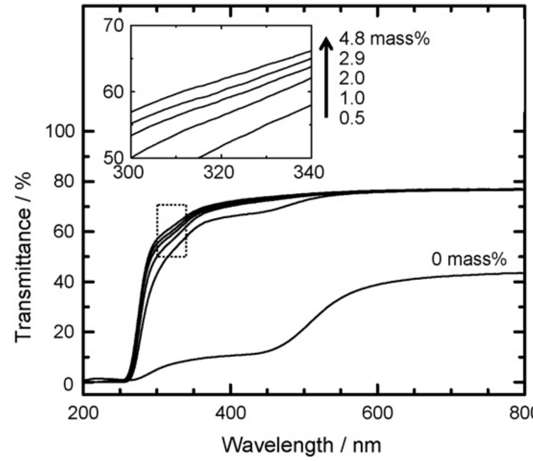


Fig. 4. Transmission spectra of AlN ceramics sintered with various amounts of $C_3A$.

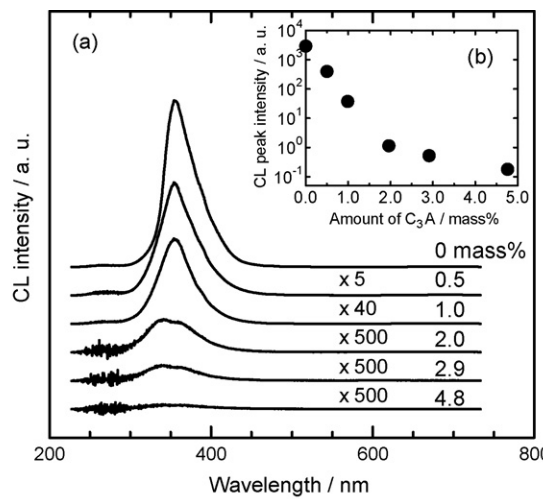


Fig. 5. (a) CL spectra of AlN ceramics sintered with various amounts of $C_3A$. (b) Relationship between CL peak intensity and amount of $C_3A$.

The densification is the essential factor for the transmittance of AlN ceramics. However, in the extremely dense ceramics (>99%) the defects in the samples may be more important. In this study, the increase of the transmittance of AlN ceramics

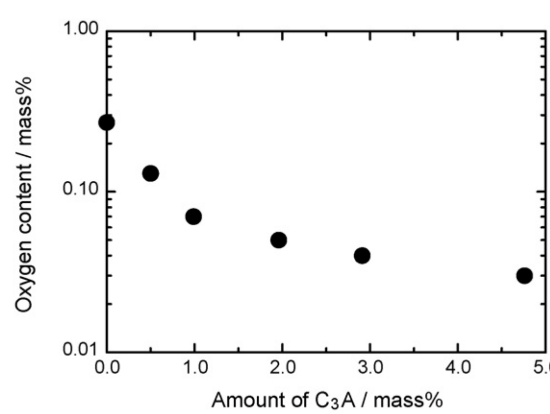


Fig. 6. Relationship between oxygen content in AlN ceramics and amount of $C_3A$.

may be attributed to the decrease of the oxygen-induced defect density caused by increasing amount of $C_3A$.

## 4. Conclusions

The relative densities of AlN ceramics sintered with 0–4.8 mass% of $C_3A$ as a sintering additive were >99%. With increasing amount of $C_3A$, the transmittance in the range of 260–550 nm increased, the CL intensity decreased, and the oxygen content decreased. The CL was related to the oxygen-induced defects in the AlN. The increase of the transmittance in the range of 260–550 nm was considered to be related to the decrease of the oxygen-induced defect density caused by increasing amount of $C_3A$.

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