Influence of SrF₂-doping in AlN ceramics on Scintillation and Dosimeter Properties

Kaori Kojima ^{a,*}, Go Okada ^a, Kentaro Fukuda ^b, Takayuki Yanagida ^a

^aGraduate School of Materials Science, Nara Institute of Science and Technology, 8916-5 Takayama, Ikoma, Nara 630-0192, JAPAN

^bTokuyama Corp., 1-1 Mikage-cho, Shunan-shi, Yamaguchi 745-8648, JAPAN

Abstract

In this study, we synthesized **undoped** AlN and SrF₂-doped AlN (AlN-SrF₂) ceramics by Spark Plasma Sintering (SPS), and we characterized their optical, scintillation and dosimeter properties. The prepared **undoped** AlN ceramic had gray color and visually non-transparent whereas, with an addition of SrF₂, the transparency improved and became translucent. The measured in-line transmittance was approximately 0.2 % at wavelengths longer than 500 nm. While the addition of SrF₂ decreased the scintillation intensity, the decay time was **significantly** fastened, which is a great advantage for fast photon counting-based measurements. Both the thermally-stimulated luminescence (TSL) and optically-stimulated luminescence (OSL) showed good linear response from the milli-gray range to over 10 Gy. The sensitivity seems to decrease by an addition of SrF₂ as it suppresses structural defect centers which are responsible for dosimeter properties. However, the main TSL glow peak position shifts to higher temperature with the addition of SrF₂, which indicates that inclusion of SrF₂ improves the TSL signal stability.

Key-words: X-ray, dosimeter, Scintillation, AlN, Thermally Stimulated Luminescence, Optically Stimulated Luminescence.

1. Introduction

Ionizing radiation detectors are currently widely applied in many fields; for example, physics, medicine and geology. Those radiation detectors often use solid states luminescent materials, which are known as scintillators and dosimeters. A scintillators absorbs an incident ionizing radiation and immediately converts the energy into thousands of low energy photons such as UV/Vis/NIR light via energy migration from the host to emission centers (Yanagida et al., 2013). On the other hand, a dosimeter material absorbs and accumulates the incident radiation energy as a form of trapped carriers. These carriers can be de-trapped by an optical or thermal stimulation, which is followed by a light emission. These emissions are often referred as an optically-stimulated luminescence (OSL) (McKeever, 1985) and thermally-stimulated luminescence (TSL) (Yukihara et al., 2011), respectively. Some examples of practical TSL dosimeter materials are Mg- and Ti-doped LiF (Mayhugh et al., 1970), and carbon-doped aluminum oxide ($\text{Al}_2\text{O}_3\text{:C}$) is a particularly well-known OSL dosimeter (McKeever, 2011).

AlN has a highly covalent-bonded wurtzite crystal structure and wide bandgap ($E_g = 6.2 \text{ eV}$). One of the practical applications of AlN is a heat sink due to its high thermal conductivity ($320 \text{ W m}^{-1}\text{K}^{-1}$) with high electrical insulation properties. Also, AlN is an attractive semiconductor material to be used for UV-LED (Taniyasu et al., 2006). Furthermore, in the previous work, we have shown that an AlN ceramic plate, which is a commercial product as a heat sink, is applicable for TSL and OSL dosimeter applications (Yanagida et al., 2013a; Okada et al., 2015). For dosimeter applications, the detector materials are preferably those with the effective atomic number (Z_{eff}) equivalent to human tissue ($Z_{\text{eff}} \sim 7.4$). Tissue equivalent dosimeter material interact with radiations as in actual tissue, so any post-irradiation corrections (often done mathematically) are required. In this point of view, AlN is an attractive material as the Z_{eff} of AlN is 11.7 and very close to the Z_{eff} of Al_2O_3 (11.3) which is one of the most widely used tissue-equivalent dosimeter materials. For those reasons, AlN is of our particular interest as a potential dosimeter material. In addition, earlier studies have shown that doping of CaF_2 to AlN improves some properties such as the densification process (Xiong et al., 2013), thermal conductivity (Qiao et al., 2003; He et al., 2010) and optical transmittance (Xiong et al., 2005; Xiong et al., 2006). Strontium and calcium

are members of the alkaline earth metals, and they share similar physiologic and chemical properties (Chi, 1979)

In this study, we prepared undoped AlN and SrF₂-doped AlN by the Spark Plasma Sintering (SPS) (Tokita, 1999) and studied the effects on the optical and dosimeter properties of AlN in relation with an addition of SrF₂.

2. Experimental procedure

The undoped and SrF₂ doped AlN ceramics were synthesized by SPS. The doping concentrations of SrF₂ were 1, 2 and 5 wt.%. In this paper, the SrF₂-doped AlN samples are denoted as AlN-SrF₂. The starting raw materials of AlN and SrF₂ were supplied by Tokuyama Corp. These compounds were mixed homogeneously, and the mixture of 0.5 g batch was loaded into a cylinder graphite die with the inner diameter of 10 mm, which was sealed by inserting two punches inside the die. This assembly was next loaded to the SPS furnace (La-BOX110, Sinter Land) to sinter at 1800 °C for 15 min under 3 kN pressure. The obtained sample size was typically 10 mmΦ × 1mmt, and the sample surfaces were polished for characterizations.

The microstructures of samples were observed by using a scanning electron microscope (SEM; Hitachi S-3400). The photoluminescence (PL) emission spectrum and PL-decay were measured by using Hamamatsu Quantaurus-τ. For both the measurements, the excitation wavelength was 280 nm, and the monitoring wavelengths of PL decay were 330, 500 and 600 nm.

The Scintillation spectra were evaluated at room temperature under X-ray irradiation by utilizing our original setup (Yanagida et al., 2013b). The irradiation source was an X-ray generator (Spellman, XRB80P & N200X4550) equipped with W target (OURSTEX Corporation) supplied with 80 kV DC voltage and 2.5 mA tube current. The emission spectra were digitized by using Andor DU-920-BU2 CCD spectrometer (cooled at 188 K by a Peltier module) equipped with a monochromator SR163 (Andor, 1200 grooves/mm and 300 nm blaze wavelength). The scintillation light was fed into the spectrometer through a 2 m optical fiber. The scintillation decay time was separately measured by our original setup, a pulsed X-ray equipped afterglow characterization system (Yanagida et al., 2014) having a timing

resolution of ~1 ns. In this measurement, all the emission wavelengths were integrated and digitized by the PMT. The spectral sensitivity of the system was from 160 to 650 nm, which covers the entire emission range of AlN.

As a dosimeter property, the TSL glow curves after X-ray irradiation ($1\text{-}10^4$ mGy) were evaluated by using TL-2000 (Nano Gray) (Yanagida et al., 2013a). The photodetector installed in the reader has a sensitivity over 300–500 nm. The heating rate was $1\text{ }^\circ\text{C/s}$. Prior to a TSL measurement, a sample was irradiated by X-rays using the same generator used for the RL measurement described above. The X-ray dose was calibrated by the ionization chamber (TN30013, PTW). The OSL was measured by using Hamamatsu Quantaurus- τ . The stimulation light source used here was a 630 nm LED. The LED equipped in this instrument is very stable which allows us to measure the OSL response with a high reproducibility. The X-ray irradiation was performed in the same manner as in the TSL measurements described above.

3. Results and discussion

Fig. 1 shows the AlN ceramic samples doped with 0, 1, 2 and 5 % of SrF_2 . The undoped sample has gray/green color without any visual evidence of optical transparency. On the other hand, AlN- SrF_2 (1, 2 and 5 %) were translucent and the strip patterns behind the samples can be clearly seen through. Interestingly, the outer edge of only AlN- SrF_2 (2 %) was blue, and the rest were gray color. Fig. 2 illustrates SEM images of selected samples: AlN and AlN- SrF_2 (5 %). The grain sizes were estimated to be several μm , and the grain size is larger when SrF_2 is added.

Fig. 1 Synthesized (a) undoped and AlN-SrF₂ ceramics samples. The concentrations of SrF₂ are (b) 1, (c) 2 and (d) 5 %.

Fig.2 SEM images of (a) undoped AlN and (b) AlN-SrF₂(5 %) ceramics synthesized by SPS.

Fig. 3 shows the optical in-line transmittance spectra of AlN-SrF₂ samples. The distortion seen around 800 nm was an instrumental artifact caused by switching of diffraction grating and lamp. The transmittance was approximately 0.2 % at wavelengths longer than 500 nm. This value is not so high compared with an earlier work (Honma et al., 2008), in which AlN ceramics have shown to be translucent with an addition of Ca₂Al₂O₆.

Fig.3 Transmittance spectra of 1-5 % AlN-SrF₂.

The PL of undoped AlN appeared around 400 nm with a very broad structure. In contrast, earlier works (Sun et al., 2001; Matoussi et al., 2010) have shown emissions around 505 and 550 nm. Interestingly enough, we did not observe the same emissions in our AlN sample. It is possible that these emissions are related to some defects and oxygen impurities which are strongly affected by the preparation method and starting materials. In our case, any oxide materials were used, and the sintering was performed under a strong vacuum environment. Instead, AlN-SrF₂ samples showed other emissions around 330, 500 and 600 nm, which were not observed in the undoped AlN sample. Therefore, we assign these emissions due to some additional defects created by doping with SrF₂.

Fig.4 PL spectra of AlN and AlN-SrF₂ ceramic samples under 280 nm excitation.

PL-decay time profiles of 405, 490 and 595 nm emission bands are displayed in Fig.5.

To quantify the decay curves, they were fitted with a sum of exponential decay functions as:

$$I = \sum_{i=1}^n A_i \exp(-t/\tau_i) \quad (1)$$

where τ_i is the decay time constant and A_i is emission intensity at $t = 0$. For PL decay, the number of decay term was selected to be 2 ($n = 2$).

The fast decay time around 1 ns is due to the instrumental response. The obtained PL-decay times are summarized in Table 1. All the samples show relatively fast lifetime of a few ns. The lifetime at 490 nm decreases with increasing the concentration of SrF₂, but the other emissions were consistent regardless of the concentration of SrF₂.

Fig.5 PL-decay time profiles of (a)AlN monitoring at 405 nm, (b) AlN-SrF₂(1-5%) monitoring at 330 nm (c) AlN-SrF₂(1-5%) monitoring at 490 nm and (d) AlN-SrF₂(1-5%) monitoring at 595 nm under 280 nm excitation.

Table 1 Summary of PL decay times measured. The excitation wavelength is 280 nm.

λ_{em} (nm)	AlN (ns)	AlN-SrF ₂ (ns)		
		1%	2%	5%
330	—	2.7	2.7	2.4
400	6.2	—	—	—
490	—	6.2	5.5	4.7
595	—	4.4	4.6	4.7

Fig. 6 shows the radioluminescence spectra of undoped and AlN-SrF₂ ceramic samples. The emission peak of the undoped AlN appeared around 380 nm with a very broad feature. By an addition of SrF₂, the emission intensity of this peak decreased by a factor of approximately 7 or larger, and the emission peak appeared around 350, 450 and 600 nm. These tendencies were similar with those in PL.

Fig.6 X-ray induced emission spectra of the samples.

The scintillation decay time profiles are shown in Fig. 7. Their curves were fitted by Equation (2) with three exponential terms ($n = 3$) to extract decay times. The obtained scintillation decay times are summarized in Table 2.

Both undoped AlN and AlN-SrF₂ (1-5%) show fast decays. As observed for the 490 nm emission in PL, the decay time decreases with increasing the SrF₂ concentration. However, due to the energy transportation process involved in the scintillation process, the scintillation decay time was slower than that of PL. It is instructive to note here that the energy transfer process is referred as, in general, migration of electrons and holes generated by interacting with radiations into luminescent centers. In PL, only luminescent centers are directly excited so the above transportation process is not involved. Therefore, scintillation decay time was slower than that of PL.

Fig.7 Scintillation decay time profiles of undoped AlN and AlN-SrF₂(1-5 %).

Table 2 Summary of scintillation decay times measured

	AlN (ns)	AlN-SrF ₂ (ns)		
		1%	2%	5%
τ_1	9.8	10.4	9.6	9.1
τ_2	130.1	100.4	95.8	65.9

Fig.8 (left) shows TSL glow curves of AlN and AlN-SrF₂(1-5%). In the previous work (Yanagida et al., 2013a), TSL glow peaks of AlN appeared around 80 and 350 °C. The peak around 350 °C could not be observed in our samples since this high temperature glow peak was due to an addition of sintering aids. By doping with SrF₂, the TSL intensity decreased by a factor of approximately 200 or larger, and the glow peak shifted to higher temperature, from ~160 to 180 °C. It indicates that a large amount of defects acting as shallow trapping centers in AlN are suppressed by doping with SrF₂; as a result, charge carriers are only captured by deeper trapping centers. However, the population of the deeper trapping centers are much less than the shallow centers, so the measured TSL signal is much smaller. Nevertheless, the increase of glow peak temperature is an indication of improvement in the TSL stability. Since it is difficult for the charge carriers captured at deeper centers to escape at low temperature, such material can hold the dose information for longer term without fading. Fig.8 (right) shows the dose response curves of TSL by undoped AlN and AlN-SrF₂(5 %). For both the samples, a linear TSL response against the X-ray dose was confirmed. The dynamic range confirmed was from 1 mGy to 10 Gy for the undoped AlN while AlN-SrF₂ did not show a measurable signal below 100 mGy.

Fig.8 TSL glow curves (left) and dose response functions (right) of AlN and AlN-SrF₂ ceramics.

The TSL glow curves were measured after an X-ray irradiation of 1 Gy.

Fig.9 (left) shows the OSL spectra of undoped AlN and AlN-SrF₂(1%). For both the samples, the emission is very broad and the spectral position is very similar. The emission peak may be slightly

shorter for AlN-SrF₂(1%) (340 nm) than undoped AlN (360 nm). For the samples with higher concentrations of SrF₂, no measurable OSL signal was observed. As seen in TSL, we think that an addition of SrF₂ suppresses the OSL signal by reducing the amount of defect centers, which capture charge carriers generated by radiations. Fig.9 (right) shows the dose response curves of OSL by the undoped AlN and AlN-SrF₂(1%) tested in the dose range 1 mGy to 10 Gy. On one hand, the undoped AlN showed a linear response over the dose range of 1 mGy to 10 Gy; on the other hand, the OSL signal of AlN-SrF₂(1%) was too small to measure below 100 mGy. However, a linear response was confirmed over 100 mGy to 10 Gy.

Fig.9 OSL emission spectra (left) and dose response functions (right) of AlN and AlN-SrF₂ ceramics. The stimulation light wavelength was 630 nm. The emission spectra were measured after an X-ray irradiation of 10 Gy.

4. Summary and Conclusions

undoped AlN and AlN-SrF₂(1, 2 and 5 %) ceramics were synthesized by SPS. Although the undoped AlN sample was visually non-transparent and the in-line transmittance was not measurable, an addition of SrF₂ improved the transmittance to 0.2 % at the wavelengths longer than 500 nm and the opposite side of sample could be seen through with eye. Under UV and X-rays, PL and scintillation emissions, respectively, of undoped AlN ceramic sample appeared around 400 nm only. In contrast, an addition of SrF₂ significantly changed the spectrum and showed PL and scintillation emission peaks around 330, 500

and 600 nm and 350, 450 and 600 nm, respectively. Also, the addition of SrF₂ decreased the PL and scintillation decay times. Although the scintillation decay time was much longer than those in PL. In TSL, an addition of SrF₂ increased the glow peak temperature (from ~160 °C to ~180 °C), in other words a stability of TSL signal, at a cost of sensitivity. An OSL emission was observed in the undoped and AlN-SrF₂(1%) around 460 and 430 nm by stimulation at 630 nm. For those with a larger amount SrF₂ added (2 and 5 %), no measurable signal was observed. Despite the reduced sensitivity at lower doses, a linear response was confirmed up to 10 Gy. For the future work, we will continue to optimize the AlN ceramics as a dosimeter with better sensitivity and stability.

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