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## Electroluminescence of Oxygen Deficient $\text{YAIO}_3$ Crystals

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### 1. Introduction

Much attention has been directed to perovskite-type transition-metal oxides due to the unique opto-electronic, electronic and magnetic properties reflecting the strongly correlated nature of the electrons in the oxides. The perovskite-type oxides  $\text{YAIO}_3$  and  $\text{LaAlO}_3$  have large oscillator strength of the charge-transfer excitation reflecting the large overlap integral between the transition metal 3d-orbital and the oxygen 2p-orbital [1]. Kawabe, Yamanaka and Hanamura reported that the oxygen deficient  $\text{YAIO}_3$  and  $\text{LaAlO}_3$  single crystals prepared in a reducing atmosphere show strong photoluminescence (PL) originating from the excited state formed at oxygen defect sites [2,3]. The doping of ions of different valence stabilizes the oxygen vacancies and results in the significant increase of the PL intensity of the oxides [2,3]. The strong PL and large mobilities of photo-excited carriers in these oxides make us expect to observe electroluminescence (EL). There is a growing needs for novel inorganic EL materials and devices [4-6], because the usage of EL as a non-thermal light emission process has expanded in the areas such as display and lighting applications, and inorganic EL generally has superior thermal stability than organic EL. We have preliminarily reported on the EL of doped  $\text{YAIO}_3$  crystal films [7]. Here we report mainly on the EL of Ti-doped  $\text{YAIO}_3$  crystal films and Ca-doped  $\text{YAIO}_3$  crystal films. EL property of  $\text{YAIO}_3$  crystal films with other dopant will also be presented at the Conference.

### 2. Experimental

Films of oxygen deficient  $\text{YAIO}_3$  crystals with dopants such as Ti and Ca were prepared from single crystals grown by the floating-zone (FZ) method in a reducing atmosphere. The rod-shaped single crystals were grown in the FZ furnace heated by using either a Xe lamp or a halogen lamp [2,3]. High purity powders of oxides such as  $\alpha\text{-Al}_2\text{O}_3$ ,  $\text{Y}_2\text{O}_3$ ,  $\text{TiO}_2$  and  $\text{CaO}$  were used as the starting materials. The concentration of the dopants in the obtained crystals ranged from 0.1 to 3%. The films of 0.1-0.25 mm thick were prepared by cutting the crystals perpendicular to the direction of growth, followed by polishing. The Au and Al electrodes were deposited on the front and rear surfaces of the crystal films by DC sputtering and vacuum evaporation, respectively. For generating EL from the crystal films, a bipolar high voltage power supply (Kepco

BOP-1000M) and a waveform generator (Agilent Technologies 33220A) were used to apply high voltage with several waveforms such as a bipolar symmetrical drive form, a square form, a triangular form and a sinusoidal form. The applied electric field intensity and the drive frequency were in the range  $\pm 10^6$ - $10^7$  V/m and 0.2 Hz-1 kHz.

EL spectra of the crystal films were measured in the visible wavelength range at room temperature using a Otsuka Electronics MCPD-7000 spectro-multichannel photodetector with a quartz optical fiber.

### 3. Results and Discussion

Visible EL was observed in the oxygen deficient  $\text{YAIO}_3$  crystal films except 3% Ti-doped  $\text{YAIO}_3$  film in which the application of voltages higher than  $\pm 10^5$  V/m was difficult due to the relatively high electrical conductivity of the film. The 0.1% and 1% Ti-doped  $\text{YAIO}_3$  films and the 0.1% Ca-doped  $\text{YAIO}_3$  film showed visible EL at electric field intensities greater than  $\pm 0.7 \times 10^6$ ,  $\pm 0.7 \times 10^6$  and  $\pm 1 \times 10^6$  V/m, respectively. The EL intensity of these three crystal films was strongest in the drive frequencies around 10 Hz, however, the emission was not very stable.

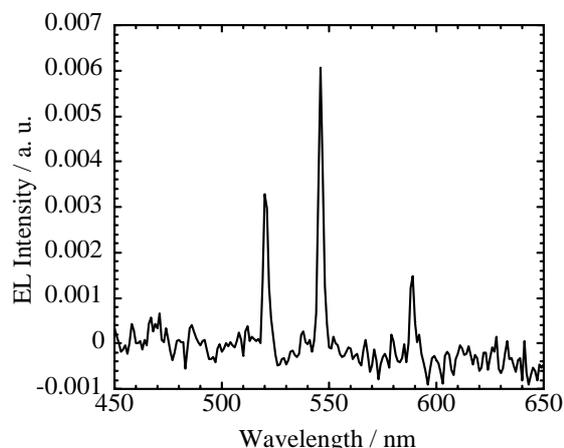


Fig. 1 EL spectra for the 0.1% Ti-doped  $\text{YAIO}_3$  film at an electric field of  $\pm 6.6 \times 10^6$  V/m and a drive frequency of 1 Hz.

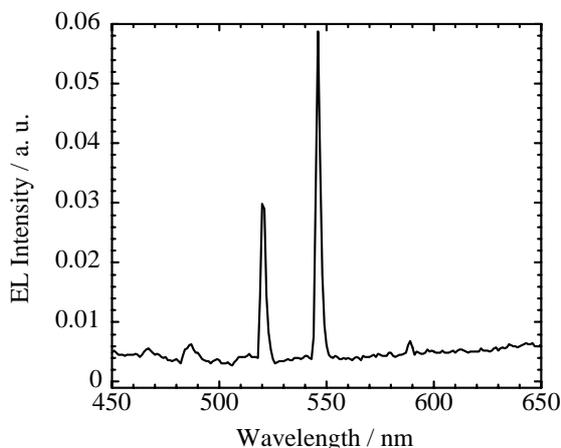


Fig. 2 EL spectra for the 1% Ti-doped  $\text{YAlO}_3$  film at an electric field of  $\pm 1.5 \times 10^6$  V/m and a drive frequency of 10 Hz.

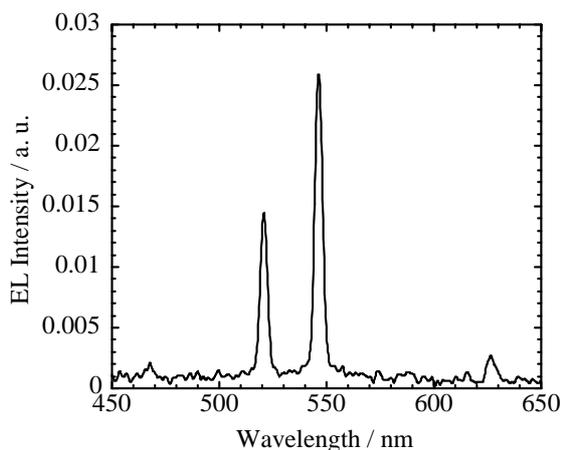


Fig. 3 EL spectra for the 0.1% Ca-doped  $\text{YAlO}_3$  film at an electric field of  $\pm 3.9 \times 10^6$  V/m and a drive frequency of 10 Hz.

At drive frequencies around 10 Hz, the color of the EL of the three films was green, indicating that the EL color observed under the above condition was almost independent of the dopant species and concentration. The green EL was observed when the waveforms of the applied electric field were square waves with and without a relaxation period. In contrast, the use of sinusoidal and triangular waveforms did not result in EL emission, showing that a rapid change of electric field is necessary for generating EL emission in these oxides. The use of a symmetrical waveform with a relaxation period during which no voltage was applied was better than a simple square waveform without such a relaxation period for generating clearly ob-

servable EL, suggesting that the relaxation period for equilibrating the charge distribution is effective for enhancing the EL.

Figures 1 and 2 show typical EL spectra for the 0.1% Ti-doped  $\text{YAlO}_3$  and 1% Ti-doped  $\text{YAlO}_3$  films, respectively, measured at drive frequencies of 1 and 10 Hz. In both cases, the strongest emission line centered at 546 nm and the second strongest line at 521 nm appeared. In addition to these two strong emission lines, weak emissions of other colors were also present. These EL wavelengths were shorter than the PL peak wavelength (600 nm) of the 0.1% and 1% Ti-doped  $\text{YAlO}_3$  single crystals. The FWHM of the EL emission lines were 3-5 nm and were much narrower than the FWHM of the PL, suggesting that the EL of the oxygen deficient  $\text{YAlO}_3$  crystals has potential for use as a new type of monochromatic light source. The 0.1% Ca-doped  $\text{YAlO}_3$  crystal film also showed strong emission lines at 546 and 521 nm at drive frequencies around 10 Hz (Fig. 3). Since yttrium does not have emission lines at 546 and 521 nm [8,9], the above results strongly suggest that the EL emission would not mainly come from the dopant ions, but rather from the luminescent centers formed at the oxygen defect sites in  $\text{YAlO}_3$ . The mechanism of the EL is still unclear. A possible process is that the electrons in these oxide crystals are accelerated by the high electric field and excite the luminescent oxygen vacancy centers on impact, followed by radiative transitions of the excited electrons back to the ground state.

## References

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