

# Growth and characterization of high-quality Mn-doped LiAlO<sub>2</sub> single crystal

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The growth of a Mn-doped LiAlO<sub>2</sub> single crystal by the Czochralski (CZ) method and the characterization of its spectroscopy and thermoluminescence (TL) are presented. The X-ray rocking curve and chemical etching analysis show that the as-grown crystal has good crystallinity. The full-width at half-maximum (FWHM) of the LiAlO<sub>2</sub> (200)  $\omega$  rocking curve is 23.2 arcsec and the etching pits density of the (100) plane is  $(1.6\text{--}4.0) \times 10^4 \text{ cm}^{-2}$ . The transmission spectrum indicates that the crystal is highly transparent in the 200–1500-nm wavelength range. The emission spectrum of the crystal consists of a peak around 579 nm when excited with 428-nm light. The TL spectra show that the LiAlO<sub>2</sub>:Mn crystal has glow peaks at 150 and 172 °C. The change of TL characteristics of the crystal before and after thermal annealing in the air is discussed, and the effect of annealing and irradiation on the evolution of defect types is analyzed.

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In recent years,  $\gamma$ -LiAlO<sub>2</sub> (LAO) single crystal as a substrate material has attracted a lot of attention for growing non-polar GaN or ZnO layers<sup>[1–4]</sup>. LAO is also a suitable host lattice for investigating the optical characteristics of doping ions, given that all ions in the structure are tetrahedrally coordinated, and only one type of vacancy exists in the crystal which can avoid the overlap of absorption and emission bands from different impurity centers<sup>[5]</sup>. The luminescence properties of LAO powder doped with transition metal (Mn<sup>2+</sup> and Fe<sup>3+</sup>) and rare-earth ions (Ce<sup>3+</sup>, Eu<sup>3+</sup>, and Tb<sup>3+</sup>) have been studied for applications in phosphor, thermoluminescence (TL) dosimetry, and so on<sup>[6–8]</sup>. However, spectroscopic studies on ions doped in LAO crystals are very few<sup>[9,10]</sup>, which is likely due to difficulty in crystal growth. In addition, as compared with phosphor powder, bulk crystal materials as used for TL or optically stimulated luminescence (OSL) dosimetry have some advantages such as higher sensitivity to radiation, higher repeatability, and lower background noise. Moreover, LAO could be enriched with <sup>6</sup>Li isotope which has a high cross-section for neutron capture<sup>[8]</sup>. The introduction of LAO crystal would extend the advantages of the neutron-sensitive TL or OSL dosimetry.

In this work, a Mn-doped LiAlO<sub>2</sub> single crystal is grown by the Czochralski (CZ) method. Crystal quality is examined by X-ray rocking curve measurement. The corrosion morphology of the (100) plane of the as-grown crystal is observed by optical microscopy and scanning electron microscopy (SEM). The spectroscopic and TL characteristics of the crystal are also investigated.

Starting materials of Li<sub>2</sub>CO<sub>3</sub> (99.999%), Al<sub>2</sub>O<sub>3</sub> (99.999%), and MnO<sub>2</sub> (99.99%) were prepared for the Mn-doped LiAlO<sub>2</sub> single crystal growth. The molar ratio of Al:Li:Mn was 1:1:0.003. The raw materials were initially mixed thoroughly, then compressed into pieces

and calcined at 1200 °C for 10 h. Afterwards, they were loaded into Ir crucible. The crystal was grown by the radio frequency (RF) heating CZ pulling method. The temperature was controlled by a precision temperature controller (Eurotherm 818, UK) with a precision of  $\pm 0.5$  °C. The melt temperature kept at  $1750 \pm 5$  °C should be favorable for starting the growth. High-purity nitrogen was adopted to protect the Ir crucible from oxidation. A ZrO<sub>2</sub> after-heater was used for preventing the crystal from cracking by decreasing the vertical temperature gradient. A ZrO<sub>2</sub> lid was added to the top of the after-heater to reduce Li-evaporation. A (100) *a*-axis LAO seed was used to dip the center of the melt surface and start the pulling progress. The pulling rate and the rotation rate were 1–3 mm/h and 15–30 rpm, respectively. After the growth process, the crystal was cooled down to room temperature (RT) for a few days. The segregation of Mn in LiAlO<sub>2</sub> was measured by inductively coupled plasma (ICP, IRIS Intrepid), and the sample was selected from the start point of the as-grown crystal. The (100) wafers were cut from the boule and chemo-mechanically polished. The thickness of all polished wafers was 1 mm.

The as-grown crystal was analyzed by high-resolution X-ray diffraction (HRXRD, Philips X'Pert-MRD, Netherlands) using Cu *K* $\alpha$ 1 ( $\lambda=0.154056$  nm) radiation. The optical system of HRXRD was equipped with a Ge (220) four-crystal monochromator, and the angular resolution ratio was 0.0001°. The X-ray tube was operated at 30 kV and 15 mA. The (100) wafers of the crystal were immersed into HCl (30%) solution at 80 °C for 10 min, and the dislocation etching pits were observed under optical microscope (Leitz) and SEM (JSM-6360LA JEOL, Japan). The transmission spectrum of the crystal was measured at RT by an ultraviolet/visible/near-infrared (UV/Vis/NIR) spec-

trophotometer (V-750, JASCO, Japan). Excitation and emission spectra were measured by employing a fluorescence spectrometer (FP-6500/6600, JASCO, Japan). TL spectra were recorded immediately after the  $\text{LiAlO}_2\text{:Mn}$  crystal samples had been irradiated under X-ray ( $\text{Cu } K\alpha$ ) for 20 s, and the measurement was performed in the air from RT to 350 °C at a heating rate of 1 °C/s using a thermally stimulated spectrometer (FJ427-Al, Beijing Nuclear Instrument Factory).

Figure 1 shows the photograph of the as-grown  $\text{LiAlO}_2\text{:Mn}$  crystal. The crystal is transparent and colorless, but the left part looks darker in color than the right ones, because the left part has an obvious crack parallel to the  $a$ - $c$  plane, which is related to the stress in this part from the voltage fluctuation in the growth process. This is also reflected in the variation in the diameter of the body. The crystal is free of any visible bubbles and inclusions. A green laser was used to evaluate the crystal's quality. The laser beam scattering caused by voids and inclusions is even slighter than that in the pure LAO single crystals, in which these defects are usually difficult to eliminate thoroughly. It is probable that a small amount of  $\text{Li}_2\text{O}$  evaporation during the growth makes it easy for the dopant ions to enter into the Li sites in the host lattice. Also, the substitution of Mn for Li could compensate for the loss of O, so the formation of  $\text{LiAl}_5\text{O}_8$  was reduced, which was identified as the phase of inclusions<sup>[11]</sup>. The segregation coefficient of Mn in the crystal is 0.11 based on the Mn concentration of 0.034 at.-% at the growth starting position and 0.3 at.-% in the melt, which is the reason for the limited incorporation of Mn in the LAO host being similar to that of the  $\text{YAlO}_3\text{:Mn}$  crystal<sup>[12]</sup>. The phase of the as-grown crystal is the LAO phase identified by X-ray diffraction (XRD). The X-ray rocking curve of the (100) wafer was measured to assess the crystalline quality of the as-grown crystal. The full-width at half-maximum (FWHM) of the LAO (200)  $\omega$  rocking curve was 23.2 arcsec, indicating the good crystalline formation of the material. Dislocation sites on the surface of the polished wafer were revealed by chemical etching. Figure 2(a) shows the optical microscopic image of an etched (100) wafer of the crystal. As expected, the etching pits are rhomboidal shaped and align along the same direction, the same as those of pure LAO crystals. The linear arrangement of these etching pits is attributed to the subgrain boundaries by dislocations<sup>[13]</sup>. The overall etching pit density is about  $(1.6\text{--}4)\times 10^4 \text{ cm}^{-2}$ . Figure 2(b) shows the detailed morphology of etching pits analyzed by SEM. The elongated side of the etching pits is along the [010] direction, and the shape of these etching pits reveals the structural



Fig. 1.  $\text{LiAlO}_2\text{:Mn}$  single crystal grown by the CZ pulling method.

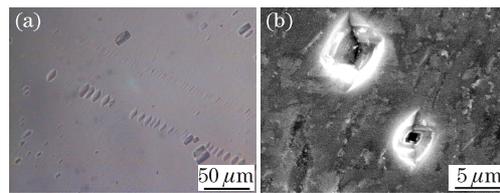


Fig. 2. (a) Optical microscopic and (b) SEM images of the etched (100) wafer of the as-grown crystal.

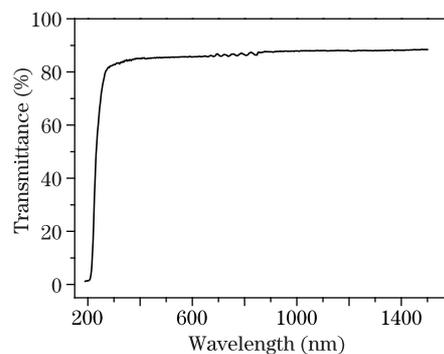


Fig. 3. UV/Vis/NIR transmission spectrum of the  $\text{LiAlO}_2\text{:Mn}$  single crystal.

symmetry of this plane.

The UV/Vis/NIR (190–1500 nm) transmission spectrum of the  $\text{LiAlO}_2\text{:Mn}$  (100) wafer is shown in Fig. 3. It is obvious that the crystal has a high optical transmission in the whole recorded wavelength range, whose transmittance is above 85 % in the wavelength range of 400–1500 nm, and decreases to 60% with the wavelength reducing from 400 to 238 nm. The absorption edge of the crystal is estimated to be about 200 nm, and the optical band-gap is about 6.2 eV. In Fig. 3, no special absorption band about Mn ions is observed, probably because of the very low intensity of the parity- and spin-forbidden character of this transition at a low dopant concentration<sup>[14]</sup>. The colorlessness of the crystal is consistent with the absence of absorption bands in the Vis spectrum.

Figure 4 shows the RT excitation (curve (a)) and emission (curve (b)) spectra of the  $\text{LiAlO}_2\text{:Mn}$  single crystal. An intensive tail-like band in the range of 220–250 nm is observed in the excitation spectrum of  $\lambda_{\text{em}} = 579 \text{ nm}$ , which is attributed to the  $\text{Mn}^{2+}\text{--O}^{2-}$  charge transfer transition<sup>[15]</sup>. The excitation spectrum also consists of a broad band ranging from 350 to 490 nm including peaks at 360, 385, 412, 428, and 450 nm, which can be attributed to the d-d transition of  $\text{Mn}^{2+}(3d^5)$  configuration from the multiplets  ${}^4E$  (D),  ${}^4T_2$  (D),  ${}^4A_1$  (G),  ${}^4E$  (G), and  ${}^4T_2$  (G) respectively to the ground state  ${}^6A_1$  (S) of the  $\text{Mn}^{2+}$  ions in tetrahedral coordination<sup>[16]</sup>. As compared with the  $\text{LiAlO}_2\text{:Mn}$  phosphor powder<sup>[7]</sup>, the excitation peaks of the crystal are relative difficult to discriminate, probably because of its more integrated crystal field and the strong interaction between the open 3d electron shell of Mn and crystal lattice vibration, which causes the very broad bands of spin-allowed transitions<sup>[5]</sup>. This is why transition ions are considered to be the activator ions in generating tunable lasers. In the emission spectrum a wide emission band peaked at 579 nm is observed. According to Ref. [7], tetrahedrally

coordinated  $Mn^{2+}$  ions will emit green luminescence corresponding to the transition of  $Mn^{2+}$  ions from  ${}^4T_1$  to  ${}^6A_1$ . However, in our case, the  $Mn^{2+}$  ions emitted a yellow-green luminescence. Considering ionic radius ( $r_{Mn^{2+}} = 0.08 \text{ nm}^{[17]}$ ,  $r_{Li^+} = 0.068 \text{ nm}$ , and  $r_{Al^{3+}} = 0.057 \text{ nm}^{[18]}$ ), it is unlikely for  $Mn^{2+}$  ions to substitute  $Al^{3+}$  ions in LAO crystal. The incorporation of  $Mn^{2+}$  ions on Li sites requires Li vacancies for charge compensation, which leads to the distortion of the tetrahedral crystal field of Li sites and thus a bathochromic shift of luminescence band caused by the increased crystal field<sup>[19]</sup>. Even so, it cannot be disregarded that the  $Mn^{3+}$  ions can substitute the  $Li^+$  ions with a higher coordination number. The emission of the  $Mn^{3+}$  ions contains several bands in a very wide spectral range (500–1100 nm) and also includes allowed transitions at about 600–700 nm<sup>[20]</sup>, in which it is difficult to discriminate the luminescence between  $Mn^{2+}$  and  $Mn^{3+}$ .

Figure 5 shows the TL curves of the two samples after X-ray irradiation under the same conditions. Both samples (a) and (b) were taken from the as-grown crystal, while for sample (b), we adopted 900 °C annealing temperature in the air for 30 min before irradiation. Both samples show a glow peak at 150 °C accompanied by the peak at 172 °C. Two weak TL peaks at 255 and 315 °C also appear in curve (b), while in curve (a), these are not obvious. In addition, the peak intensity of sample (b) is nearly one order of magnitude higher than that of sample (a). Generally,  $Li_2O$  volatilizes from LAO crystal above 900 °C<sup>[11]</sup>, and a large amount of  $Li^+$  and  $O^{2-}$  ion vacancies are left in the host

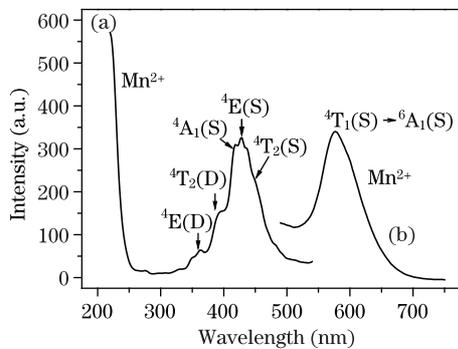


Fig. 4. (a) Excitation ( $\lambda_{em} = 579 \text{ nm}$ ) and (b) emission ( $\lambda_{ex} = 428 \text{ nm}$ ) spectra of the  $LiAlO_2:Mn$  single crystal.

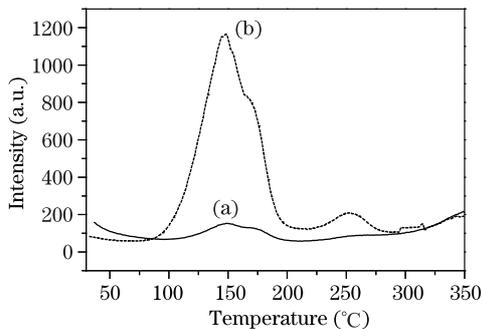


Fig. 5. TL spectra of the  $LiAlO_2:Mn$  single crystal. (a) Sample without thermal annealing before irradiation, (b) sample with 900 °C annealing temperature in the air for 30 min before irradiation.

lattice; some  $O^{2-}$  ion vacancies can capture free electrons and become  $F^+$  centers. Dhabekar *et al.* demonstrated the TL peaks around 150 and 320 °C of  $LiAlO_2:Mn$  powder and attributed TL luminescence to the  ${}^4T_1$  to  ${}^6A_1$  transition of  $Mn^{2+}$ <sup>[7]</sup>. The increase in peak intensity of sample (b) is probably due to the increased electron traps, such as  $F^+$  centers and  $O^{2-}$  ion vacancies, which provide more opportunities for the recombination of electrons and holes at  $Mn^{2+}$  centers when thermally stimulated. On the other hand,  $Li^+$  ion vacancies increased after the annealing because of Li-evaporation, and V-type centers formed by holes trapping should be the defect centers corresponding to the peak around 172 °C. It is also possible for  $F^+$  centers to be formed through  $O^{2-}$  ion vacancies capturing the excited electrons of the irradiated crystal host.  $F^+$  centers usually have a deeper trap level than V-type centers, and they release electrons at a relatively high temperature. Dhabekar *et al.* also proved the center decay of  $F^+$  in the 225–325 °C range<sup>[7]</sup>. This may be the same with our case in which the TL peak at 255 °C becomes obvious for the annealed sample after X-ray irradiation.

In conclusion,  $LiAlO_2:Mn$  single crystal has been grown by the CZ pulling method. The as-grown crystal has high quality, with the FWHM of the X-ray rocking curve at 23.2 arcsec. The etching pits density of the (100) plane is  $(1.6\text{--}4.0)\times 10^4 \text{ cm}^{-2}$  throughout the crystal boule. The optical transmission spectrum from UV to IR exhibits that the crystal is transparent from 200 to 1500 nm. A wide emission band peaked at 579 nm is observed when excited with 428-nm light for the incorporation of  $Mn^{2+}$  ions on the Li sites in the crystal. TL spectra show that the crystal has glow peaks at 150, 172, 255, and 315 °C, and two types of defect centers are tentatively identified to the V-type centers and  $F^+$  centers respectively in the annealed  $LiAlO_2:Mn$  crystal after irradiation. A systematic study on the growth of  $LiAlO_2:Mn$  and its spectra features is currently in progress.

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