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Light-induced coloration and transformation process in $YAlO_3$ crystal

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ABSTRACT

The nature of point defects in $YAlO_3$ (YAP) which brings great influence on the crystal properties has not been fully established. The UV-irradiated crystal exhibits broad additional absorption bands in the range of 200–800 nm while the additional absorption bands 200–800 nm can be reduced, with a re-irradiation of a 457 nm green laser. The light-induced coloration and transformation mechanism is studied and it is found that the increase or decrease of both UV and visible absorption bands are related to the creation and annihilation of anion vacancies (V_O^{2+} and F^+) and cation vacancies (V_{Al}^{3-} and V_Y^{3-}). It is proposed that the creation and annihilation of V_O^{2+}, F^+, V_{Al}^{3-} and V_Y^{3-} may be caused by the separation and recombination of the vacancy clusters [V_O^{2+}–V_{Al}^{3-}–F^+] and [V_O^{2+}–V_Y^{3-}–F^+], which play important roles in the formation and transformation process of light-induced color centers in YAP crystal.

1. Introduction

The optical properties of ionic crystals are affected by the presence of point defects. These defects may act as carrier traps and suppress the emission of light [1]. Because of that, the development of many oxide crystals into efficient scintillators has been hindered [2]. YAP crystals have good optical, thermal and mechanical properties similar to YAG crystals. YAP single crystals doped with rare-earth and transition metal ions are prospective materials for laser engineering, scintillators, holographic recording, data storage and substrate materials for thin films of high-temperature superconductors [3–5]. Point defects created during crystal growth or under different external stimulus (irradiation, thermal treatment, etc.) bring great influence on the properties of YAP crystals. Recently, point defects were considered as the origin of nonradiative transitions and carrier traps [6,7], which are a limiting factor for the performance of YAP crystal as excellent host material for laser, scintillation and data-recording applications [8–11]. So it is imperative to analyze in detail the color centers (CCs) related to point defects, which under the action of low-energy (optical pumping) or high-energy (scintillation processes) quanta on the crystal, forming additional channels of excitation energy dissipation.

The nature of CCs in YAP has not been fully established though many color models were proposed [7,12–16]. The photo-chromic effect was also not given satisfied explanation. In this paper, the light irradiation induced CCs creation and transformation were investigated deeply by measuring the spectra of as-grown YAP, the UV-irradiated YAP, the difference spectra of UV-irradiated and 457 nm laser re-irradiated YAP crystal. The difference absorption spectrum, defined as the spectrum of the crystal after irradiation subtracted by the spectrum of the crystal before irradiation, is employed to see the sensitivity of the absorption features to the light irradiation. Based on the results mentioned above, new CCs model was proposed that the defect clusters [V_O^{2+}–V_{Al}^{3-}–F^+] and [V_O^{2+}–V_Y^{3-}–F^+] may play an important role in the color forming and transforming processes.

2. Experiment

The pure YAP samples were grown from Y_2O_3 and Al_2O_3 raw material powders with purity 5 N by the traditional Czochralski technique with radio-frequency induction heating. The growth process was carried out in an iridium crucible of 110 mm in diameter at the pulling rate of 1.4 mm/h and a rotation rate of 18 rpm in pure Ar atmosphere. Good quality single crystal of Ø 50 mm × 120 mm was grown using pure YAP seed oriented along ⟨0 0 1⟩ crystallographic direction in *Pnma* setting. The picture of as-grown pure YAP crystal just taken out from Czochralski furnace is shown in Fig. 1. The samples for absorption measurements were cut from the same part of the YAP crystal ingot in dimension of 10 mm × 10 mm × 1 mm, with the 10 mm × 10 mm polished surface perpendicular to the *c* axis of the crystal. The UV-irradiations were performed by a sample exposed to an Hg lamp (8 W) for 10 min, 20 min, 40 min, and 10 h, respectively. The sample irradiated by a UV light for 10 h is subsequently re-

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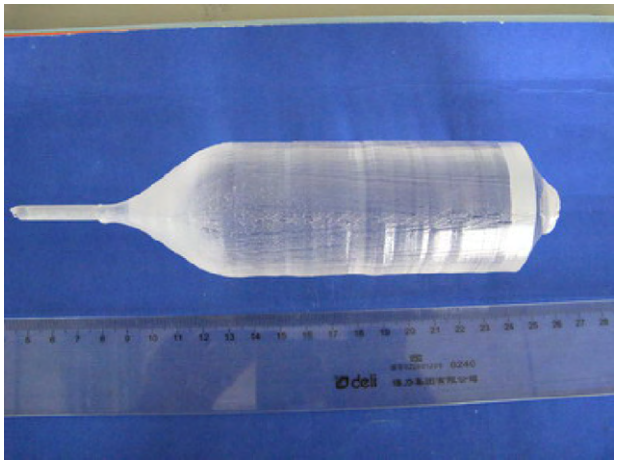

Fig. 1. The picture of pure YAP crystal with size of Ø 50 mm × 120 mm.

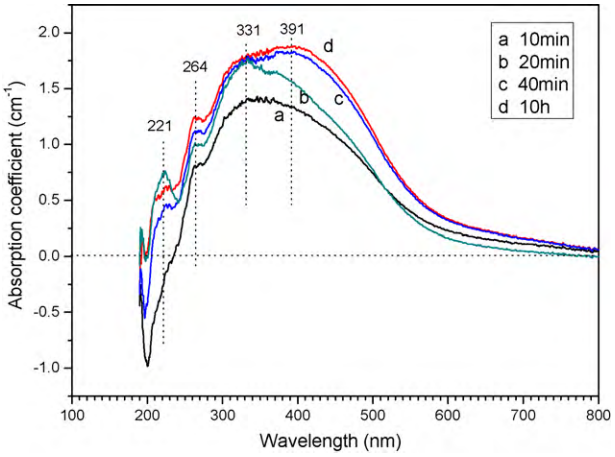

Fig. 3. The DA spectra of YAP with different UV-irradiation time intervals. (a) 10 min, (b) 20 min, (c) 40 min, and (d) 10 h.

irradiated by a 457 nm laser (200 mW) within variant time intervals of 1 min, 4 min, 16 min, and 64 min. The Jasco V-570 UV/VIS/NIR spectrophotometer with an accuracy of 0.002 abs is aligned to measure the optical absorption spectra from 190 nm to 800 nm. The YAP crystal is colorless when it was just taken out from the Czochralski furnace and it turned salmon pink in air gradually and the color will be deeper and turn into brown after longer time UV-irradiation.

3. Results and discussion

Fig. 2 shows the absorption spectra of a different UV-irradiated YAP sample. The optical absorption of the as-grown YAP sample is shown by curve (a). There is obvious absorption in the range 200–380 nm. These absorption bands are labeled as the absorption of intrinsic defects and unintentional impurities [17–19]. Curves (b)–(e) are corresponding to the variant UV-irradiation time intervals of 10 min, 20 min, 40 min and 10 h. It can be seen that all these UV-irradiations increase the absorption bands from 200 nm to 800 nm. Fig. 3 shows the DA spectra of YAP after different UV-irradiation. Curves (a)–(d) are corresponding to the DA spectra of different UV-irradiation time intervals of 10 min, 20 min, 40 min and 10 h, respectively. It can be seen that all the DA spectra increase from 200 nm to 800 nm after UV-irradiations. However, the effect is significant at the beginning of the irradiation, and it tends to saturate after longer time irradiation.

The sample after UV-irradiation for 10 h is then subsequently re-irradiated by a 457 nm laser within variant periods of 1 min, 4 min, 16 min, and 64 min. The corresponding difference spectra are shown in Fig. 4. In this case, the re-irradiation causes a decreasing of the 200–800 nm bands, which implies that the 457 nm laser re-irradiation acts as a reverse process of the UV-irradiation.

As a rule, the CCs existing in unactivated crystals of complex oxides owe their origin to point defects of the matrix and appear in the region of localization of cationic vacancy (V_C) and anionic vacancy [20]. So V_C (V_{Al}^{3-} and V_Y^{3-}) and anionic vacancy (V_O^{2+}, F^+ and F center) are the most possible intrinsic defects existed in pure YAP. Zorenko et al. studied the absorption and luminescence of V_O^{2+} related defects F^+ and F centers in YAP at 9 K and 295 K under synchrotron radiation and suggested that the absorption bands peaking at 191 nm, 220 nm and 288 nm are caused by the F^+ center while the absorption bands peaking at 167 nm, 212 nm and 241 nm are caused by F center [17]. We simulated the F center in YAP crystal using a first-principles method and found that isolated F center is responsible for the new appeared absorption bands appeared in the region 200–300 nm [18]. The kinds of V_C (V_{Al}^{3-} and V_Y^{3-}) in YAP were also simulated and it is found that V_C is responsible for the additional absorption bands in the visible region [21]. Based on the facts above, it can be concluded that the absorption bands of point defects including V_O^{2+}, F and F^+ in pure YAP crystal overlap in the range of 200–300 nm. That is to say, the coloration of YAP after UV-irradiation has nothing to do with

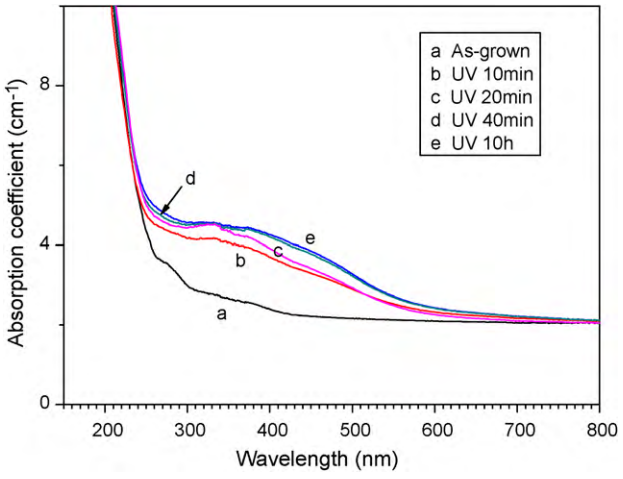

Fig. 2. The UV-irradiated induced absorption spectra of YAP within different time intervals. (a) As-grown, (b) 10 min, (c) 20 min, (d) 40 min, and (e) 10 h.

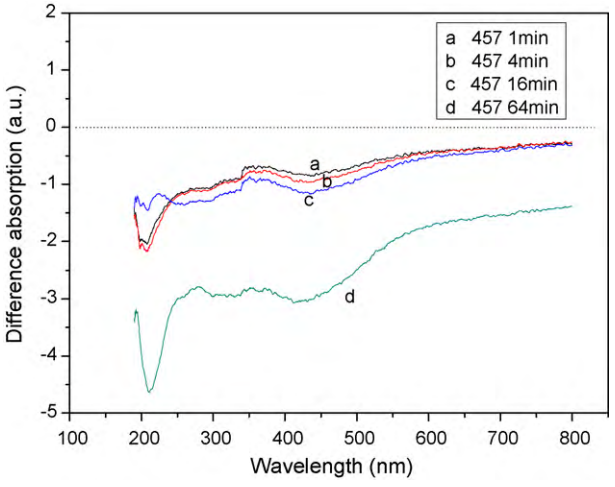

Fig. 4. The 457 nm laser re-irradiated difference spectra of YAP with different time respectively: (a) 1 min, (b) 4 min, (c) 16 min, and (d) 64 min.