Journal of Alloys and Compounds 506 (2010) 500–503

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

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

Jianyu Chen [a,b], Guangjun Zhao [a,*], Qin Dong [a,b], Yuchong Ding [a,b]

[a] Key Laboratory of Materials for High Power Laser, Shanghai Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, Shanghai 201800, PR China
[b] Graduate School of Chinese Academy of Sciences, Beijing 100039, PR China

ARTICLE INFO

Article history:
Received 10 May 2010
Received in revised form 7 July 2010
Accepted 7 July 2010
Available online 15 July 2010

PACS:
76.30.Mi
78.30.Hv
78.40.−q

Keywords:
$YAlO_3$ crystal
Irradiation
Green laser
Color center

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-

---

* Corresponding author.
E-mail addresses: zhaoguangjun@163.com, giep2008@163.com (G. Zhao).

0925-8388/$ – see front matter
doi:10.1016/j.jallcom.2010.07.063

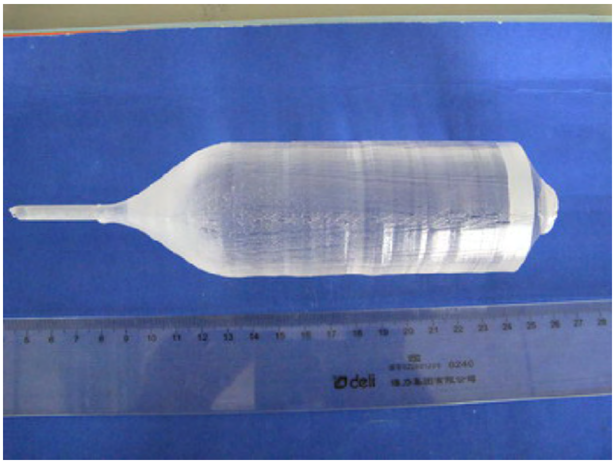

Fig. 1. The picture of pure YAP crystal with size of Ø 50 mm × 120 mm.

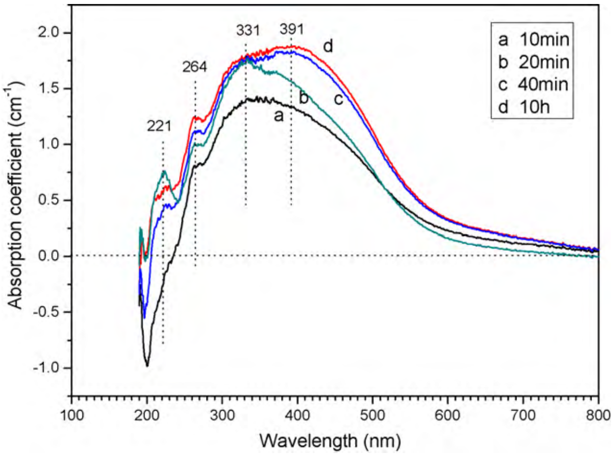

Fig. 3. The DA spectra of YAP with different UV-irradiation time intervals. (a) 10 min, (b) 20 min, (c) 40 min, and (d) 10 h.

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

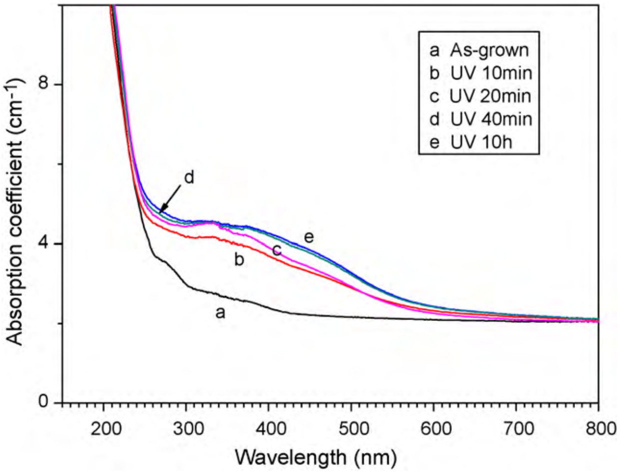

Fig. 2. The UV-irradiated induced absorption spectra of YAP within different time intervals. (a) As-grown, (b) 10 min, (c) 20 min, (d) 40 min, and (e) 10 h.

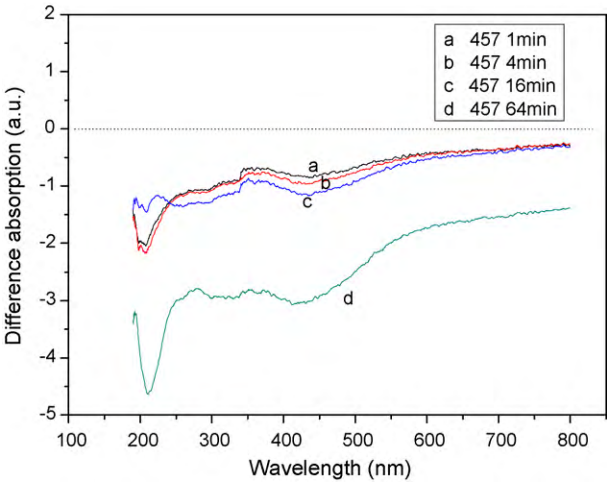

Fig. 4. The 457 nm laser re-irradiated difference spectra of YAP with different time respectively: (a) 1 min, (b) 4 min, (c) 16 min, and (d) 64 min.

the isolated point defects related to oxygen vacancy and the additional absorption bands in the visible range are caused by V_C. Since the 380–780 nm bands are negligible in the as-grown pure YAP, the amount of isolated V_C in as-grown pure YAP crystal could be neglected.

The problem is in what forms of V_{Al}^{3-}, V_Y^{3-}, V_O^{2+}, F^+ and F may exist in YAP crystal. The negative V_C, positive V_O^{2+} and F^+ are very inclined to form electrical neutral vacancy clusters with no optical absorption. In a perfect crystal, it requires the potential minimum. This means that it should satisfy the local electric neutrality and no large defect aggregate everywhere. Based on the results above, it can be concluded that the vacancy clusters should be $[V_O^{2+}–V_{Al}^{3-}–F^+]$ and $[V_O^{2+}–V_Y^{3-}–F^+]$ rather than larger vacancy clusters $[2V_{Al}^{3-}–3V_O^{2+}]$ and $[2V_Y^{3-}–3V_O^{2+}]$ or $[V_{Al}^{3-}–3F^+]$ and $[V_Y^{3-}–3F^+]$.

The Coulomb interaction among charge carriers depends on the electricity of the charge carriers. The $[V_O^{2+}–V_{Al}^{3-}–F^+]$ and $[V_O^{2+}–V_Y^{3-}–F^+]$ in the as-grown YAP are stable because of the strong attraction among the three different charged ions deficiencies. However, once the crystal sample are irradiated by UV light, the neighbor ions nearest to the $[V_O^{2+}–V_{Al}^{3-}–F^+]$ and $[V_O^{2+}–V_Y^{3-}–F^+]$ are excited to produce hot electrons and holes, the hot electrons and holes may be trapped by V_{Al}^{3-}, V_Y^{3-}, V_O^{2+} and F^+ in certain forms, respectively, which reduce the interaction between vacancy clusters and thus cause $[V_O^{2+}–V_{Al}^{3-}–F^+]$ and $[V_O^{2+}–V_Y^{3-}–F^+]$ to separate into isolated V_O^{2+}, F^+ and V_{Al}^{3-}, V_Y^{3-} easily. It has well established that oxygen vacancy related defects and O^{2-} ions are movable in oxide crystals [22–24]. The V_O^{2+} and F^+ centers separated from $[V_O^{2+}–V_{Al}^{3-}–F^+]$ and $[V_O^{2+}–V_Y^{3-}–F^+]$ may hop in the crystal, leaving isolated V_{Al}^{3-}, V_Y^{3-} at the original site, and tends to be distributed evenly in the crystal. The isolated V_O^{2+}, F^+ centers and V_{Al}^{3-}, V_Y^{3-} trap electrons and holes, respectively, and hence result in the formation of new color centers. The whole defect chemistry processes under UV-irradiation may be expressed as

$$[V_O^{2+}–V_{Al}^{3-}–F^+] + 3[e + h] = [V_O^{2+} + 2e] + [V_{Al}^{3-} + 3h] + [F^+ + e], \tag{1}$$

$$[V_O^{2+}–V_Y^{3-}–F^+] + 3[e + h] = [V_O^{2+} + 2e] + [V_Y^{3-} + 3h] + [F^+ + e], \tag{2}$$

$$[V_O^{2+}–V_{Al}^{3-}–F^+] + 2[e + h] = [V_O^{2+} + e]^+ + [V_{Al}^{3-} + 2h]^- + [F^+ + e], \tag{3}$$

$$[V_O^{2+}–V_Y^{3-}–F^+] + 2[e + h] = [V_O^{2+} + e]^+ + [V_Y^{3-} + 2h]^- + [F^+ + e]. \tag{4}$$

This is to say, high photon irradiation may result into the formation of the electrical neutral defect pair $[V_{Al}^{3-} + 3h]$, $[V_Y^{3-} + 3h]$ and F centers or electrical univalent $[V_{Al}^{3-} + 2h]^-$, $[V_Y^{3-} + 2h]^-$ and F^+ centers. In the former case [Eqs. (1) and (2)], the V_O^{2+} can escape easily from the defect clusters. If the result is the latter [Eqs. (3) and (4)], the interattraction between $[V_O^{2+} + e]^+$ and $[V_{Al}^{3-} + 2h]^-$ or $[V_O^{2+} + e]^+$ and $[V_{Al}^{3-} + 2h]^-$ is weak, and thus these vacancies may change the form from tightly bound to weakly bond, or further they can even separate from each other.

The color of YAP sample turned to brown after long time UV-irradiation, while the monochromatic 457 nm light re-irradiations reduce the coloration of the sample, as shown in Fig. 4, which implies that the 457 nm laser re-irradiation acts as a reverse process of the UV-irradiation. The experimental results also indicate that the 457 nm re-irradiations reduce the amount of V_C which are responsible to the additional absorption bands in visible region, leading to the recombination of the defect clusters $[V_O^{2+}–V_{Al}^{3-}–F^+]$ and $[V_O^{2+}–V_Y^{3-}–F^+]$ again. The possible process is as follows: Electrons and holes in $[V_O^{2+} + 2e]$, $[F^+ + e]$, $[V_{Al}^{3-} + 3h]$ and $[V_Y^{3-} + 3h]$ are ionized by the 457 nm laser. Once the moveable isolated V_O^{2+} and F^+ center is close to V_{Al}^{3-} and V_Y^{3-}, it recombines the V_{Al}^{3-} and V_Y^{3-} and thus form defect clusters $[V_O^{2+}–V_{Al}^{3-}–F^+]$ and $[V_O^{2+}–V_Y^{3-}–F^+]$. This results in the decrease of the visible absorption bands as shown in Fig. 4. However, the 200–800 nm absorption bands cannot completely be quenched, which means that $[V_O^{2+} + 2e]$, $[F^+ + e]$, $[V_{Al}^{3-} + 3h]$ and $[V_Y^{3-} + 3h]$ cannot be fully excited to recombine the defect clusters $[V_O^{2+}–V_{Al}^{3-}–F^+]$ and $[V_O^{2+}–V_Y^{3-}–F^+]$.

The defect model proposed above can explain the light-induced coloration and transformation phenomena in YAP crystal well. However, the model proposed is based on the absorption measurements of those crystals irradiated by UV light and 457 nm lasers and certain literature models, which is not supported by direct proof of proposed structure of defects. So the real defect structures in YAP crystal need more advanced experimental methods to confirm.

4. Conclusion

Pure YAP single crystal with large dimensions of Ø 50 mm × 120 mm was grown by Czochralski method. New defect structures based on experimental results and certain literatures are proposed and the possible pictures of light-induced coloration and transformation mechanism in YAP crystal are as follows: (1) in the as-grown YAP crystal, isolated oxygen defects are the main defects corresponding to the absorption bands in the range of 200–300 nm, while the forms of V_C (V_{Al}^{3-} and V_Y^{3-}) which cause the absorption in visible region may be mainly in vacancy clusters $[V_O^{2+}–V_{Al}^{3-}–F^+]$ and $[V_O^{2+}–V_Y^{3-}–F^+]$. (2) UV-irradiation break the $[V_O^{2+}–V_{Al}^{3-}–F^+]$ and $[V_O^{2+}–V_Y^{3-}–F^+]$ and increase the absorption in the range of 200–800 nm by creation of isolated defects V_O^{2+}, F^+, F, V_{Al}^{3-} and V_Y^{3-}. (3) The absorption spectra of YAP crystal re-irradiated by the 457 nm monochromic light exhibit a decrease of the 200–800 nm bands, which is caused by the recombination of the defect clusters $[V_O^{2+}–V_{Al}^{3-}–F^+]$ and $[V_O^{2+}–V_Y^{3-}–F^+]$.

Acknowledgment

This work has been supported by Acknowledge Innovation Program of Chinese Academy of Science.

References

[1] F.A. Selim, D. Solodovnikov, M.H. Weber, K.G. Lynn, Appl. Phys. Lett. 91 (2007) 104105.
[2] M. Nikl, V.V. Laguta, A. Vedda, Phys. Status Solidi (b) 245 (2008) 1701.
[3] C.K. Duan, P.A. Tanner, V.N. Makhov, M. Kirm, Phys. Rev. B 75 (2007) 195130.
[4] S. Baccaro, K. Blazek, F. de Notaristefani, P. Maly, J.A. Marser, R. Pani, R. Pellegrini, A. Soluri, Nucl. Instrum. Methods Phys. Res. A 361 (1995) 209.
[5] G.B. Loutts, M. Warren, L. Taylor, R.R. Rakhimov, H.R. Ries, G. Miller, M.A. Noginov, M. Curley, N. Noginova, N. Kukhtarev, H.J. Caulfield, P. Venkateswarlu, Phys. Rev. B 57 (1998) 3706.
[6] P. Rodnyi, Physical Processes in Inorganic Scintillaltors, CRC, Baca Raton, FL, 1997.
[7] D.J. Singh, Phys. Rev. B 76 (2007) 214115.
[8] W. Drozdowski, D. Wisiewski, A.J. Wojtowicz, A. Lempicki, P. Derenbos, J.T.M. de Haas, C.W.E. van Eijk, A.J.J. Bos, J. Lumin. 72–74 (1997) 756.
[9] A. Vedda, M. Martini, F. Meinardi, J. Chval, M. Dusek, J.A. Mares, E. Mihokova, M. Nikl, Phys. Rev. B 61 (2000) 8081.
[10] A.J. Wojtowicz, P. Szupryszczynski, D. Wisniewski, J. Glodo, W. Drozdowski, J. Phys.: Condens. Matter 13 (2001) 9599.
[11] M. Nikl, J.A. Mares, J. Chval, E. Mihokova, N. Solovieva, M. Martini, A. Vedda, K. Blazek, P. Maly, K. Nejezchleb, P. Fabeni, G.P. Pazzi, V. Babin, K. Kalder, A.

Krasnikov, S. Zazubovich, C. D'Ambrosio, Nucl. Instrum. Methods Phys. Res. A 486 (2002) 250.
[12] M.J. Weber, M. Bass, K. Andringa, R.R. Monchamp, E. Comperchio, Appl. Phys. Lett. 15 (1969) 342.
[13] O.F. Schirmer, K.W. Blazey, W. Berlinger, R. Diehl, Phys. Rev. B 11 (1975) 4201.
[14] T. Li, G.J. Zhao, X.M. He, J. Xu, S.K. Pan, J. Synth. Cryst. 31 (2002) 456.
[15] J. Kvapil, B. Perner, B. Manek, K. Blazek, Z. Hendrich, Cryst. Res. Technol. 20 (1985) 473.
[16] D. Sugak, A. Matkovskii, D. Savitskii, A. Durygin, A. Suchocki, Y. Zhydachevskii, I. Solskii, I. Stefaniuk, F. Wallrafen, Phys. Status Solidi (a) 184 (2001) 239.
[17] Yu.V. Zorenko, A.S. Voloshinovskii, I.V. Konstankevych, Opt. Spectrosc. 96 (2004) 532.
[18] J.Y. Chen, G.J. Zhao, D.H. Cao, H.J. Li, S.M. Zhou, Comput. Mater. Sci. 46 (2009) 225.
[19] A. Matkovski, A. Durygin, A. Suchocki, D. Sugak, G. Neuroth, F. Wallrafen, V. Grabovski, I. Solski, Opt. Mater. 12 (1999) 75.
[20] P. Dorenbos, M.V. Korzhik, A.P. Kudryavtseva, S.V. Lyubetskii, B.I. Minkov, V.B. Pavlenko, A.A. Fyodorov, J. Appl. Spectrosc. 59 (1993) 633.
[21] J.Y. Chen, G.J. Zhao, D.H. Cao, S.M. Zhou, Curr. Appl. Phys. 10 (2010) 468.
[22] W. Van Loo, J. Solid State Chem. 14 (1975) 359.
[23] J.A. Groenink, H. Binsma, J. Solid State Chem. 29 (1979) 227.
[24] J.Y. Chen, et al., Physica B 40 (2009) 3405.