A New Absorption Band of Ti-Doped Al_2O_3 Crystals after Thermal Annealing and γ-Irradiation

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Z. Naturforsch. **61a,** 564 – 568 (2006); received June 2, 2006

Al_2O_3 single crystals doped with titanium ions were grown by the Czochralski method in a pure N_2 atmosphere. The titanium ion content reached up to 0.08 – 0.1 wt%. After thermal annealing and γ-irradiation, the optical absorption spectra were measured at room temperature for samples of high optical quality. Many previously reported absorption spectra of Al_2O_3:Ti^{3+} have a distinct double-peak shape in the visible region. However, the absorption spectra in this work present three peaks at 480 nm, 500 nm, and 550 nm. The triple-peak shape absorption bands in the visible region are reported for the first time. The reason for forming a triple-peak in the absorption spectra is discussed. – PACS numbers: 78.40.Ha, 78.30.Hv, 71.70.Ch

Key words: Ti^{3+}:Al_2O_3; Crystal Growth; Optical Absorption Spectrum.

1. Introduction

The Ti^{3+}:Al_2O_3 laser is one of the most successful solid state lasers and the first to use Ti^{3+} as active ion. The broad, intense fluorescence emission band of Al_2O_3:Ti^{3+} provides a wider tuning range and higher gain cross section than other transition metal ion tunable lasers. Researches of this material have attracted considerable attention for a long time [1 – 13].

The optical absorption spectra of titanium-doped Al_2O_3 crystals were first studied by McClure [14]. Tippins [15] studied the charge-transfer spectra, Nelson et al. [16] and Joyce and Richards [17] investigated the far-infrared spectra, Gather and Koningstein [18] measured the zero phonon lines of Al_2O_3:Ti^{3+} crystal. According to the previously reported spectroscopic investigations of this material, the optical absorption spectrum consists of a double-structured absorption band with overlapping peaks at 490 and 550 nm and a weak infrared absorption band around 800 nm.

In our work, several single crystals of high optical quality, grown by the Czochralski method, were selected for absorption measurements. The absorption spectra between 200 and 900 nm all exhibited triple-peak bands in the visible region. This phenomenon has not been reported before.

2. Crystal Growth

Al_2O_3 and Ti_2O_3 with 5N purity were used as starting material. Several crystals of 0.08 – 0.1 wt% Ti-doped Al_2O_3 were grown from iridium crucibles using the Czochralski method in N_2 atmosphere. When the process of crystal growth finished, the crystals were annealed in H_2 atmosphere at 1900 °C for 48 h. After the thermal annealing, the crystals, oriented in the [001] plane, were cut into disc-shaped samples with a diameter of 10 mm and a thickness of 2 mm, and the discs were on both sides polished for the spectroscopic measurements. Then the samples were irradiated by gamma photons up to 10^6 rad at room temperature.

Thermal annealing and γ-irradiation were applied with the aim of changing the valency of titanium ions (e. g. increasing the amount of Ti^{3+} ions).

3. The Measurement of the Optical Absorption Spectrum

The optical absorption spectra were obtained at room temperature in the spectral range 200 – 900 nm, using a SHIMADZU UV-2100 spectrophotometer.

Figure 1 shows the absorption spectrum measured at room temperature. Clear bands are seen in the visible region with extremes at 480 nm (20833 cm^{-1}), 500 nm (20000 cm^{-1}), and 550 nm (18182 cm^{-1}). They are as-

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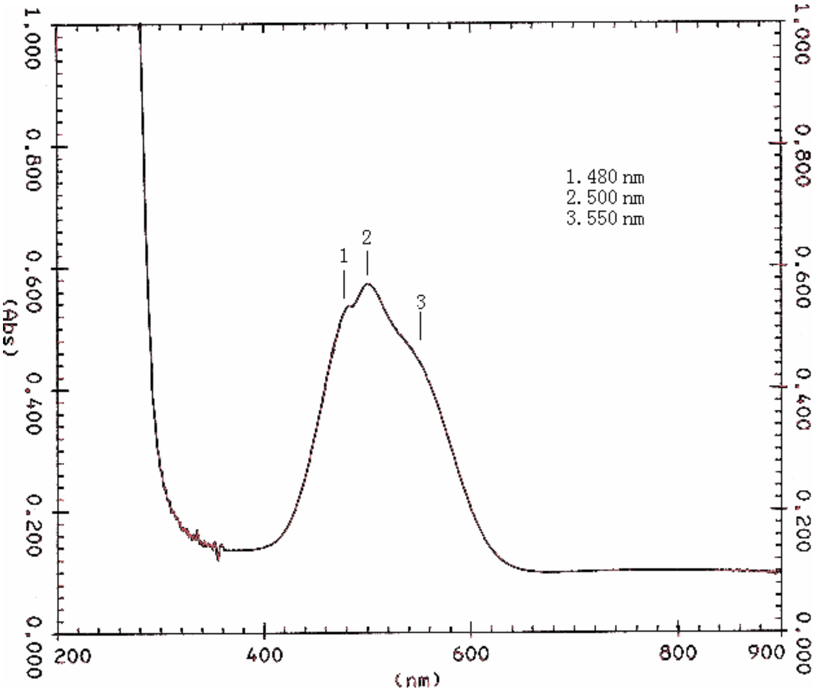

Fig. 1. The absorption spectrum of Ti-doped Al_2O_3 at room temperature after thermal annealing and γ-irradiation treatments.

sociated with impurities introduced to the crystal during its growth. The shoulder to shorter wavelengths at 480 nm has not been reported before. The infrared absorption band is not clearly seen.

4. Thermal Annealing and γ-Irradiation

Ti-doped sapphire is a well known solid state laser material in the red to near infrared spectral range (700 – 1100 nm). Achieving efficient operation of cw or flashlamp-pumped Ti : sapphire lasers and obtaining high output energy from such lasers requires the use of highly doped crystals of good optical quality. An ideal Al_2O_3:Ti^{3+} laser crystal requires a uniform distribution of titanium in its trivalent state. However, a high Ti ion concentration in the sapphire matrix brings about the serious problem of a considerable increase of the parasitic infrared absorption (near 800 nm) in the laser emission band. It raises the lasing threshold and significantly diminishes the overall laser efficiency. For Ti-doped Al_2O_3, Ti^{4+} ions are responsible for the parasitic infrared absorption [7, 13]. For this reason, the titanium-doped crystals must be grown in mildly reducing or neutral atmospheres to prevent oxidation to the Ti^{4+} state. In our experiments, crystals were prepared in a nitrogen atmosphere to prevent oxidation of Ti^{3+} to Ti^{4+}. All the same, we could not absolutely prevent all the Ti^{4+} ions from entering the crystal lattice during the crystal growth process. In practice, we could decrease this unwanted infrared absorption by a thermal annealing process or by γ-irradiation (two effective methods to decrease the concentration of Ti^{4+} ions in Al_2O_3 crystals [3, 13, 19]).

In our spectroscopic measurements, no such parasitic infrared band is present in the absorption spectra. This indicates that after the thermal annealing and γ-irradiation changes in the valency of titanium ions take place and the concentration of Ti^{4+} is greatly decreased.

5. The Energy Level Splittings of Al_2O_3:Ti^{3+}

Over the past decades, numerous spectroscopic studies have been undertaken to determine the origin of the optical absorption bands in Ti-doped Al_2O_3 crystals. Most of the observed bands have been unequivocally assigned.

For Al_2O_3 crystals doped with Ti ions, the impurity ion is substituting directly an Al^{3+} ion. The Al^{3+} lattice symmetry is trigonal, but the six O^{2-} ions adjacent to an Al site lie at the corners of a not too badly distorted octahedron (see Fig. 2), thus the crystalline field seen by an ion substituted for Al can be viewed

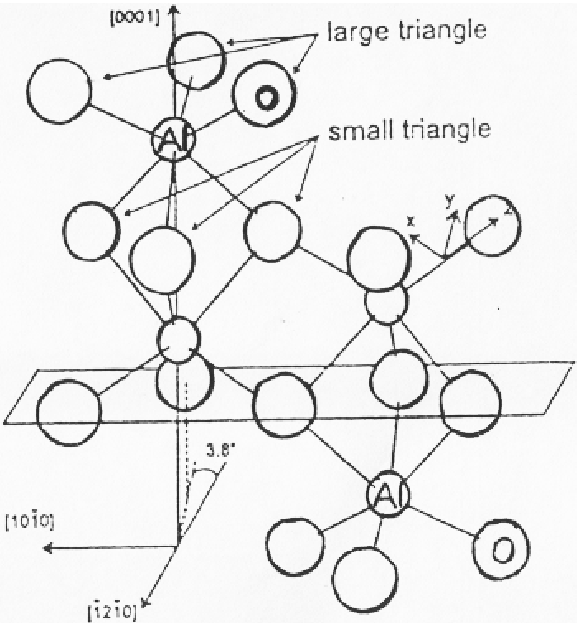

Fig. 2. The local structure of Al_2O_3 crystal.

as a large cubic field with a small trigonal distortion [1, 13, 16, 17].

Since the Ti^{3+} ion has the $3d^1$ electron configuration outside a closed shell, the free-ion level is the 10-fold degenerate ^{2}D. According to the crystal-field theory [20 – 22], the cubic field alone splits the 10-fold degenerate ^{2}D level into a four-fold degenerate ^2E_g state and a six-fold degenerate $^2T_{2g}$ state. The separated energy between ^2E_g and $^2T_{2g}$ is $10Dq$. Addition of the trigonal field does not further split the ^2E_g, but it does split the $^2T_{2g}$ into a doubly degenerate $^2A_1(^2T_{2g})$ and a four-fold degenerate $^2E(^2T_{2g})$, the $^2E(^2T_{2g})$ level being the lower one. In addition, the lower $^2E(^2T_{2g})$ level is split by spin-orbit coupling (labeled δ_1), and the upper $^2E(^2E_g)$ level is split by the Jahn-Teller effect (labeled δ_3) [14]. Thus, the original 10-fold degenerate level of the free ion splits into five doubly degenerate Kramers levels. These Kramers doublets can be split only by the application of a magnetic field. Figure 3 shows the energy-level scheme for Ti^{3+} in Al_2O_3 crystal.

The optical absorption spectra are associated with impurities introduced to the crystal during the growth process, and the values of the relevant energy level splittings can be obtained by optical spectra. The consequences of the strong static Jahn-Teller effect in the $^2E(^2E_g)$ excited state are the two overlapping absorption bands in the visible region (so called double-peak band). McClure [14] measured the peak splitting to be 1850 cm^{-1} at 77 K. The excited state energy $10Dq \approx 19000$ cm^{-1} is also estimated from the average of experimentally determined peak energies of the double-peak absorption band.

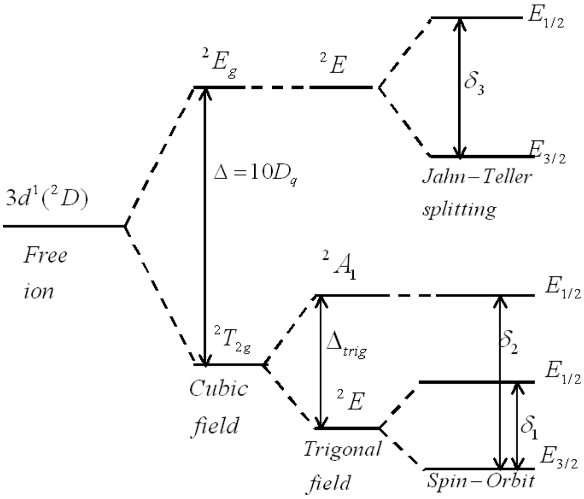

Fig. 3. Energy-level diagram of Al_2O_3:Ti^{3+} including crystal-field, spin-orbit coupling and the Jahn-Teller effect. According to [14, 16 – 18], $10Dq \approx 19000$ cm^{-1}, $\delta_1 = 37.8$ cm^{-1}, $\delta_2 = 107.5$ cm^{-1}, and $\delta_3 = 1850$ cm^{-1}.

The measured values of δ_1 and δ_2 are 37.8 and 107.5 cm^{-1}, respectively, as determined by infrared absorption spectroscopy [16, 17] and zero phonon lines measurement [18]. The level spacings of δ_1 and δ_2 are much smaller than predicted by the crystal-field theory. Macfarlane [23] pointed out that for the splittings of the $^2E(^2T_{2g})$ ground state, the dynamic Jahn-Teller effect plays an important role. After considering the dynamic Jahn-Teller effect, he calculated the values of δ_1 and δ_2, and his theoretical calculations agree satisfactorily with these experimental data.

6. Discussion

In our work, three overlapping broad bands in the visible region are observed, peaking at 480, 500, and 550 nm. The bands at 500 and 550 nm agree well with the previous reports [1, 14] and correspond to transitions from the ground $^2T_{2g}$ state to the excited $^2E(^2E_g)$ state split by a static Jahn-Teller effect. The band at 480 nm has not been reported before.

Our experiments adopted two treatments (thermal annealing and γ-irradiation) to decrease the concentration of Ti^{4+} ions and to reduce the unwanted parasitic IR absorption. However, the γ-irradiation may also cause a change of valency from Ti^{3+} to Ti^{2+} and a change of local structures of impurity centers, thus decrease the symmetry of crystal-field surrounding the impurity ions.

Morrison [24] investigated the crystal-field parameters of Ti^{3+} and Ti^{2+} ions doped in YAG crystals and pointed out that the crystal-field parameters of B_{44} and B_{40} of Ti^{2+}:YAG are approximately two times larger than those of Ti^{3+}:YAG. Meanwhile, the expectation values $\langle r^k \rangle$ of Ti^{2+} ions are about 1.7 times larger than those of Ti^{3+} ions [25]. Therefore, we could reasonably assume that the cubic field parameter Dq of Al_2O_3:Ti^{2+} is also much larger than that of Ti^{3+} ions doped in Al_2O_3. For the case of Ti^{3+}-doped Al_2O_3 crystal, $Dq = 1900\ \text{cm}^{-1}$ [14]. In our approximate calculation, we take $Dq \approx 2850\ \text{cm}^{-1}$ for Al_2O_3:Ti^{2+} which is about 1.5 times larger than the value of the Ti^{3+} ions. Because the spectral intensity of spin-allowed transitions is much stronger than that of spin-forbidden transitions, we only considered the transitions among the spin-triplet states. The calculation shows that for the Ti^{2+}-doped Al_2O_3 crystal, the spin-allowed transition from the ground state $^3T_1(F)$ to the lowest excited state $^3T_2(F)$ is 26991 cm^{-1}. This value is much larger than the new absorption peak at 480 nm (20833 cm^{-1}) in our experiment.

This approximate calculation shows that the new absorption peak at 480 nm is not corresponding to the Ti^{2+} ions. It suggests that the prolonged γ-irradiation brings about the change of local structures of the impurity centers and the lower symmetry of the crystal-field further leads to the appearance of new energy level transitions of impurities.

7. Conclusion

In this work, a number of Al_2O_3 single crystals doped with titanium ions was obtained by the Czochralski method. In order to increase the concentration of Ti^{3+} ions and decrease the parasitic infrared absorption, the as grown crystals were annealed at 1900 ℃ and underwent the γ-irradiation treatment. The absorption spectra measurements on those crystal samples were presented. Besides the previously reported bands at 500 nm and 550 nm, associated with Ti^{3+} substituting Al^{3+} in trigonally distorted octahedral crystal-field positions, we found a new band at 480 nm. Our approximate calculation showed that the decreasing symmetry of the crystal-field surrounding the impurities after γ-irradiation is responsible for this new band.

Acknowledgement

This research has been supported by the National Natural Science Foundation of China (Grant No. 50372053) and Chengdu Science Foundation (Grant No. 2005 – 38 – 162).

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