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Characteristics of KTP Crystals

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We have studied the influence of 3d impurity (Fe atoms), and the effects of annealing on KTP ($KTiOPO_4$) single crystals. It has been found that the iron concentration should be reduced to less than 1-3 weight ppm for use in high-power second harmonic generation, and that annealing at 800 °C causes the optical absorption edge to shift 5-10 nm toward shorter wavelengths. A high recovery capability against irradiation damage is obtained after annealing. The measured FWHM of X-ray diffraction is apparently decreased in annealed crystals. This means that lattice ordering proceeds during annealing.

1. Introduction

Recently, the KTP($KTiOPO_4$) single crystal has attracted much attention because it possesses superior qualities for use as a non-linear optical material transparent at 350-4500 nm. Many papers on the characteristics and the growth techniques for KTP single crystals have been reported 1-4). However, there are few papers on the influence of residual impurities or thermal history on the characteristics of the crystals, while the influence of iron impurity on $LiNbO_3$ has been well studied. We have studied the influence of the 3d impurity (Fe atoms) and the effects of annealing, on the KTP crystals. It has been found that the iron concentration should be reduced to less than 1-3 weight ppm for use in high-power second harmonic generation, and that annealing at 800 °C causes the optical absorption edge to shift 5-10 nm toward shorter wavelengths. The damage threshold increased and a high recovery capability was obtained after annealing. This paper reports the effects of impurities and thermal annealing on the crystal's potential for use in optical devices based on impurity concentration analysis, optical transparency measurements and X-ray analysis. These results imply that durable optical devices will require heating systems for recovery from laser damage. The annealing effects on the crystals depending on atmosphere and temperature are discussed. The differences in crystals grown by the flux technique and the hydrothermal technique are also discussed.

2. Experimental

KTP single crystals have been obtained by the flux growth technique without a seed crystal. The viable solvent used was $K_6P_4O_{13}$ referred to as the K_6 flux [1]. KTP and the phosphate fluxes were synthesized using TiO_2, KH_2PO_4, and K_2HPO_4. The solvent and solute were both made in situ by reacting TiO_2 with appropriate amounts of mono-basic and di-basic orthophosphates. These were dehydrated to form KPO_3 and $K_4P_2O_7$, respectively.

Crystalline KTP is soluble in the flux composition $2KPO_3.K_4P_2O_7$ (designated K6) in a platinum crucible of 50 mm in diameter and 50 mm in height. The growth of the KTP crystals was accomplished by slow cooling in a furnace with an appropriate temperature gradient. The cooling rate was 1.0°C/h. Utilizing these processes, single crystals as large as 1-2 cm were obtained after removing the flux by dissolving in distilled water. Some crystals were doped with iron which was directly added into the flux. The amount of dopant to the flux and KTP was 100 mg for a 100 g total charge. The KTP crystals doped with iron were obtained without any trouble. To study the influence of the impurity,iron concentrations , the output power of SHG was measured by the powder technique using a YAG laser. In order to study the annealing effects , the crystals were annealed in air at 800 °C and 200 °C. Their optical transparency was measured after mirror polishing the samples. The KTP crystals doped with iron have a tendency to generate a color center by exposing them to X rays. Their irradiation damage was studied by using an X ray with a 20 mA and 40 kV electric field using a Cu target.

3.Result and Discussion

3-1 Influence of iron impurity

To study the influence of iron impurity concentration on the characteristics of the KTP crystals, iron was doped to the crystals. Optical transmittance was measured for doped and undoped KTP crystals, as shown in Fig.1. As shown in this figure, the transmittance decreased and the absorption edge shifted toward a longer wavelength by doping iron. The amount of iron concentration in this crystal was 75 weight ppm measured by the ICP (inductively coupled plasma) technique. Irradiation damage was clearly observed in the iron -doped crystals by exposing to X-ray for 2 hours. The transmittance variation before and after the exposure to X-ray is shown in Fig 2. The transmittance decreased greatly for iron doped crystals by exposing to X-ray. This transmittance decrease may cause a reduction in the output power of the second harmonic generation. The output power was measured by the powder technique with 200 μm particle size. The input laser was 1 w in average and the pulse width was 100 psec with an 82 MHz repetition rate by using a 1064 nm wavelength YAG laser. The result is shown in Fig.3. The output power clearly decreased with increasing amount of iron concentration in the crystals . The iron concentrations less than 10 wt ppm were residual concentration. Residual iron concentration in the crystals varied widely from boule to boule. The laser irradiated crystals with iron

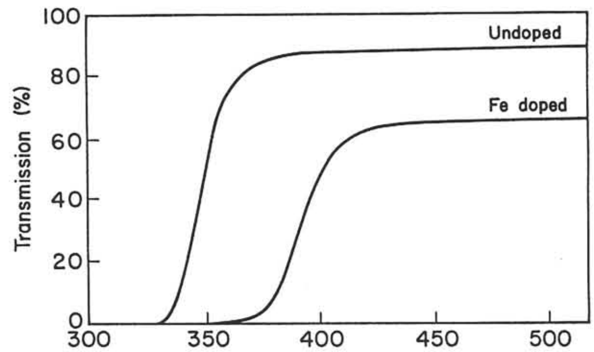


Fig.1 Optical transmittance for iron-doped and undoped KTP crystals

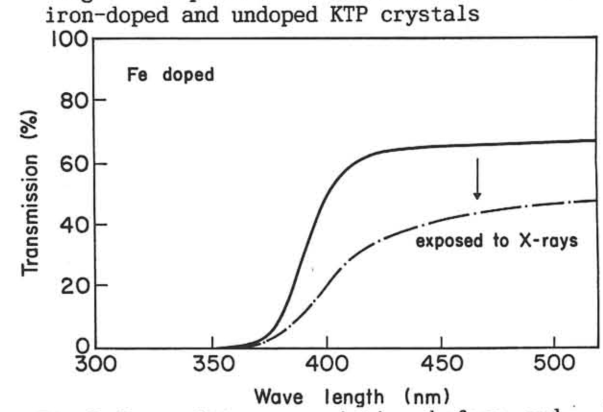


Fig.2 Transmittance variation before and after the exposure to X-ray

concentrations of more than 70 wt ppm were colored to brown. The result in Fig.3 indicates that the iron concentration should be reduced to less than 1-3 wt ppm for use in high-power second harmonic generation. This may be due to the reduction of transparency.

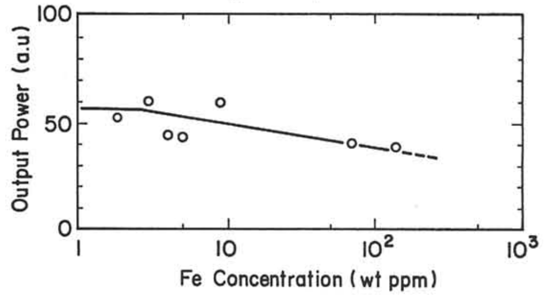
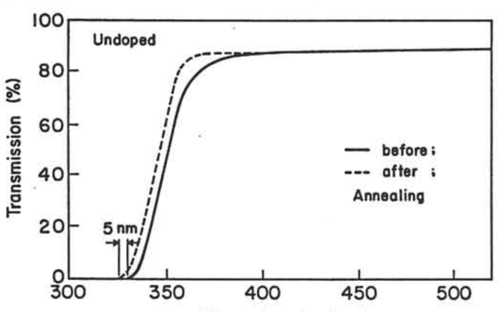


Fig.3 SHG output power as a function of iron concentration in the crystal

3-2 Effects of annealing

Annealing effects for KTP crystals have been studied for obtaining more reliable crystals. The optical absorption edge shifts towards shorter wavelengths when KTP single crystals are annealed at 800 °C for 48 hours in air, as shown in Fig.4 a). The iron doped crystals show a similar tendency, as shown in Fig.4 b). The

a)



b)

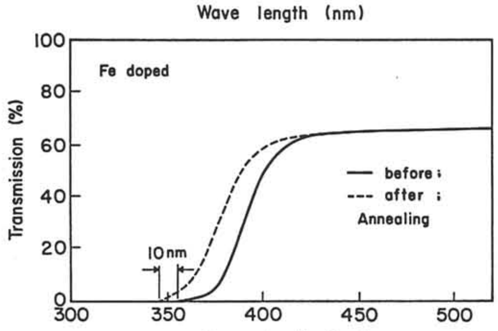


Fig.4 Optical absorption edge variation by annealing a) undoped b) iron doped

absorption edge shifts about 5-15 nm toward shorter wavelengths, which is a favorable tendency for optical use. The X-ray irradiation damage was studied for crystals before and after the annealing. The damage caused by X-rays was found to decrease when the crystals were annealed before exposure ,as shown in Fig.5. This tendency was the same for undoped crystals, but it was clearly observed for iron doped crystals. These improvements in the crystals have also been achieved by annealing at a lower temperature ,i. e. 200 °C. Transparency has a tendency to increase by annealing. The X-ray diffraction was studied for crystals before and after annealing at 800 °C. The signals for (800) reflection are shown in Fig.6 for comparing the differences. The measured FWHM apparently decreased in annealed crystals, as shown in this figure. The peak signal had a tendency to be slightly strong for annealed crystals.

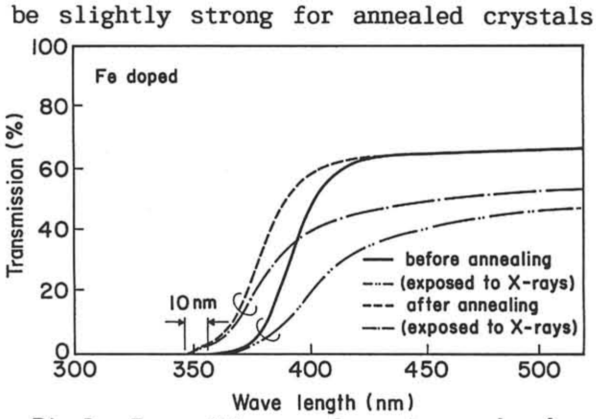


Fig.5 Transmittance for iron doped crystals before and after annealing

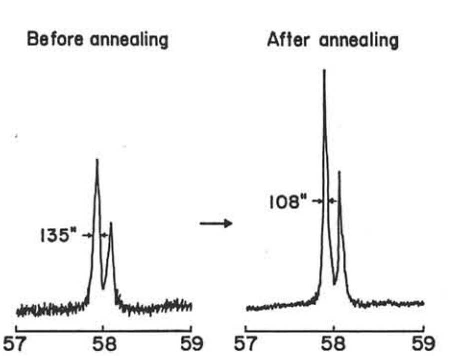


Fig.6 Variation of (800) reflection signal measured by X-ray diffraction before and after annealing

This means that lattice ordering proceeds during annealing. These obtained results imply that durable optical devices will require heating systems for recovery from irradiation damage.

3-3 Comparison between flux and hydrothermal grown crystals

The characteristics of KTP single crystals grown by the flux and hydrothermal growth techniques were compared, from the viewpoint of improving the crystal quality for optical use. Differences were seen at the onset of transmission; the onset shifts about 20 nm toward a longer wavelength for a hydrothermal material than a flux grown crystal, as shown in Fig.7. The transmittance increased steeply near the onset for the flux grown crystals, whereas optical absorption from 360 to 530 nm was observed in hydrothermal crystals. The annealing effects have been studied for the hydrothermal material. No improvement has been obtained by annealing at 200 °C and 400°C. The annealing at 800°C made the hydrothermal crystals opaque, smoky white, which is detrimental for optical use. The inner parts of the above two types of crystals are shown in Fig.8 a),b),respectively. The details of this phenomenon is now under investigation.

4. Summary

The characteristics of KTP single crystals have been studied. The iron impurity should be reduced to less than 1-3 weight ppm. Annealing in air for flux grown crystals causes the optical absorption edge to shift 5-10 nm toward shorter wavelengths. A high recovery capability against irradiation damage is obtained after annealing. Hydrothermal crystals did not show such improvement.

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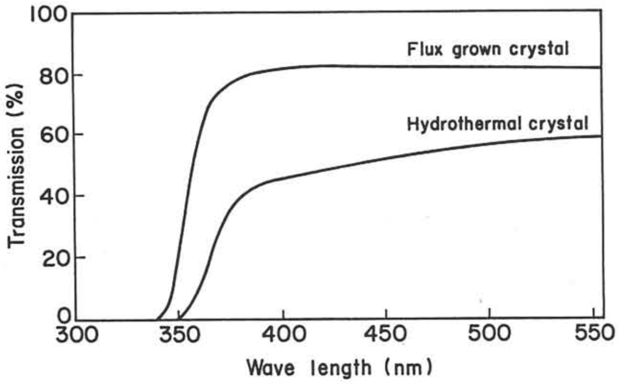
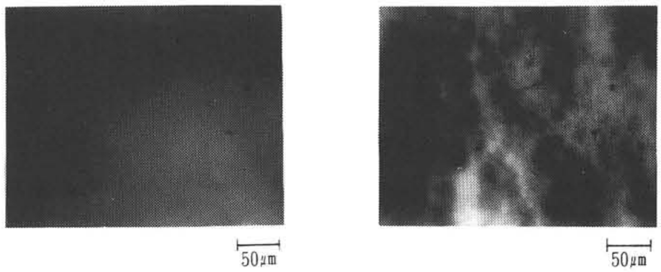


Fig.7 Optical transmittance differences between flux and hydrothermal grown crystals



a) Flux grown crystal

b) Hydrothermal crystal

Fig.8 Inner · part of crystals after annealing a)flux grown crystal b)hydrothermal grown crystal