

Growth and Properties of Co-doped Ce,Mn:LiTaO₃ Single Crystals

Bonghoon Kang[†], Bum Ku Rhee*, Ki-Soo Lim**, Sung-Ho Bae*** and Gi-Tae Joo

Electro-optic Ceramics, KIST, Seoul 136-791, Korea

**Department of Physics, Sogang University, Seoul 121-742, Korea*

***Department of Physics, Chungbuk National University, Chungchungbuk-do 361-763, Korea*

****Daejoo Fine Chemical Co. Ltd., Kyunggi-do 429-450, Korea*

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ABSTRACT

The Ce,Mn:LiTaO₃ crystals were grown by Czochralski method in congruent $\Phi 3"$ LiTaO₃ single crystal growing conditions. Concentrations of Ce and Mn in melt were respectively 0.1 and 0.01 mole%. As-grown crystals were red, transparent and the grown crystals were tested with oxidation/reduction treatment for color and other properties. Influence of Ce and Mn dopants on LiTaO₃ crystal properties was discussed. And the nonlinear optical properties of the Ce,Mn:LiTaO₃ crystal are being studied.

Key words : Ce,Mn:LiTaO₃ single crystals, Czochralski method, Absorption coefficients

1. Introduction

Lithium tantalate(LiTaO₃) crystal is one of attractive materials because of its application of Surface Acoustic Wave(SAW) filters for telecommunication systems and optoelectronic devices such as Quasi-Phase Matched(QPM) Second-Harmonic Generators(SHG). LiTaO₃ has the same crystallographic structure as lithium niobate(LiNbO₃) and a very similar electronic structure. Both crystals are piezo-, pyro- and ferro-electric, photorefractive and nonlinear with large electro-optic and nonlinear coefficients. They can be grown by the Czochralski growth to single crystals with good optical quality.¹⁾ Recently, there has been a significant renewed interest on the growth and investigation of their properties when rare earth and transition metal ions are doped.²⁻⁴⁾ Doped LiTaO₃ and LiNbO₃ crystals exhibit excellent photorefractive properties and this attractive feature makes them important for applications in optical computing, image processing, phase conjugation and laser hardening.

The effect of various dopants in crystal is different on the nonlinear optical property. In a set, two kinds of dopants have been added in crystal in order to enhance the nonlinear optical property. For example, the photorefractive effect of Ce,Fe:LiNbO₃ crystal was enhanced compared with Ce:LiNbO₃ and Fe:LiNbO₃ and the photorefractive efficiency depends on the dopant concentration, oxidation/reduction treatment and light wavelength.^{5,6)} Similarly, the saturation value of the photorefractive effect in Ce,Fe:LiTaO₃ crystal was one and a half times as large as that of Fe:LiTaO₃ at

the same light intensity.⁷⁾ For laser application, LiTaO₃ crystal has the advantage over LiNbO₃ crystal in its considerably higher threshold for photorefractive damage.

In this study, LiTaO₃ single crystals doped with Ce and Mn transition ions were grown by the Czochralski method and optical properties were investigated with poling condition and oxidation/reduction treatments. The absorption coefficients of the crystals were measured in the UV-VIS wavelength range.

2. Experimental

Co-doped Ce,Mn:LiTaO₃ crystals were grown by the Czochralski method. 0.1 mol% CeO₂ and 0.01 mol% MnO₂ were added to the congruent composition LiTaO₃ powder which was prepared from high purity raw chemicals of Li₂CO₃ (99.99%) and Ta₂O₅ (99.99%). The dopants CeO₂ and MnO₂ were GR grade. Mixing was carried out in an urethane pot with urethane balls for 2 h. After melting the mixed powder in Ir crucible of Czochralski apparatus, seeding, necking, shouldering, body growing and tailing procedure were followed to normal $\Phi 3"$ LiTaO₃ crystals growing method. The seed was 36° Y-cut LiTaO₃ crystal. The as-grown crystals are 80 mm in diameter and 80 mm in length. Nitrogen gas was flowed continuously in order to prevent the oxidation of Ir crucible. Typical technical parameters for $\Phi 3"$ LiTaO₃ crystal growth are listed in Table 1.

After annealing at 1400°C for 24 h, the crystal specimens were cut into about 5×5×1 mm³ by diamond wheel saw.

[†]Corresponding author : Bonghoon Kang

E-mail : bonfeel@kist.re.kr

Tel : +82-2-958-5516 Fax : +82-2-958-5489

Table 1. Growth Conditions for Ce,Mn:LiTaO₃ Crystals

Atmosphere	Pulling rate	Rotation	Melt volume
N ₂ +O ₂ (~1%)	2 mm/h	7~20 rpm	85% of crucible

During oxidation and reduction treatments in the tube furnace, heating and cooling rate was 100°C/h.

The crystals were poled at 650°C under the DC electric field of 5 V/cm.

Structures of Ce,Mn:LiTaO₃ crystal and congruent LiTaO₃ crystal were identified by XRD(Rigaku Geigerflex) using CuK α radiation at 30 kV and 20 mA. Dielectric constant(ϵ') and Curie temperature(T_C) of the crystals were measured by a LCR meter(Wayne Kerr, Automatic Precision Bridge B905) at 10 kHz using parallel equivalent circuit model.

The absorption spectra of the specimens in the wavelength from 300 nm to 900 nm were obtained using a UV-VIS spectrometer(Acton Research Co., SpectraPro-500i grating groove). The optical transmission was recorded with unpolarized light at normal incidence on CCD in the wavelength range of 300~900 nm. The surrounding medium was air and all the measurements were done at room temperature. The absorption coefficient α was calculated from the transmission data.

3. Results and Discussion

One of the as-grown $\Phi 3''$ Ce,Mn:LiTaO₃ crystals is shown in Fig. 1. All of the grown crystals showed good symmetry, transparent and dark-red color. And they have some cracks which were created during cooling, but the cracks counted for nothing in measuring the properties. We have good growing conditions for $\Phi 3''$ congruent LiTaO₃ crystals without cracks and $\Phi 3''$ Ce,Mn:LiTaO₃ crystals were grown on the same conditions. But all grown Ce,Mn:LiTaO₃ crystals have cracks in same way. Ce and Mn ions might give effects on crystal as bad impurities. To prevent cracks, the growing conditions may be changed, for example, to slower thermal gradient on melt.

Fig. 2 is XRD patterns for powder obtained by as-grown crystals. We cannot find any differences in XRD patterns between congruent LiTaO₃ and Ce,Mn:LiTaO₃. Ce and Mn ions did not change LiTaO₃ structure but it may be effective on the characteristic of electrical and linear/nonlinear opti-

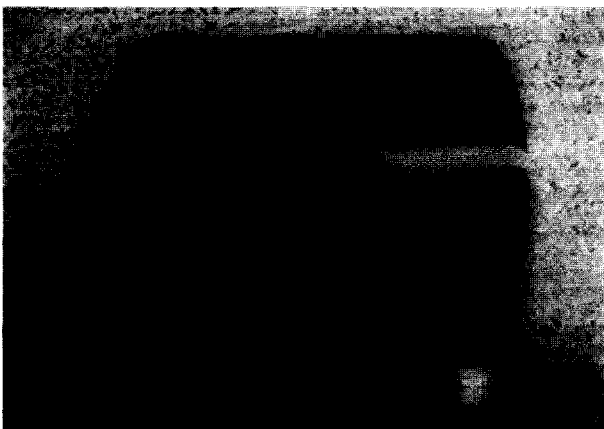


Fig. 1. Ce,Mn:LiTaO₃ crystal boule.

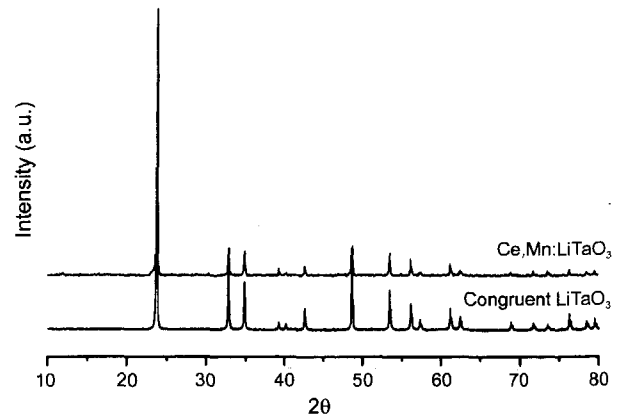


Fig. 2. Powder XRD patterns of Ce,Mn:LiTaO₃ and congruent LiTaO₃.

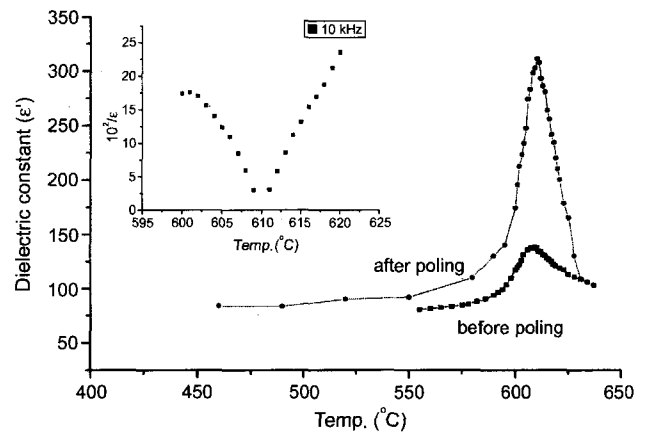


Fig. 3. Temperature dependence of the dielectric constant of Ce,Mn:LiTaO₃ crystal (inset. reverse real dielectric constant).

cal properties. In an application of photorefractive effect, for example, hologram, the goal in sensitization is electron transfer from the deep to shallow trap. The energy level of Ce ion is similar to Fe ion in the energy level and Mn ion is known as deep centers and known to be effective trap centers. Recently, many researchers present experimental observation of their properties.⁶⁻⁸⁾

Temperature dependence of the dielectric constant of the Ce,Mn:LiTaO₃ crystal was shown in Fig. 3. Curie temperature T_C was 610°C in this study. Measured dielectric constant of Ce,Mn:LiTaO₃ before and after poling appeared different value but T_C was equal to each process. And thermal hysteresis was not appeared. Inset figure within Fig. 3 show Curie-Weiss behaviour, i.e. $(\epsilon')^{-1} = (T - T_C) / C$ for several degrees above the phase transition. The ratio of the slopes $\partial(1/\epsilon) / \partial T$ below and above T_C is about -1.6 for Ce,Mn:LiTaO₃ to be compared with the values -2 expected for conventional phenomenological theory.⁹⁾ These results may be explained a temperature gradient in sample and inhomogeneous of electrode.

The transmission spectra of Ce,Mn:LiTaO₃ shown in Fig.

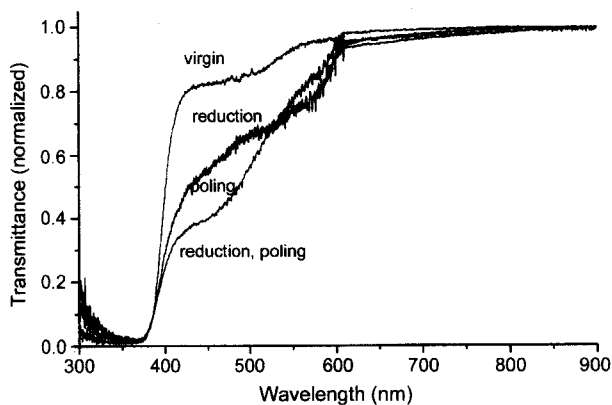


Fig. 4. Transmission spectra of virgin Ce,Mn:LiTaO₃ crystal and treated crystals.

Table 2. Specimens of Ce,Mn:LiTaO₃ Single Crystals for Oxidation and Reduction

Treatment	Color	Atmosphere
as grown	dark-red	N ₂ +O ₂ (~1%)
annealing	colorless	air
reduction	brown yellow	N ₂
oxidation	light violet	O ₂

4 were obtained with non-polarized light. All specimens were transparent at visible region, but appeared different tendency at UV region.

For oxidation and reduction treatments, the temperature of oxidation and reduction was 1400°C and the treatment time were 24 h. The treated specimen was lapped and optically polished for characterization. The color of crystals was changed by treatment (see Table 2). As-grown Ce,Mn:LiTaO₃ crystal has dark-red color because of reduction atmosphere condition on growing, it became to be colorless after annealing in air, brown yellow after reduction at 1400°C and light violet by oxidation. Ce doped crystals or photosensitive glasses containing CeO₂¹⁰⁾ are sometimes red or brown. But LiTaO₃ crystal becomes to be black or brown by reduction of some Ta⁵⁺ ions to Ta⁴⁺. In Ce,Mn:LiTaO₃ crystal, Ce, Mn and Ta ions look to be the color center of crystal but we did not yet analyzed the valence of those ions of colored crystals.

Optical absorption by other defects than impurities can also give rise to intense coloring of crystals. It is known that the crystals are often photochromic if two kinds of trap centers exist between the valence and conduction bands, which means that the absorption can be changed by illumination because of the redistribution of charge carriers between these different traps. As well-known, modest treatment of oxidation and reduction can change the valence state of the doped ions and the other defects' distribution. The influences of the oxidation and reduction are also clearly observed (Fig. 5). The absorption coefficient have a form of $\alpha l \propto -\log(I/I_0)$. Here l , I and I_0 are active length, output

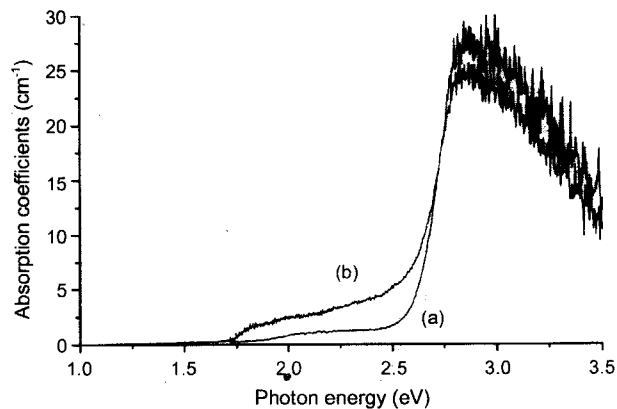


Fig. 5. Absorption coefficient of Ce,Mn:LiTaO₃ (a) before reduction (b) after reduction.

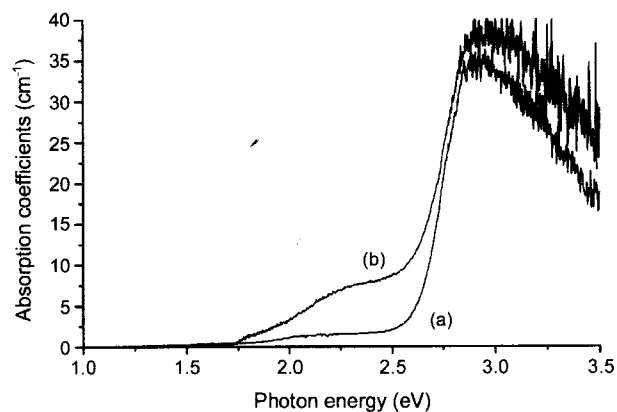


Fig. 6. Absorption coefficient of Ce,Mn:LiTaO₃ (a) before poling (b) after poling.

intensity and input intensity, respectively. There is a broad absorption band located at 460~550 nm, which is induced by Ce²⁺ ions and Mn²⁺ ions and oxygen vacancies V_O^{••}. It is obvious that with more Ce²⁺ and Mn²⁺ in crystal the absorption become heavier. The intensity of the absorption band at 460~550 nm increases as reduction and decreases as oxidation. The absorption coefficient increases monotonously with the incident energy and suddenly it begins to increase rapidly at a threshold on the higher-energy side. On increasing the degree of reduction, more and more oxygen vacancies are created in the LiTaO₃ system; thus, the internal electric fields arising due to these charged defects also increase, producing a pronounced effect on the absorption edge, which is broadened further. Dhar *et al*¹¹⁾ and Yang *et al*⁶⁾ have also observed a similar tailing in reduced LiNbO₃, Ce,Fe:LiNbO₃, respectively.

Because LiTaO₃ is a ferroelectric material, the electric field was applied along the uniaxial direction in the poling process. The domain-wall contribution to the free energy will affect most of the macroscopic properties of ferroelectrics.^{12,13)} The specimen was soaked at 650°C for 10 min and the heating and cooling rate was 3.5°C/min. After the soaking process, electric field was applied with 5 V/cm during

the cooling process.

Fig. 6. shows the absorption spectra of the Ce,Mn:LiTaO₃ single crystal poled under 5 V/cm. The entire absorption edge is formed to shift in a rigid manner toward higher energies in an applied electric field. But our experimental results showed different feature, that the polar faces of a crystal during cooling could, in principle, be sufficient to produce the single-domain state, but in practices this is not usually sufficient because of temperature gradients, internal strains and surface effects. Experiments for these poling condition are being tried.

4. Conclusion

Φ3" co-doped Ce,Mn:LiTaO₃ single crystals were grown by the Czochralski method. Its structural variation was not appeared in comparison with Φ3" LiTaO₃ and Curie temperature was unchanged. The transmission spectra of Ce,Mn:LiTaO₃ crystal was a induced broad absorption in the range from 460 nm to 550 nm. Ce doping gives active ultraviolet sensitivity. Oxidation or reduction treatments of the co-doped Ce,Mn:LiTaO₃ give variation of absorption coefficients. The absorption variation in the crystal is originated from the filling of Ce traps with the help of ultraviolet light and not to some kinds of background impurities.

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