The effect of NaCl melt-additive on the growth and morphology in LiB_3O_5(LBO) crystals

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Lithium triborate(LiB_3O_5; LBO)[1] is one of the important nonlinear optical crystals in the spectral range of ultraviolet wavelength. Because of its interesting optical properties[2] such as a relatively large [illegible] nonlinear optical coefficient (d_{32} = 1.4 pm/V), high laser damage threshold (25 [illegible], 1.064 μm, 0.1 ns), wide transparency range (0.16-2.5 μm), and good mechanical and chemical stabilities, LBO is widely used for second harmonic generation, optical parametric oscillation and more recently planar waveguide.

LBO crystals belong to the orthorhombic space group $Pna2_1$ and point group mm2 with cell parameters a = 8.4473 Å, b = 7.3789 Å, c = 5.1395 Å, and Z = 4. Single crystals of LBO have been grown successfully from an excess B_2O_3 solution by the top seeded solution growth(TSSG) method with or without pulling[3]. However, the high viscosity inherent in B_2O_3 solution hinders mass transport and results in the depletion of material at the melt-crystal interface. So, it has been difficult to obtain crystals of large size and good quality in a short period of time. To overcome this problem, we introduce NaCl as a dopant to modify the characteristic of the solution. High viscosity of the B_2O_3 solution is originated from the presence of [illegible] BO_3 and BO_4 chain-like structures. The structure of the B_2O_3 solution forms a three-dimensional network, mainly consisting of randomly oriented boroxol rings [illegible] by B-O-B bridges, and alkali oxide (Li_2O) contributes to the changes of the network structure. The viscosity of the alkali borate melts is independent of the choice of alkali ions and is simply a function of the O/B ratio. The region for LBO crystal growth in the phase diagram is placed in the vicinity of the [illegible] of the viscosity curve, so small addition of other alkali cations gives little effects on the viscosity. It was reported that the doping of Cl^- ions and F^- ions can reduce the network strength in the alkali borate melts[4]. The Cl^- ions in the melt do not couple with the boron-oxygen network and lie in the interstitial sites as free ions. As a consequence, the [illegible] effect of the Cl^- ions, and the chemical equivalent between the Cl^- ions and $[BO_3]^{3-}$ ions make the network less tight. On the other hand, the F^- ions take part in the network and form B-F non-bridge bond, so the viscosity of the solution becomes also reduced. We employed NaCl as a modifier.

LBO crystals of large size and good quality have been grown successfully by the TSSG method with different concentration of the modifier, 2 mol %, 4 mol % NaCl and without NaCl. Changes in growth and morphology were observed. In tables 1 and 2, the growth conditions and the comparison for the as-grown LBO crystals of different NaCl concentration are summarized. It is remarkable to note that the growth rate increased by a factor of two for the crystals of 4 mol % NaCl concentration.

In order to investigate the adverse effect of NaCl, bulk laser damage threshold was measured using a Nd:YAG laser operating at 1.064 μm with the pulse width of 9 ns and the repetition rate of 10 Hz. The result is shown in table 2.

Table 1. Growth conditions for LBO crystals of different NaCl concentration.

NaCl concentration (mol %)	0	2	4
Seed orientation	[001]	[001]	[001]
Seeding temperature	849 °C	845 °C	845 °C
Temperature gradient	0.20 °C/cm	0.20 °C/cm	0.20 °C/cm
Cooling rate	< 1.0 °C/day	< 1.2 °C/day	< 1.5 °C/day
Crucible rotation speed	20 RPM	20 RPM	20 RPM
Seed rotation speed	40-50 RPM	40-50 RPM	30-40 RPM

Table 2. Comparison for as-grown LBO crystals of different NaCl concentration.

NaCl concentration (mol %)	0	2	4
Size (mm^3)	25.8×25.7×23.8	30×30.5×26	23.5×25.6×27.7
Growth period(days)	10	12	7
Growth rate (g/day)	3.9	4.2	6.8
Faces	{110}, {100}, {011}, {201}	{110}, {100}, {011}, {201}	{110}, {011}, {201}
Crack	free	free	one crack in {201}
$[Na^+]$ concentration in crystal	0	below detection limit	0.019 %
Inclusion	free	free	free
Laser damage threshold	2.2 GW/cm^2	2.1 GW/cm^2	1.6 GW/cm^2

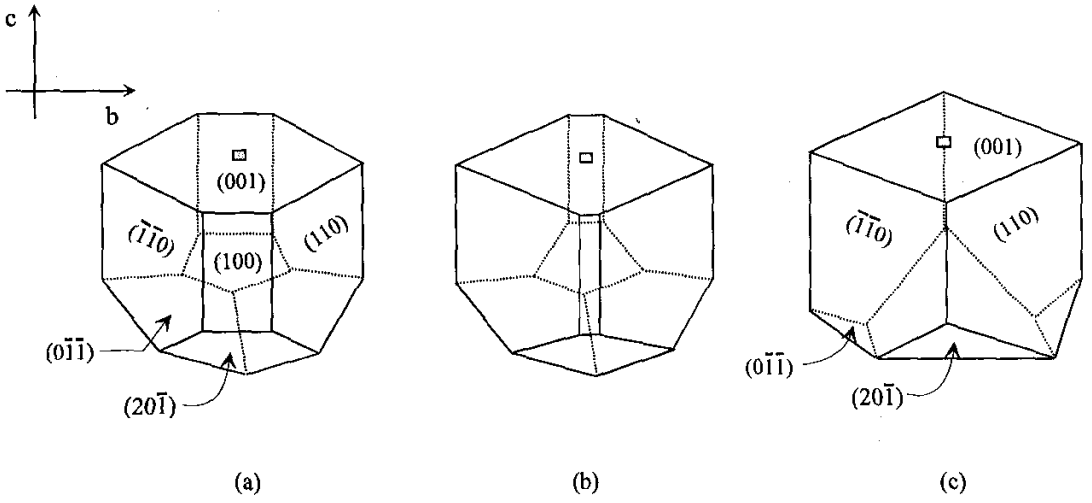

Fig. 1. Crystal morphology for as-grown LBO crystals of different NaCl concentration;

(a) 0 mol %, (b) 2 mol %, and (c) 4 mol %.

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