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Growth of neodymium lanthanum calcium borate (NdLCB) single crystals by the Czochralski method and its characterisation

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ABSTRACT

The synthesis of neodymium lanthanum calcium borate (NdLCB) was carried out using solid state reaction method. The NdLCB single crystals were grown by the Czochralski method using platinum wire as a seed. The single phase of NdLCB is confirmed by powder X-ray diffraction analysis. EDAX analysis is carried out to find the presence of constituent elements of NdLCB. Single crystal X-ray diffraction analysis was performed to find the lattice parameters and crystal system. Nd concentration in the crystal is determined using ICP-OES measurements. Optical studies such as UV–vis–NIR and photoluminescence were carried out for the NdLCB crystal and the results are analysed. SEM and etching analysis were carried out to analyse the surface morphology and the growth pattern of the as grown NdLCB crystals respectively.

1. Introduction

The development of nonlinear optics (NLO) gained technological importance and usage from their wide application ever since the first observation of optical second harmonic generation is reported [1]. Inorganic nonlinear optical materials have been developed very rapidly during the past decade on the borate series since the chemical bonding and the mechanical properties of these crystals are superior over other organic and semi-organic crystals. These inorganic borate compounds are reliable materials for effective nonlinear processes and very good candidates for device applications. Excellent mechanical strength and temperature withstanding capabilities lead them to be utilised in high power laser sources and for frequency conversion applications.

Borate crystals are not only employed for frequency conversion but also used as self-frequency doubling (SFD) active laser sources. Borate family of crystals were developed in the recent years. Potassium penta borate ($KB_5O_8 \cdot 4H_2O$) [2] was the first borate crystal described for UV light generation in the borate series. Since then, the search for new NLO borate crystals got momentum after the invention and development of β-BaB_2O_4 (BBO) and LiB_3O_5 (LBO) which are very useful for second harmonic generation from the visible to the UV ranges down to 200 nm. A complete review on borate based single crystals was reported by Becker [3] and Sasaki et al. [4].

Among the borate class of materials, lanthanum calcium borate exhibits second harmonic generation effect about twice as large as that of KDP. Also these single crystals are good candidates for applications in the ultraviolet region, since the lanthanum ion has no absorbing peak in the UV wavelength range. Hence it can act as good NLO crystal for the realisation of UV sources. In this crystal due to the presence of the La^{3+} ions, it is expected to show a self-frequency doubling effect when doped with other rare-earth elements. Presently, neodymium doped LCB single crystals with different concentrations of Nd^{3+} are of good interest as it is considered to be a potential multifunctional crystal for the second harmonic generation, frequency conversion and for ultraviolet light generation. The LCB crystal offers suitable sites for substituting them with laser active ions such as neodymium (Nd^{3+}), erbium (Er^{3+}), and ytterbium (Yb^{3+}) as their ionic radii are similar and further they exists in the trivalent state. These rare earth ions can be doped with LCB crystal to convert as a laser crystal and found to possess good spectroscopic and laser properties. Rare earth doped LCB crystal has potential applications in medicine, opto-communication, and lidar systems [5–7].

In our present work, the synthesis and the growth of NdLCB compound (5 mol% of Nd) was carried out and structure, composition and optical properties of the as grown crystal was analysed. For the first time, this paper reports the surface morphological features of NdLCB single crystals using SEM and etching analysis and the results are presented in detail.

2. Experiment

2.1. Nd^{3+} doped LCB: Materials synthesis

The synthesis of neodymium lanthanum calcium borate was carried out using neodymium oxide, lanthanum oxide, calcium carbonate and boric acid as the starting materials. For the preparation

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of NdLCB compound, 5% of neodymium (mole ratio) was taken along with other starting materials La_2O_3, $CaCO_3$ and H_3BO_3 with purity of 99.99% were taken and well mixed using agate mortar. Initially, the starting materials were kept at a temperature of 450 °C for 12 h to eliminate the moisture and carbonate present in the reactant. The reactants were once again grounded and sintered at 930 °C for 36 h. The synthesis of NdLCB compound given by the equation

$$(0.05)Nd_2O_3+(0.95)La_2O_3+CaCO_3+10H_3BO_3\rightarrow Nd_{0.10}La_{1.90}CaB_{10}O_{19}+15H_2O+CO_2\uparrow$$

The powder X-ray diffraction pattern of polycrystalline NdLCB after second step of synthesis is reported as shown in Fig. 1(a). As grown LCB crystal was powdered and the powder X-ray diffraction pattern was recorded as shown in Fig. 1(b) as reference. From the X-ray powder diffraction profiles, it is observed that the main 100% peak of NdLCB powder profile matches with that of the powder XRD pattern of LCB crystal powder. Occurrence of new peaks along with few peak shifts may be observed due to the incorporation of $Nd3^+$ ions in the LCB compound.

2.2. NdLCB single crystal growth

The synthesised NdLCB compound was subjected to DTA analysis to find the melting of the compound before performing growth procedure. Among the borate crystals, LCB is reported as

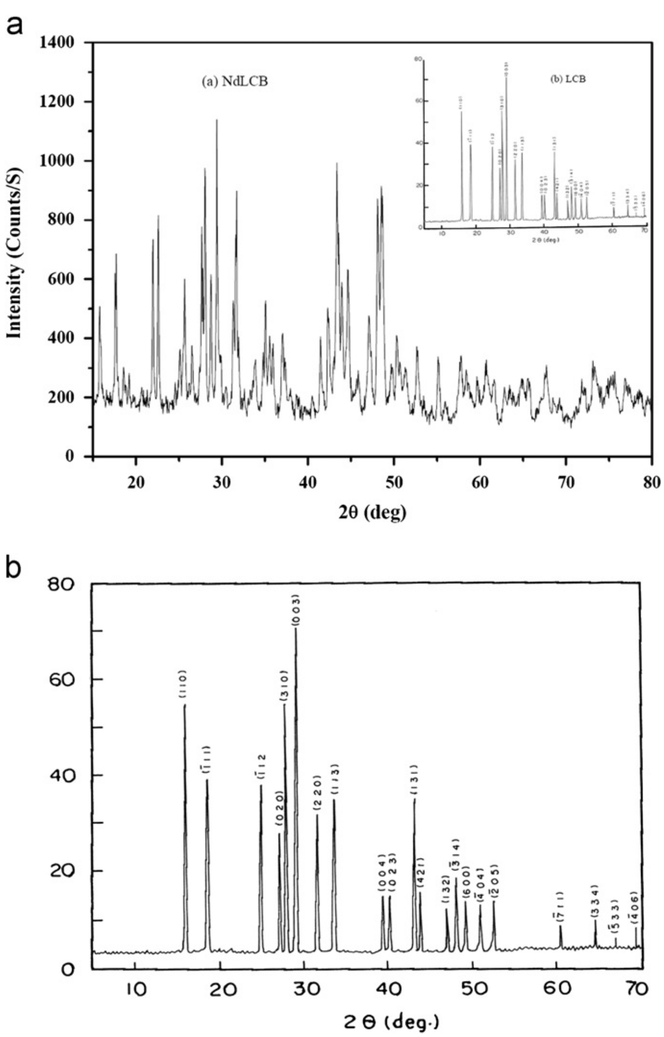

Fig. 1. Powder XRD Pattern of NdLCB compound.

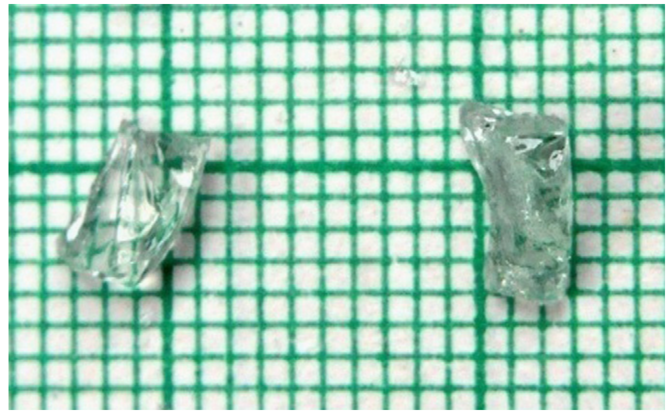

Fig. 2. As grown NdLCB crystal removed from platinum wire.

one of the non-hygroscopic material in borate crystal family. Similar to LCB, the non-hygroscopic nature was observed during NdLCB crystal growth processes. From the analysis, it is observed that the compound LCB with 5 mol% of Nd concentration have the melting point of 1043.8 °C and is confirmed that the material does not decompose before melting. In the rare earth doped borate class of materials, the melting point of crystals decreases with the increase in the ionic radius of the rare earth ion present in it [8]. Based on the thermal analysis, suitable thermal cycle was adopted for the growth of NdLCB crystals. The NdLCB polycrystalline material was taken in a platinum crucible and was heated to 1050 °C and is completely melted. Further the temperature was raised to 1080 °C for the homogenisation of the melt and to expel the bubbles formed during the melting process and then slowly reduced to 1055 °C. The conditions for the growth parameters were optimised and the growth of NdLCB single crystal was performed using the crystal pulling method. During the growth process, the cooling rate was varied between 0.5–0.2 °C in the temperature range of 1055 °C–1040 °C. In the growth experiments the platinum wire has been used as the seed for the growth of crystals. The as grown NdLCB crystals are shown in Fig. 2.

3. Characterisation

3.1. EDAX analysis

Energy dispersive analysis by X-rays (EDAX) analysis is one of the powerful tools in determining the presence of elements in a given sample. The EDAX spectrum of the NdLCB crystal was obtained using the instrument Hitachi energy dispersive X-ray microanalyser (model S-3400 N). The presence of the constituent elements of the NdLCB crystal was confirmed by the occurrence of their respective peaks in the EDAX spectrum which is as shown in Fig. 3 and the Table 1 shows the percentage of the constituent elements present in the NdLCB sample.

3.2. ICP-OES measurements

The inductively coupled plasma-optical emission spectrometer (ICP-OES) is used to determine concentrations of a wide range of elements in solution. It is a type of emission spectroscopy that uses the inductively to produce excited atoms and ions that emit electromagnetic radiation at wavelengths characteristic of a particular element. The intensity of this emission is indicative of the concentration of the element within the sample solution. For the present investigation, Perkin Elmer Optima 5300 DV instrument was