A New Nonlinear Optical Borate Crystal $Na_3La_2(BO_3)_3$

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A new nonlinear optical (NLO) borate crystal $Na_3La_2(BO_3)_3$ (sodium lanthanum borate, NLBO) has been discovered. The bar-shaped crystal with sizes up to $8 \times 3 \times 2$ mm^3 was grown by the Top-Seeded Solution Growth (TSSG) method using Na_2CO_3–H_3BO_3–NaF as fluxes. The measurement of the infrared spectrum indicated that the basic anionic group is the BO_3 group. Furthermore, NLBO crystal exhibits an optical second harmonic generation effect about twice as large as that of KDP(KH_2PO_4).

It is well known that rare earth ions have similar coordination structure and physical–chemical properties. From crystal-chemistry principle, when the rare earth ion is replaced partly or completely by different rare earth elements, the crystal structure and property do not change dramatically, and the improvement of material properties could be easily achieved. Over the past 30 years, complex borate of rare earth and other elements as a unique nonlinear optical material has received much attention. As a results of intensive studies, many complex borate NLO crystals have appeared, including $YAl_3(BO_3)_4$ (YAB),[1] $Nd_xY_{1-x}Al_3(BO_3)_4$ (NYAB),[2] $GdCa_4O(BO_3)_3$(GdCOB)[3] and their isomorphers, in which the anionic groups are planar BO_3 groups, and possess larger SHG coefficients. Recently, Khamaganova et al.[4] have discovered a new class of rare earth borate of composition $Ba_3Ln(BO_3)_3$(Ln=La–Lu,Y) which their basic structure units are also the BO_3 groups and exhibit second harmonic generation (SHG) effect. To our knowledge, information of SHG on double borate with $A_3Ln_2(BO_3)_3$ (A= alkali metal elements, Ln = rare earth elements) has been absent. So it will be of practical value to investigate complex borates with $A_3Ln_2(BO_3)_3$.

Early in 1983, $Na_3La_2(BO_3)_3$ with an orthorhombic structure (space group *Amm*2) had been synthesized in a nitrogen atmosphere, but single crystal had been prepared from $Na_4B_2O_5$ flux.[5] Since then, no reports on $Na_3La_2(BO_3)_3$ have been published. In the present study, we describe the synthesis in air, crystal growth from Na_2CO_3–H_3BO_3–NaF flux and SHG of $Na_3La_2(BO_3)_3$.

Polycrystalline samples of $Na_3La_2(BO_3)_3$ were prepared by using solid state reaction techniques. The initial substances were 99.99% purity La_2O_3, analytical grade Na_2CO_3 and H_3BO_3. The mixture of the starting charges taken in stoichiometric proportion was thoroughly homogenized in an agate mortar, then packed into a platinum crucible. The temperature was raised slowly to 500 °C in order to avoid ejection of powdered raw material from the crucible due to vigorous evolution of CO_2 and H_3BO_3 decomposition. After preheating at 500 °C for 10 h in air in a muffle furnace, the products were cooled, ground again, compressed, and sintered at 940 °C for 24 h. The purity of sample was checked by X-ray powder diffraction. A single phase powder of $Na_3La_2(BO_3)_3$ was obtained when repeated heat treatment caused no further changes in the X-ray powder diffraction pattern. The solid products were then pulverized, and ground into fine powder. The chemical equation can be expressed as follows:

$$3Na_2CO_3+2La_2O_3+6H_3BO_3=2Na_3La_2(BO_3)_3+3CO_2\uparrow+9H_2O$$

The crystals of the title compound were grown under flux conditions. According to the choice rules of fluxes, when a surplus of a constituent of the compound can act as the flux for the growth of the crystal of that compound, it will be possible to prevent the flux from contaminating the growth crystal. The crystal growth in such a melt will therefore be of high purity and good quality. So several self-fluxes and fluxes having common ions were firstly investigated for growing NLBO crystal, such as Na_2CO_3, H_3BO_3, Na_2CO_3–H_3BO_3, NaF and LaF_3. The results indicate that the Na_2CO_3–H_3BO_3–NaF flux system is more suitable. Several ratios of Na_2CO_3: H_3BO_3: NaF were tested for growing NLBO crystals. The suitable molar ratios of Na_2CO_3: H_3BO_3: NaF turned out to be 1:1:0.2. The growth temperature decreased with decreasing of solute concentration. The solute concentration about 30–50 mol% and the growth temperature at 1000–1030 °C proved suitable for growth of NLBO in our experiment.

At the beginning of our experiment, a suspending platinum wire method was performed in order to obtain seed. The raw materials were polycrystalline form $Na_3La_2(BO_3)_3$ powder, analytical grade Na_2CO_3, H_3BO_3 and NaF. The charges were weighted in the appropriate ratio, ground, mixed thoroughly, and melted in a platinum crucible of 30 cm^3 capacity in several batches. The experiments were carried out in a resistance-heated furnace. An A1-708P controller was used to control the temperature. The procedure was as follows: the fully charged crucible was placed in the growth furnace. The temperature was raised at about 100–150 °C/h to 1100 °C and held at for 10–24 h to ensure the solution melts completely and mixes homogeneously. After the melt was firstly cooled at a rate of 10 °C/h to 1040 °C, a platinum wire used as seed was slowly introduced into the furnace and dipped into the melt, then followed by a slow cool at a rate of 1–2 °C per day. Thus, some crystals crystallized on the platinum wire.

To obtain larger crystals, the TSSG method was adopted. The saturation temperature was determined to be 1030 °C by the testing seed crystal method. The seed contacted the melt at a temperature 10 °C above the saturation temperature and was kept at constant temperature for 30 min to dissolve the outer surface of the seed. The temperature was first decreased at a rate of 5 °C/h to the initial growth temperature and then decreased at a rate of 0.5 °C per day. The growing crystal was rotated at a rate of 20 rpm. When the growth was completed, the crystal was drawn out of the melt surface and cooled down together with the furnace to room temperature at a rate of 50

°C/h. Finally, the bar-shaped colorless transparent single crystal with a dimension of 8 × 3 × 2 mm^3 was obtained.

The obtained crystal was identified by X-ray powder diffraction (XRD), using a MXP18 AHF(MAC. Science Co. Ltd.) powder diffractometer with Cu $K\alpha_1$ radiation (λ = 0.15405 nm) by a graphite monochromator. The scanning step width of 0.02° and the scanning rate of 0.1° s^{-1} were applied to record the patterns in the 2θ range of 10–70°. Figure 1 shows the X-ray powder diffraction pattern of the crystal NLBO.

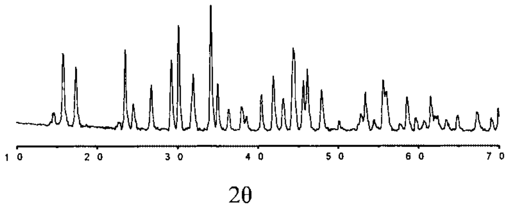

Figure 1. X-ray powder diffraction pattern of NLBO crystal.

The crystal structure of NLBO was investigated. The crystallographic data and experimental conditions are listed in Table 1.

Table 1. Crystallographic data and experimental conditions for $Na_3La_2(BO_3)_3$

Diffractometer, Temperature	Rigaku Raxis IV, 293(2) K
Radiation	0.71073 Å graphite monochromated Mo Kα
Crystal size, color	0.20 × 0.10 × 0.10 mm, Colorless
Formula, formula weight	$B_3 La_2 Na_3 O_9$, 523.22
Crystal system, space group	Orthorhombic, *Amm*2
Unit cell dimensions	*a* = 5.1580(10) Å α= 90°
	b= 11.350(2) Å β= 90°
	c = 7.3230(15) Å γ = 90°
Volume, Z, calculated density	428.71(15) $Å^3$, 2, 4.053 g /cm^3
Absorption coefficient, F(000)	10.012 mm^{-1}, 468
Absorption correction	Empirical
Theta range for data collection	3.31 to 27.54°
Index ranges	$0 \le h \le 6, -14 \le k \le 0, 0 \le l \le 9$
Reflections collected / unique	300 / 300 [R(int) = 0.0000]
Program	SHELXL-97[6]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	300 / 1 / 55
Final *R* indices [*I*>2sigma(*I*)]	R_1 = 0.0232, wR_2 = 0.0530
R indices (all data)	R_1 = 0.0237, wR_2 = 0.0532
Goodness-of-fitonF², Extinction coefficient	0.985, 0.173(10)
Largest diff. Peak and hole	1.120 and -1.155 e. $Å^{-3}$

At room temperature, the infrared (IR) spectrum of the NLBO crystal powder was recorded on a 170SFT-IR model infrared spectrophotometer with KBr pellet as the reference in the region 2000–400 cm^{-1}(see Figure 2). The results obtained are compared with the characteristic values of the BO_3 group.[7] For the planar, triangular BO_3 group, the vibration are in the region ν_3=1000–1300 cm^{-1} (asymmetric stretch B–O), ν_1=900–1000 cm^{-1} (symmetric stretch of B–O), ν_2=700–900 cm^{-1} (out-of-plane bend), ν_4=590–680 cm^{-1} (in-plane bend). Obviously, the NLBO crystal contains characteristic BO_3 groups as its basic structural units.

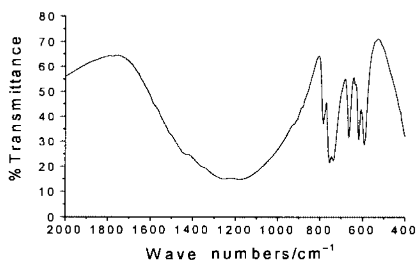

Figure 2. Infrared spectrum of sample at room temperature.

The element contents in the crystal were determined by using an Atomscan Advantage plasma spectrometer. The ratio of Na to La to B atoms in the crystal is 3 to 2 to 3, which agrees with the composition of the compound $Na_3La_2(BO_3)_3$ confirmed by determining crystal structure.

The investigation of optical SHG was carried out on the $Na_3La_2(BO_3)_3$ sample. Fundamental 1064 nm light was generated with a Q-switched Nd:YAG laser. Microcrystalline KDP(KH_2PO_4) served as the standard. Green light was observed and its intensity was about twice as large as that of KDP. On the basis of determined crystal structure data, the calculated SHG coefficient $\chi^{(2)}_{113}$ of NLBO by Gaussian'92 and $\chi^{(2)}$ calculated program[8] is 0.843 pm/v, which is about two times that of KDP (0.435 pm/v)[9] and in line with experimental value. According to the anionic group theory,[10] the nonlinearity of a borate crystal originates in the boron-oxygen groups, so borates containing BO_3 groups could be expected to possess a larger SHG effect. Our result is in agreement with this theory. It means that NLBO crystal is probably used as a kind of nonlinear optical material.

In summary, sodium lanthanum borate $Na_3La_2(BO_3)_3$ was synthesized in atmosphere. Na_2CO_3–H_3BO_3–NaF flux was successfully used as a new flux to grow NLBO crystal. NLBO crystal contains the BO_3 group as basic structural unit. The intensity of second harmonic generation effect was about twice as large as that of KDP. It is possible for NLBO crystal to possess potential for application as a new nonlinear optical crystal. In near future, large NLBO crystals of high optical quality will be obtained, and the linear and nonlinear optical properties of NLBO will be measured completely.

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