Journal of Crystal Growth 344 (2012) 27–30

Contents lists available at SciVerse ScienceDirect

Journal of Crystal Growth

journal homepage: www.elsevier.com/locate/jcrysgro

Growth and piezoelectric features of $La_2CaB_{10}O_{19}$ crystals doped with Pr^{3+} ions

K. Ozga [a,*], A. Majchrowski [b], N. AlZayed [c], E. Michalski [b], L. Jaroszewicz [b], P. Rakus [d], I.V. Kityk [d], M. Nabialek [e], M. Szota [f]

[a] Chair of Public Health, Czestochowa University of Technology, 36B Armii Krajowej, 42-200 Czestochowa, Poland
[b] Institute of Applied Physics, Military University of Technology, 2 Kaliskiego, 00-908 Warsaw, Poland
[c] Physics & Astronomy Department, College of Science, King Saud University, P.O. Box 2455, Riyadh 11451, Saudi Arabia
[d] Department of Optoelectronics, Faculty of Electrical Engineering, Czestochowa University of Technology, 17 Armii Krajowej, 42-200 Czestochowa, Poland
[e] Institute of Physics, Czestochowa University of Technology, 19 Armii Krajowej, 42-200 Czestochowa, Poland
[f] Institute of Materials Science, Czestochowa University of Technology, 19 Armii Krajowej, 42-200 Czestochowa, Poland

ARTICLE INFO

Article history:
Received 29 December 2011
Received in revised form
23 January 2012
Accepted 26 January 2012
Communicated by S. Uda
Available online 4 February 2012

Keywords:
A2. Growth from high temperature solutions
B1. Borates
B2. Piezoelectric materials

ABSTRACT

High quality $La_2CaB_{10}O_{19}$ single crystals doped with Pr^{3+} ions were grown by means of the top seeded solution growth method. The concentration of Pr^{3+} ions in the starting melt was equal to 4 at%, which, due to small distribution coefficient, in consequence gave single crystals containing 2.5 at% of Pr^{3+} ions. The piezoelectric coefficients were measured for the pure and Pr^{+3} doped crystals. The principal changes under influence of the nanosecond pulsed 1064 nm Nd:YAG laser were observed for the LCBO nanocrystallites incorporated into the polymer matrices. The introduction of the Pr^{3+} ions favors enhanced piezoelectric constants. In turn the nanocrystallites with enhanced piezoelectricity lead to the enhanced laser threshold damage.

1. Introduction

The use of the polymer nanocomposites containing borate nanocrystallites presents a promising way for construction of optically operated devices [1,2]. The principal physical insight for applications of such materials consists in the formation of the thin nanosheet interfaces on borders between the nanocrystallites and the surrounding polymers. The latter are very sensitive to the surface nanocrystalline ground state dipole moments determined by the polymer-nanocrystallite borders. From this reason polarizability of polymer matrix is crucial for such kinds of effects. For the traditional polymers like polymethylmethacrylate (PMMA) this nanosheet is very thin. For the photopolymer like oligoetheracrylate (OEA) this sheet possesses thickness equal to about several nanometers.

Most of the studies performed up today were done for the optical and nonlinear optical features. Following the general phenomenological consideration one can expect an occurrence of photoinduced piezoelectric changes. In the present work we present results of measurements of the photoinduced piezoelectricity in such kinds of materials containing $La_2CaB_{10}O_{19}$ (LCBO) nanocrystals under influence of the external laser light for different polymer matrices.

2. Sample preparation

LCBO single crystals doped with Pr^{3+} ions (LCBO:Pr^{3+}) were obtained by means of top seeded solution growth (TSSG) method. LCBO melts incongruently [3], so the only way to grow single crystals of this material is high temperature solution growth. The solvent chosen to our experiments contained CaB_4O_7 and $Li_2B_4O_7$ in molar ratio 1:1. Calcium borate was, due to its composition, natural candidate as the LCBO solvent. It contains the same ions as LCBO and allows crystallization of LCBO below the temperature of the peritectic phase transition in a broad temperature range [3]. However, when this solvent was used alone, uncontrolled crystallization of LaB_3O_6 on the bottom of the crucible as well as spontaneous crystallization on the surface of LCBO crystal was often observed. Addition of lithium tetraborate, similarly to Ref. [4], lowered the temperature of crystallization below 1000 °C and made the control of the growth process much easier. The LCBO:Pr^{3+} single crystals

* Corresponding author.
E-mail addresses: iwank74@gmail.com, cate.ozga@wp.pl (K. Ozga).

0022-0248/$ - see front matter © 2012 Elsevier B.V. All rights reserved.
doi:10.1016/j.jcrysgro.2012.01.050

growth was carried out from 50 × 50 mm Pt crucible in a two-zone resistance furnace. The temperature of the heating zones was controlled by two independent Eurotherm 906S programmers. The detailed description of the TSSG set can be find elsewhere [5]. The growing crystals were rotated at a rate of 10 rpm, no pulling was used, so the LCBO crystals grew in the volume of the melt and were confined with flat crystallographic faces. The cooling of the melt during the growth process was extremely slow and its rate was equal to 0.01 K/h. The typical growth on a seed lasted 2–3 weeks, then LCBO crystal was withdrawn from the melt and cooled to room temperature during four days. As-grown LCBO single crystals were of good optical quality except their central parts containing some inclusions. The starting melt contained 4 at% of Pr^{3+} ions substituting La^{3+} ions. According to Ref. [6] the distribution coefficient for Pr^{3+} ions is rather small (0.63) what results in decrease of Pr^{3+} ions concentration in as-grown LCBO single crystals. In Fig. 1 one can see as-grown LCBO:Pr single crystal weighing 3.56 g, while there was 56.26 g of LCBO in the starting melt. The small fraction of crystallized LCBO did not strongly influence the content of Pr ions in growing crystal despite small distribution coefficient of Pr^{3+} ions. In case of LCBO crystals grown from the melt containing 4 at% of Pr^{3+} it gives the real value near 2.5 at%.

Fig. 1. LCBO:Pr^{3+} single crystal grown from melt containing 4 at% of Pr^{3+} ions in the melt.

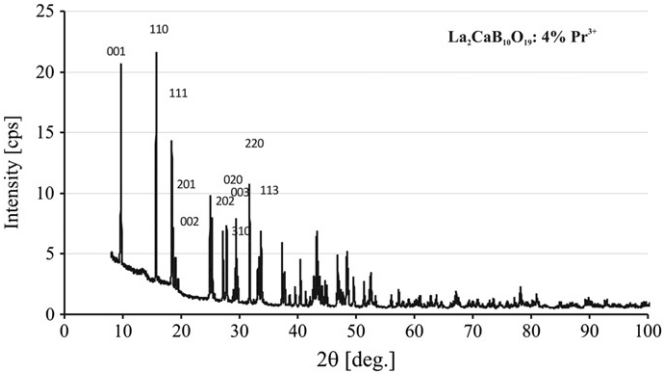

Fig. 2. X-ray powder diffraction pattern of the LCBO:Pr crystals.

To confirm that introduction of Pr^{3+} did not change the structure of the growing crystals X-ray investigations were carried out. Fig. 2 presents the powder diffraction pattern obtained for the LCBO:Pr^{3+} (4 at% in the melt) single crystal.

The nanocrystals were prepared by mechanical crushing of the LCBO:Pr Pr^{3+} bulk single crystals with additional treatment by acoustical field as described in the Ref. [7]. The nano-powder crystallites were separated by size-controlled filters. Afterwards the nanopowders were incorporated into the polymer matrices. For the case of the PMMA matrices the incorporation was done using spin coating method as described in the Ref. [7]. For the OEA photopolymer matrices the incorporation of the nanocrystallites was done using photo-solidification similarly to Ref. [8]. The optimal concentration of the nanoparticles was varied within the 6.7–7% in weighing units.

The study of NC incorporation was carried out using atomic force microscopy (AFM). The contrast imaging was performed in tapping mode. The signal was obtained by measuring the phase shift of an oscillating at resonant frequency cantilever. The NP-10 tip with Au reflectively coated films of thickness of ~15 nm was

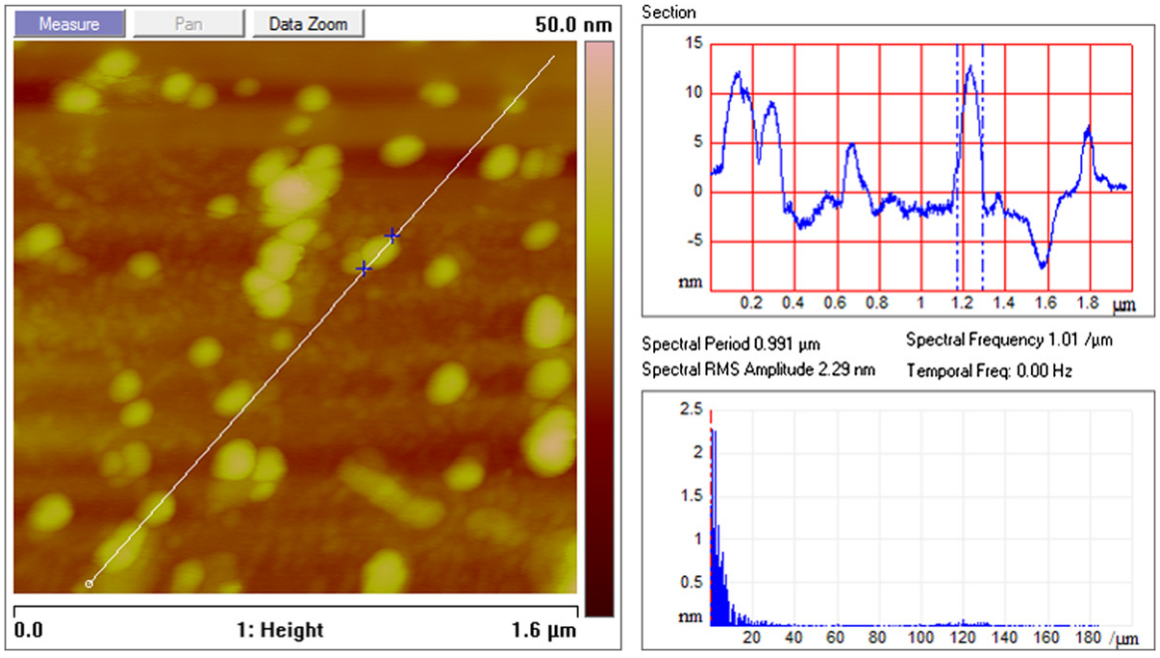

Fig. 3. Typical AFM pictures of the studied LCBO nanocomposites together with profile of the nanocomposite surfaces.