Asian Journal of Chemistry Vol. 22, No. 1 (2010), 189-193

Influence of Lanthanum(III) Dopant on Structure, Linear and Non-Linear Optical Properties of Ammonium Pentaborate Crystals

B. MUNIRATHNAM* and J. MADHAVAN†
Department of Physics, Sir Theagaraya College, Chennai-600 021, India
Fax: (91)(44)28175566; Tel: (91)(44)28178200
E-mail: jmadhavang@yahoo.com

Single crystals of pure and lanthanum doped ammonium pentaborate (AB5) have been successfully grown from aqueous solution by slow evaporation technique. The growth conditions of both pure and La^{3+} doped AB5 are optimized and the grown crystals are investigated by powder X-Ray diffraction technique. The grown crystals of pure and La^{3+} doped AB5 are subjected to FT-IR and UV-Vis-NIR spectral techniques and the influences of La^{3+} are reported. The second harmonic generation of the crystals was confirmed by Kurtz and Perry powder technique and the influence of La^{3+} is also discussed.

Key Words: Non-linear optical, Solution growth, Borates, FT-IR.

INTRODUCTION

Non-linear optical materials have a significant impact on laser technology, optical communication, optical storage technology and electro optic modulation. The experiments on non-linear optical (NLO) materials proved that borate compound materials play an indispensable role in frequency conversion when one needs a powerful or tunable laser in the deep ultraviolet region[1]. Non-linear optical (NLO) borate crystals have a wide transparency range, good chemical stability and high damage threshold. Borate crystals such as $Sr_2Be_2B_2O_7$ (SBBO)[2], LiB_3O_5 (LBO)[3], $CsLiB_6O_{10}$ (CLBO)[4] and BiB_3O_6 (BiBO)[5] have been widely studied as promising non-linear optical (NLO) crystals. In the present investigation, we report the growth of lanthanum doped ammonium pentaborate (AB5) along with pure AB5 crystal. The primary aim of the article is to investigate the influence of La^{3+} on the structural and optical properties of AB5 crystals.

EXPERIMENTAL

Synthesis and growth of pure and doped AB5 crystals: Single crystals of ammonium pentaborate with chemical formula $NH_4[H_4B_5O_6(OH)_4].2H_2O$ was synthesized by stoichiometric incorporation of ammonium carbonate and boric acid taken in the appropriate ratio. The calculated amount of salt was dissolved in deionized

†Department of Physics, Loyola College, Chennai-600 034, India.

water. Tiny crystals were formed due to spontaneous nucleation at the bottom of the container. Recrystallization was carried out more than three times to increase the purity of the crystal. The same process was repeated for synthesizing the La^{3+} substituted AB5 by taking 2 mole % of lanthanum. In order to grow bulk size single crystals, the tiny crystals formed due to spontaneous nucleation were used as seed crystals. The period of growth ranged from 45-60 d. During the growth experiments, it was observed that the presence of La^{3+} in general, increases the dimensions of the grown crystals. As grown crystals of pure and La^{3+} doped AB5 crystals are shown in Fig. 1.

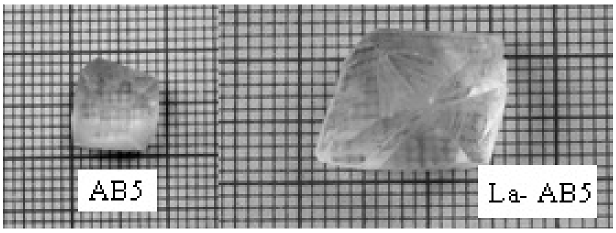

Fig. 1. Photograph of pure AB5 and La- AB5

RESULTS AND DISCUSSION

Powder X-ray diffraction studies: The unit cell parameters of pure and doped AB5 single crystals were collected by subjecting the samples to powder XRD analysis using RICH SEIFERT, XRD 3000P with monochromatic nickel filtered CuK_α (λ = 0.15406 nm) radiation X-ray diffractometer and it is shown in Figs. 2 and 3. PXRD data of pure and doped AB5 crystals indicate that they belong to orthorhombic crystal system with space group Aba2. The cell parameters are listed in Table-1. The data of the present work is in good agreement with the reported work[6]. The slight variation in the doped crystal could be attributed to the presence of dopant.

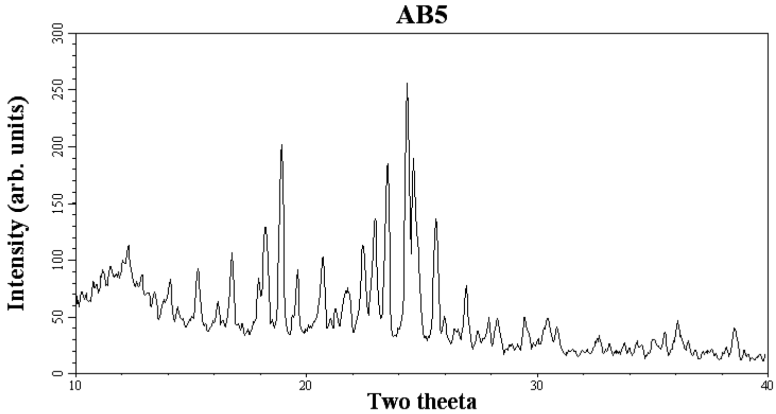

Fig. 2. Powder X-ray diffraction Analysis of pure AB5

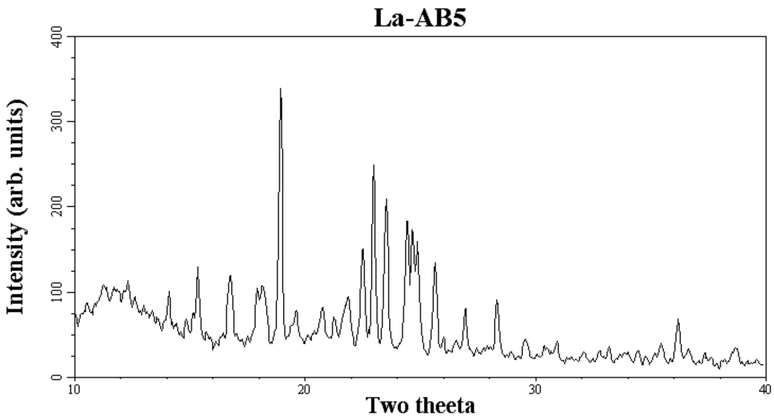

Fig. 3. Powder X-ray diffraction analysis of La^{3+} doped AB5

TABLE-1
XRD DATA OF PURE AND La^{3+} DOPED AB5

	Pure AB5	La^{2+} doped AB5
Crystal system	Orthorhombic	Orthorhombic
a(Å)	9.224	9.452
b(Å)	11.015	11.518
c(Å)	11.325	11.395
α (deg)	90	90
β (deg)	90	90
γ (deg)	90	90
Volume ($Å^3$)	1150.647	1240.55

Inductive coupled plasma analysis: The exact percentage of the lanthanum metal present in the doped crystal is determined by ICP analysis. 10 mg of fine powder of the lanthanum doped AB5 crystal was dissolved in 100 mL of triple distilled water and the prepared solution was subjected to ICP analysis. The result shows that 22 ppm of lanthanum entered into the crystal lattice of the crystal. It is seen that the amount of dopant incorporated in to the doped crystal is less than the concentration of the dopant in the corresponding solution.

FT-IR Studies: The FT-IR spectra of pure and La^{3+} substituted AB5 crystals were recorded using Bruker model IFS-66V spectrometer in the range 4000-400 cm^{-1}. In AB5, the hydroxyl groups of pentaborate anion and water are expected to contribute substantially to hold the molecules together through hydrogen bond. In the spectrum of AB5, there is a broad envelop between 3750 and 2850 cm^{-1}. It includes the O-H stretch of BO-H, water between the lattice and outside the lattice and N-H stretch of NH_4^+ ion. The higher frequency band in this region includes BO-H stretch and the O-H stretch of water that lies out of the pentaborate lattice. The low frequency band may be assigned to the OH stretch of the strongly hydrogen bonded water which lies in the lattice. Again, the BO stretching vibrations provide a broad peak between 1350 and 1240 cm^{-1}. The broadening is also observed for the bending modes of B-O bonds below 781 cm^{-1}. The OH bending mode of water is traced out as a less intense peak at 1656 cm^{-1}. In the case of La^{3+} substituted AB5 crystals, it is observed that there are slight variations in the peak as well as the intensities.

UV-Vis-NIR studies: The UV-Vis-NIR spectra of pure and La^{3+} substituted AB5 crystals were recorded using Varian Cary 5E model spectrophotometer in the region 200-2000 nm. It is observed from the spectra Fig. 4 that both pure and La^{3+} substituted AB5 are optically transparent in the entire visible and infrared region and the cutoff wavelength lies around 200 nm. It is further evident from the spectra that the presence of La^{3+} enhances the transparent nature of the AB5 crystal. This wide transparency optical window is an essential property for non-linear optical frequency conversion.

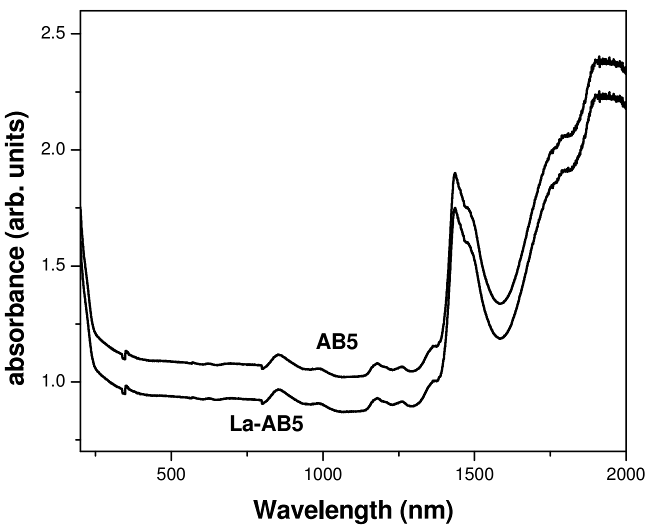

Fig. 4. UV-Vis-NIR spectra of pure and La^{3+} doped AB5

Non-linear optical test: The non-linear optical property of the pure and La^{3+} doped AB5 crystals were tested by passing the fundamental beam of Q-switched, mode locked Nd:YAG laser operating at 1.06 μm and pulse width of 8 ns laser pulse with spot radius of 1 mm[7]. The input laser beam was passed through IR reflector and then directed on the sample. An intense green radiation observed from the pure and doped AB5 crystals confirmed the second harmonic generation. The second harmonic generation efficiency of AB5 is found to be comparable with that of potassium dihydrogen phosphate and the doped crystals have 1.5 times efficiency that of potassium dihydrogen phosphate.

Conclusion

Pure and La^{3+} doped AB5 single crystals are grown by slow solvent evaporation technique. The functional groups of the sample are identified using FTIR technique. The optical absorption spectra of pure and La^{3+} substituted AB5 show the wide transparency window in the entire visible and infrared region. The second harmonic generation efficiency of the doped crystals is higher than that of the pure crystals.

ACKNOWLEDGEMENT

The authors acknowledge University Grants Commission (UGC), India for funding this research project [F.No. 33-11/2007 (SR)].

REFERENCES

1. P. Becker, *Adv. Mater.*, **10**, 979 (1998).
2. C. Chen, Y. Wang, B. Wu, W. Zeng and L. Yu, *Nature*, **373**, 322 (1995).
3. C. Chen, Y. Wu, A. Jiang, B. Wu, G. You, R. Li and S. Lin, *J. Opt. Soc. Am. B*, **6**, 616 (1989).
4. Y. Mori, I. Kuroda, S. Nakajima, T. Sasaki and S. Nakai, *Appl. Phys. Lett.*, **67**, 1818 (1995).
5. H. Hellwig, J. Liebertz and L. Bohaty, *J. Appl. Phys.*, **88**, 240 (2000).
6. G. Bhagavannarayana, R.V. Ananthamurthy, G.C. Budakoti, B. Kumar and K.S. Bartwal, *J. Appl. Cryst.*, **38**, 768 (2005).
7. S.K. Kurtz and T.T. Perry, *J. Appl. Phys.*, **39**, 3798 (1968).

(*Received*: 12 December 2008; *Accepted*: 3 September 2009) AJC-7821