

## Growth of pure APB and cobalt doped APB crystals

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### Abstract:

Ammonium pentaborate (APB) is well known nonlinear optical (NLO) material. To modify and engineer the properties of APB crystals, chalcogenide compound was added. Pure and cobalt doped ammonium pentaborate (APB) crystals were grown by slow solvent evaporation method. Cobalt chloride solution was added in the solution of APB. The Powder XRD confirms that both Pure and cobalt doped APB possessed orthorhombic crystal structure. The EDAX study confirms the presence of cobalt. Various functional groups were identified by FT-IR spectra for pure and cobalt doped APB.

### Introduction:

The crystals from boron family had good chemical stability, good optical quality and high damage threshold [1]. Pentaborates crystals were known for their polar symmetry structure, which is known as the family of hydrated pentaborates,  $X[B_5O_6(OH)_4]$  ( $X=NH_4$ , Li, Na, K, etc.). The first NLO effect was observed in

potassium pentaborate by Dewey et al.[2]. Borates have transparency in a very wide range which possess very high threshold damage, good chemical and physical stabilities. [3-5]. The theory of anionic give birth to new borate family having NLO properties. NLO borates contain various rigid and non-rigid groups and the dimensionality of the borate anions varies from 0D to 3D. [4], [6]. The main structural unit for pentaborate group is a double ring composed of two triborate rings, each formed by one boron–oxygen tetrahedron  $BO_4$  and two triangles  $BO_3$ , so that the  $BO_4$  tetrahedron is shared by the two triborate rings and form the twin crystal morphology [6]. The pentaborate groups joined through the shared oxygen atoms form a double interpenetrating framework. It is also used for the various applications like conversions of laser frequencies upto UV region, because it gives good absorption edge about 160 nm [5]. Several reported works based on APB is by doping of thiourea and amino acids [7], [8].

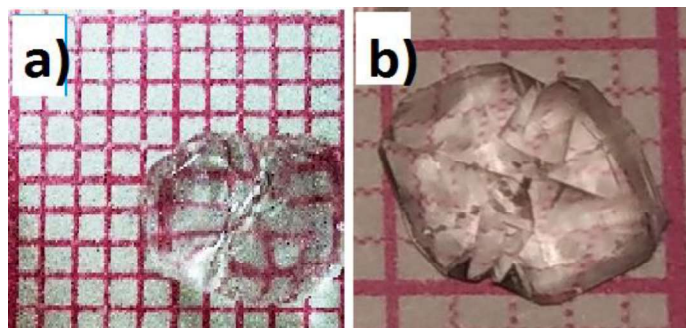
The aim of present study to investigate the effect of cobalt doped in ammonium pentaborate crystals (APB). Till date no reports were found on the impedance and complex modulus study on APB crystal. But this created novelty to this work, based on cobalt doped APB crystals along with change in their structural and functional group.

### Experimental:

The Slow Solvent Evaporation Technique was used for the growth of pure and  $\text{Co}^{2+}$  doped APB crystals at room temperature. For the growth of Pure APB crystal, 100ml APB saturated solution was prepared by adding 12gm APB in distilled water and stirred continuously for 8 hours to prepare homogeneous solution. Then the solution was filtered with the Whatman filter paper no.1. The filtered solution was covered tightly with porous lid and kept in a dust free environment for slow evaporation.

After 8-10 days transparent and good quality crystals were grown as shown in figure1.

For  $\text{Co}^{2+}$  doped APB crystals, 0.2g of  $\text{CoCl}_2$  was added in 100ml distilled water and stirred till the material dissolved (~1 hour). From that 10ml  $\text{CoCl}_2$  solution was taken and added in another homogenous solution of Pure APB and stirred for 8 hours. Then the solution was filtered by using Whatman filter paper no.1. The flatty disk was kept in dust free atmosphere with porous lid for controlled evaporation at constant temperature. After 8-10 days good quality, transparent and very light reddish color crystals were grown, which initial confirmation of  $\text{Co}^{2+}$  in APB. Figure 1 (b) shows the  $\text{Co}^{2+}$  doped APB crystals. The sizes of Crystals are 6mm x 5 mm for pure APB and 5mm x 4 mm for  $\text{Co}^{2+}$  doped APB crystals.



**Figure 1 (a)Pure APB and (b)  $\text{Co}^{2+}$ doped APB crystals**

Powdered samples of pure APB and  $\text{Co}^{2+}$  doped APB crystals were used in powder XRD. The instrument was used for the same was X'Pert MPD system and the  $\text{Cu}_\alpha$  radiation was used. The raw data of powder XRD was analysed by using Powder X software. The Thermo Nicolet 6700 instrument was used to carry out FT-IR spectroscopy and its raw data was analysed by using Omnic software which already connected to the instrument. Field Emission Gun Nano Nova Scanning Electron Microscope (FEG-SEM) 450 with EDAX.

## Result and Discussion:

### Powder XRD:

Figure 2, shows the powder XRD of Pure APB and  $\text{Co}^{2+}$  doped APB, which matched with the reported values [9]. These crystals possess orthorhombic structure. Its unit cell parameters are shown in table 1. As there was no extra peak observed in the doped crystal which indicates that the pure and doped APB crystal shows the single-phase nature.

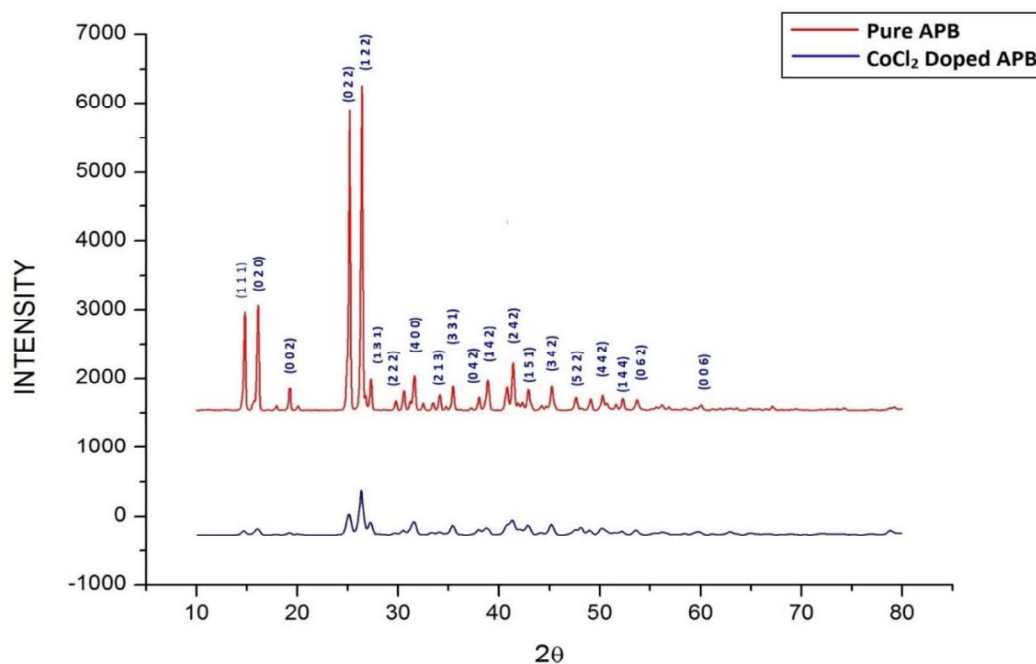


Figure 2: XRD patterns of pure and  $\text{Co}^{2+}$  doped APB crystals

**Table 1: XRD unit cell parameters**

Samples	a(Å)	b(Å)	c(Å)
Pure APB [6]	11.319	11.026	9.231
CoCl <sub>2</sub> + APB	11.335	11.028	9.288

Infrared spectrometry involves examination of the twisting, bending, rotating and Vibrational modes of atoms in a molecule. The multiplicity of vibrations occurring simultaneously produces a highly complex absorption spectrum that is unique characteristic of the functional groups that make up the molecule and of the overall configuration of the molecule as well. The group of frequency region was located between (4000 to 1300cm<sup>-1</sup>) and the fingerprint region (1300 to 650cm<sup>-1</sup>). The intermediate frequency range, 2500 to 1540 cm<sup>-1</sup> (unsaturated region) contains triple bond frequencies which appear from 2500 to 2000 cm<sup>-1</sup> and double bond frequencies

from 2000 to 1540 cm<sup>-1</sup>. In the region between 1300 and 650 cm<sup>-1</sup> there are single bond stretching frequencies and bending vibrations (skeletal frequencies) of polyatomic systems involving motions of bonds linking a substituent group to the molecule. The lower region 667 to 10 cm<sup>-1</sup> contains the bending vibrations of carbon, nitrogen, oxygen and fluorine.

Figure 3(a) and (b) shows FT-IR spectra of pure and Co<sup>2+</sup> doped APB crystals: (a) FT-IR spectrum of Pure APB crystal shows the O-H Stretching of water at 3370.7cm<sup>-1</sup>, NH<sub>4</sub> asymmetric bending at 1630.0 cm<sup>-1</sup>, B-O asymmetric stretching at 1348.0 cm<sup>-1</sup>, B-O terminal symmetric stretching at 1094.7 cm<sup>-1</sup>, B-O ring stretching Vibration at 914.9 cm<sup>-1</sup>, O-B-O ring stretching at 694.2 cm<sup>-1</sup>, O-B-O terminal bending at 530.8 cm<sup>-1</sup> and O-B-O ring bending at 461.3 cm<sup>-1</sup>.

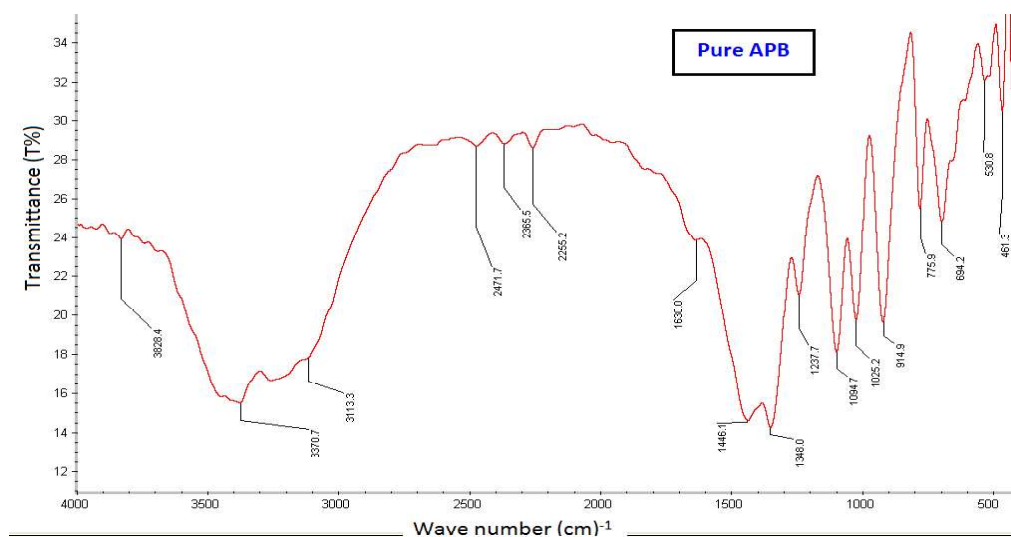


Figure 3 (a): FT-IR of Pure APB Crystals

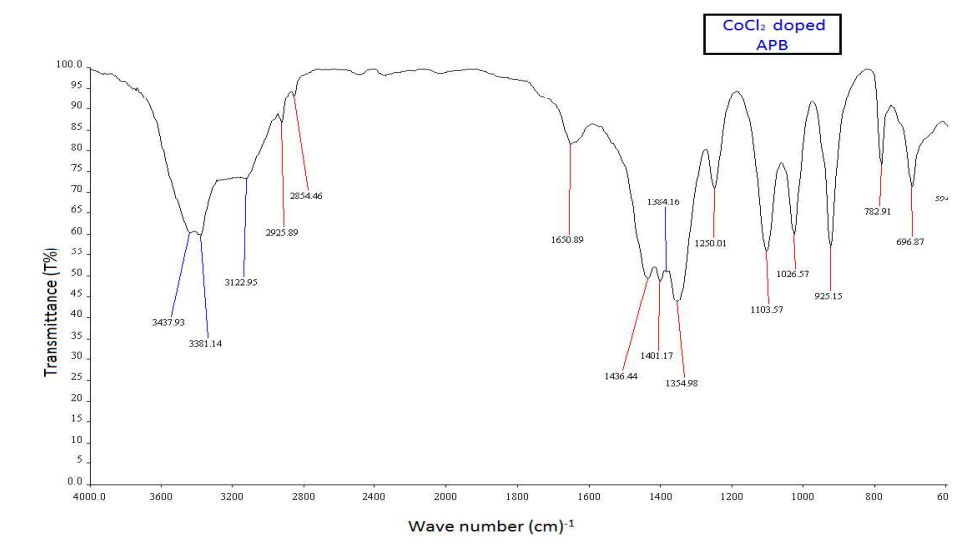


Figure 3 (b): FT-IR of  $\text{Co}^{2+}$  doped APB Crystals

Table 2: Assignments of Pure and  $\text{Co}^{2+}$  doped APB

Wave numbers ( $\text{cm}^{-1}$ )		Assignments
Pure APB	$\text{Co}^{2+}$ +APB	
3370.7	3381.14	(O-H) symmetric stretching
1630.0	1650.89	$\text{NH}_4$ asymmetric bending, (O-H) bending
1348.0	1384.16	B-O asymmetric stretching
1094.7	1026.57	B-O terminal symmetric stretching
914.9	925.15	B-O ring stretching
694.2	696.87	O-B-O ring stretching
530.8	594	O-B-O terminal bending

(b) FT-IR spectrum of  $\text{Co}^{2+}$  doped APB crystal shows that the peak positions are shifted due to presence of Cobalt in APB crystal. As for example the B-O asymmetric stretching vibration of pure APB is shifted from  $1348.0 \text{ cm}^{-1}$  to  $1384.16 \text{ cm}^{-1}$ , B-O terminal symmetric stretching of pure APB is shifted from  $1094.7 \text{ cm}^{-1}$  to  $1026.57 \text{ cm}^{-1}$ , O-B-O ring stretching of pure APB is shifted from  $694.2 \text{ cm}^{-1}$  to  $696.87 \text{ cm}^{-1}$ , O-B-O terminal bending of pure APB is shifted from  $530.8 \text{ cm}^{-1}$  to  $594 \text{ cm}^{-1}$ . The

FT-IR spectrum of Pure APB is similar to the reported work carried out by T. Balakrishnan et.al [9].

The compositional analysis of the Co doped APB, was carried out by EDAX spectroscopy to confirm the presence of Co in sample. The figure 4 is the EDAX plot for the growth of Co doped APB crystal, which confirms the presence of Cobalt (Co) and Oxygen (O).

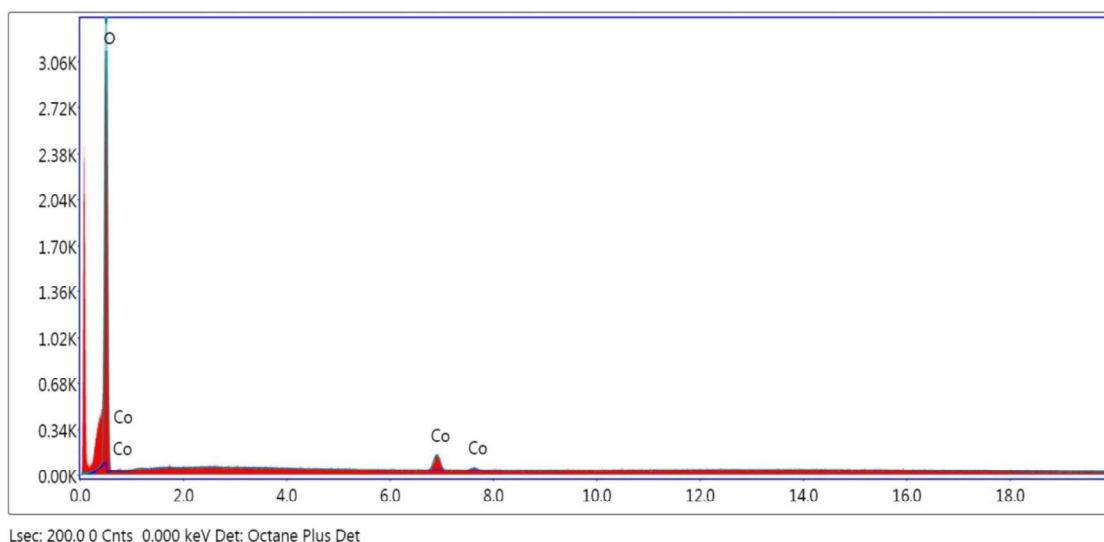


Figure (4): EDAX of  $\text{Co}^{2+}$  doped APB crystal

From EDAX data it is found that the presence of Cobalt (Co) is 6.93% and Oxygen (O) 93.07%, which indicates the successful addition of Co in APB.

**Table 3: EDAX data**

Element	Weight %	Atomic %
O	93.07	98.02
Co	6.93	1.98

## Conclusion

Pure and  $\text{Co}^{2+}$  doped APB crystals were successfully grown by slow evaporation technique. From powder XRD patterns of pure APB and  $\text{Co}^{2+}$  doped APB single phase nature was observed with slight variation in the unit cell parameters. The confirmation of Co in APB crystals was obtained from EDAX and FT-IR spectroscopy.

## References

- [1] C. Chen, Y. Wu, and R. Li, "The development of new NLO crystals in the borate series," *J. Cryst. Growth*, vol. 99, no. 1–4, pp. 790–798, 1990.
- [2] C. Dewey, W. Cook, R. Hodgson, and J. Wynne, "Frequency doubling in  $\text{KB5O8} \cdot 4\text{H}_2\text{O}$  and  $\text{NH}_4\text{B5O8} \cdot 4\text{H}_2\text{O}$  to 217.3 nm," *Appl. Phys. Lett.*, vol. 26, no. 12, pp. 714–716, 1975.

- [3] D. N. Nikogosyan, *Nonlinear optical crystals: a complete survey*. Springer Science & Business Media, 2006.
- [4] C. Chen *et al.*, *Nonlinear optical borate crystals: Principals and applications*. John Wiley & Sons, 2012.
- [5] P. Becker, "Borate materials in nonlinear optics," *Adv. Mater.*, vol. 10, no. 13, pp. 979–992, 1998.
- [6] R. Bubnova, J. Anderson, M. Krzhizhanovskaya, and S. Filatov, "Crystal structure and thermal expansion of ammonium pentaborate  $\text{NH}_4\text{B}_5\text{O}_{16}$ ," *Glass Phys. Chem.*, vol. 36, pp. 369–375, 2010.
- [7] G. Mani, K. Rajarajan, S. Selvakumar, P. Sagayaraj, and R. Mohan, "Growth, optical and thermal properties of pure and amino acid doped ammonium pentaborate NLO SINGLE CRYSTALS," *Intl J Mater Sci*, vol. 4, p. 787, 2009.
- [8] G. Mani, K. Rajarajan, M. Lydia Caroline, P. Sagayaraj, and R. Mohan, "Growth, optical and thermal studies of pure and thiourea doped ammonium pentaborate nonlinear optical single crystals," *Mater. Res. Innov.*, vol. 19, no. 5, pp. 318–323, 2015.
- [9] T. Balakrishnan, G. Bhagavannarayana, and K. Ramamurthi, "Growth, structural, optical, thermal and mechanical properties of ammonium pentaborate single crystal," *Spectrochim. Acta. A. Mol. Biomol. Spectrosc.*, vol. 71, no. 2, pp. 578–583, 2008.