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Growth and Characterization of Ag^+ doped Ammonium Pentaborate Single Crystals

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ABSTRACT

Ammonium pentaborate (APB) is a nonlinear optical material. For doping of Ag^+, 0.1M% $AgNO_3$ is added in the APB solution and the pure and Ag^+doped APB crystals are grown by slow evaporation technique at room temperature. The powder XRD study confirms that both pure and Ag^+ doped APB crystals possessed orthorhombic structure and the single phase nature. The EDAX confirms the presence of Ag^+ in APB crystals. From FT-IR spectroscopy the presence of various functional groups are identified. In present study the plots of dielectric constant, dielectric loss and a.c. conductivity versus frequency and Jonscher's plots are studied. The Ag^+ doped APB crystals exhibits slightly lower values of dielectric constant, dielectric loss and a.c. conductivity compared to pure APB.

KEYWORDS: Ag^+ doping, Powder XRD, EDAX, Dielectric study.

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INTRODUCTION

The inorganic borates exist in different structures and some crystals such as potassium pentaborate -KB5 ($KB_5O_8 \cdot 4H_2O$),beta barium borate -BBO(β-BaB_2O_4) and ammonium pentaborate –APB ($NH_4B_5O_8$), are excellent nonlinear optical (NLO) materials, particularly in the ultraviolet region [1,2]. It has been found that different chemical bonding structures of born atoms in borate compounds have strong influence of second order nonlinear optical effect. The formation B-O ring decreases the NLO property. The $[BO_3]^{3-}$ group possesses large nonlinear optical contributions than $[BO_4]^{5-}$ group [3]. Different boron crystals have an important role in modern optoelectronic devices, which have abilityof signal processing. The crystals from boron family had good chemical stability, good optical quality, high damage threshold[4]. The applications of various borate crystals in NLO and lasers are reviewed [5]. Recently, Raval et al [6] reported growth and characterization of ABP crystals.Earlier, several attempts have been made to dope APB crystal by amino acid [7] and thiourea [8].The present authors have made an attempt to dope Ag^+ in ammonium pentaborate (APB) to modify and investigate the structural, lattice strain, spectroscopic and dielectric properties.

MATERIALS AND METHODS

The Slow Solvent Evaporation Technique was used for the growth of pure and Ag^+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 15-18 days transparent and good quality crystals were harvested as shown in Fig.1 (a).For Ag^+doped APB crystals, 0.1M of $AgNO_3$ was added in distilled water and stirred till the material dissolved. From that 10ml $AgNO_3$ solution was taken and added in homogenous solution of pure APB and stirred for 8 hours. Then the solution was filtered by using Whatman filter paper no.1 and transferred in to a beaker. The beaker was kept in dust free atmosphere with porous lid for controlled evaporation at constant temperature. After 15-18 days good quality, transparent and slight grayish color crystals were grown.

The powder XRD was carried out on Philips X`pert MPD system and data were analyzed by powder-X software. The FT-IR spectra of powdered samples in KBr media were recorded on BRUKER IFS 66V FTIR spectrometer in the range of 400–4000 cm^{-1}. The EDA XXL 30 ESEM with EDAX was used for the detection of Ag^+. The dielectric property of pure APB and Ag^+ doped APB crystals were measured by using 6500B LCR meter in the frequency range from 20Hz to 1MHz at room temperature.

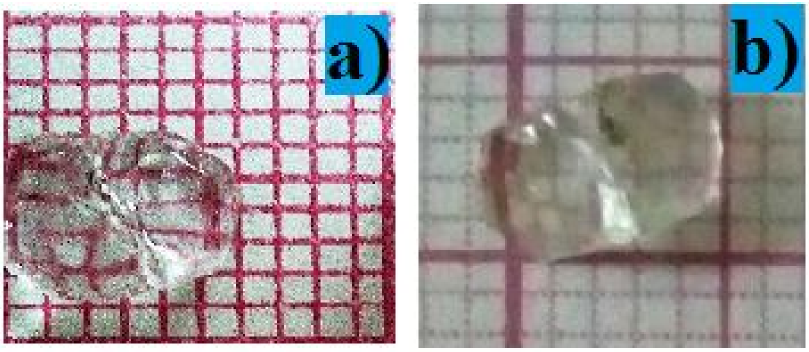

Fig.1: Grown crystals (a) Pure APB and (b) Ag+ doped APB

Fig. 1: (b) shows the Ag^+ doped APB crystals. The sizes of Crystals are 6mm x 5 mm for pure APB and 5mm x 4 mm for Ag^+doped APB crystals.

RESULTS AND DISCUSSION

Powder XRD

Fig.2 shows the powder XRD of Pure APB andAg^+ doped ABP and table 1 gives the values of unit cell parameters. Both display orthorhombic crystal structure and exhibit the single phase nature without the presence of any extra peaks for the doped APB sample. The value of unit cell parameters corresponds to the reported values for pure APB [9, 10].Fig. 3 is molecular structure of pure APB and Ag^+ doped APB.

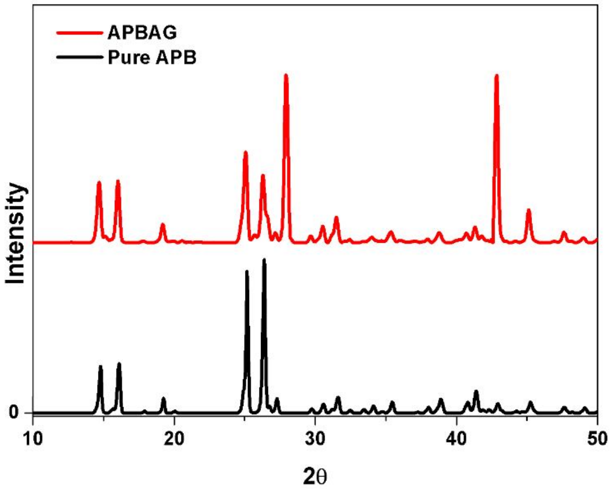

Fig.2: XRD patterns of pure APB and $^{Ag+}$ doped APB

Table No. 1: "Unit cell parameters"

Samples	a (Å)	b (Å)	c (Å)	Volume
Pure APB	11.319	11.026	9.231	1152.06
AGAPB	11.349	11.064	9.258	1162.48

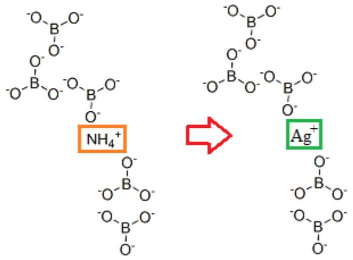

Fig.3: Molecular structure of pure APB and APBAG

FT-IR Spectroscopy

Fig.4 shows FT-IR spectra of pure and Ag+ doped APB crystals. The FT-IR spectrum of pure APB crystal shows the O-H Stretching of water at 3370 cm^{-1}, NH_4 asymmetric bending at 1630cm^{-1}, B-O asymmetric stretching at 1348cm^{-1}and 1237 cm^{-1},B-O terminal symmetric stretching at 1094 cm^{-1} , B-O ring stretching vibration at 914cm^{-1}, O-B-O ring stretching at 694cm^{-1},O-B-O terminal bending at 530cm^{-1} and O-B-O ring bending at 461cm^{-1}.The FT-IR spectrum of Ag^+ doped APB crystal shows that the peak positions are shifted due to presence of Ag^+ in APB crystal.

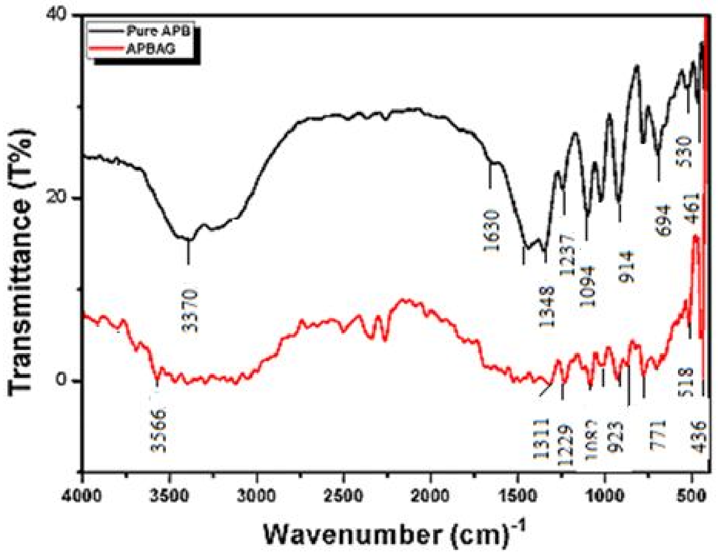

Fig.4: FT-IR spectra of pure APB and $^{Ag+}$ doped APB

For example, in Ag^+ doped ABP there was a broadening in B-O asymmetric stretching vibration is shifted from 1348cm^{-1} to 1311cm^{-1} , the O-B-O ring stretching is shifted from 694cm^{-1} to

771cm^{-1} ,the O-B-O terminal bending is shifted from 530cm^{-1} to 518cm^{-1} and the O-B-O ring bending is shifting from 461cm^{-1} to 436cm^{-1}. This indicates the removal of ammonium ion NH_4^+ by Ag^+ ion and Ag^+ ion being more massive than ammonium ion the vibrations are shifted. This indicates the successful doping of Ag^+ in APB crystals. Also one finds the absence of NH_4 asymmetric bending vibrations due to Ag^+ in doped crystals indicating the absence of ammonium. FT -IR spectrum of pure APB is similar to the reported work carried out by Balakrishnan et.al [11].

Table No. 2: "Assignments of FTIR spectra"

Wave numbers (cm^{-1})		Assignments
Pure APB	APBAG	
3370	3566	(O-H) symmetric stretching
1630	-	NH_4 asymmetric bending,(O-H) bending
1348	1311	B-O asymmetric stretching
1237	1229	B-O asymmetric stretching
1094	1082	B-O terminal symmetric stretching
914	923	B-O ring stretching
694	771	O-B-O ring stretching
530	518	O-B-O terminal bending
461	436	O-B-O ring bending

EDAX

The compositional analysis of the Ag^+ doped APB was carried out by EDAX spectroscopy to confirm the presence of Ag^+ in sample.

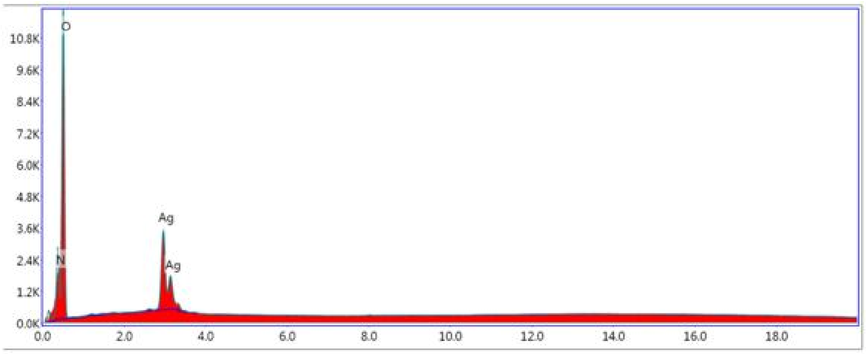

Fig.5: EDAX of $^{Ag+}$ doped APB crystal

The fig.5 is the EDAX plot for the Ag^+ doped APB crystal, which confirms the presence of Silver (Ag), Nitrogen (N) and Oxygen (O).From EDAX weight percentage data, it is found that the presence of Silver (Ag) is7.16%, Nitrogen (N) 16.15% and Oxygen (O) 76.68%, which indicates the successful doping of Ag^+ in APB.

Dielectric Study

Dielectric constant is the measure of polarization under the influence of applied alternating field and dielectric loss is the power loss under the influence of applied alternating field. Fig.6 and Fig.7 show that the both dielectric constant and dielectric loss are slightly lower in Ag^+ doped APB crystals compared to pure APB. The atomic radius of NH_4^+ is 1.44 Å and for Ag^+ is 1.15 Å, now according to the Goldschmidt rule, the dopant cations enter into the sites if the radius of the substituted ions and the replaced ions does not differ by 15–20%, otherwise, the partial substitution occurs [12].

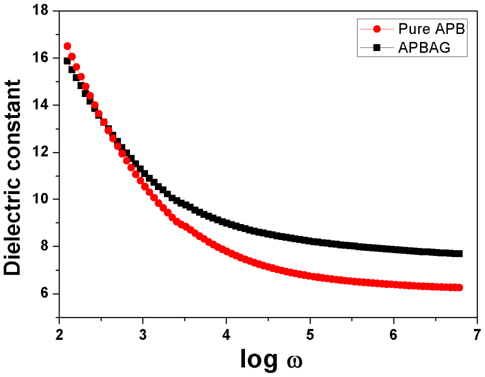

Fig.6: Dielectric constant of pure APB and $^{Ag+}$ doped APB crystal

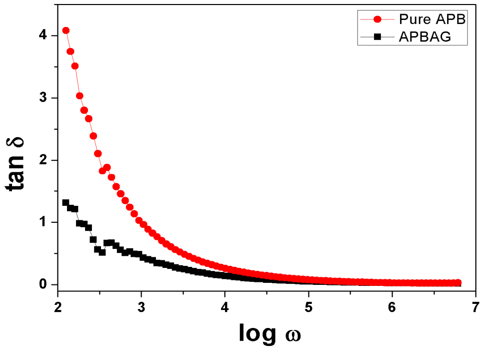

Fig.7: Dielectric loss of pure APB andAg^+ doped APB crystal

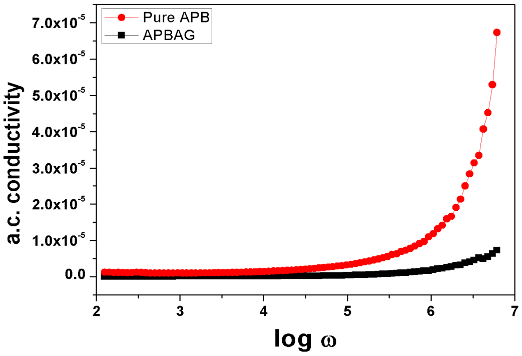

Fig.8: Conductivity of pure APB and Ag^+ doped APB crystal

From fig.6 the values of dielectric constant are high at lower frequency region due to the presence of all four kinds of polarization like ionic, electronic, space charge and orientation in pure and doped crystals. But at higher frequency the rotating dipoles cannot comply with the alternating electric field and hence exhibit low values approaching almost constant value. The similar nature is displayed by the plots of dielectric loss versus log$_{\omega}$. The comparable lower value of dielectric loss indicates the less loss taking place due to generation of defects.In fig.8 the plots of a.c. conductivity versus log$_{\omega}$ are drawn for both pure and doped crystals. The value of a.c.conductivity is slightly less in Ag^{+} doped APB crystal compared to pure APB.

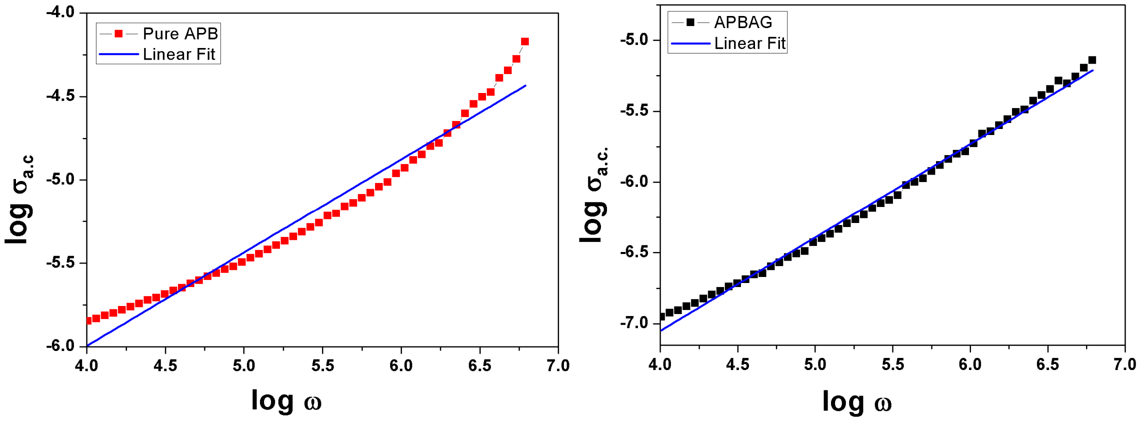

Fig.9: Jonscher's plot of pure APB and silver doped APB crystal

The frequency dependence of conductivity is related by simple expression given by Jonscher's power law:

$$\sigma_{tot}= \sigma_{dc}+A\omega^{s} \text{ ----------------- (1)}$$

Where, σ_{tot} = the sum of D.C. and A.C. conductivity, "A" is the strength of polarizability and "s" is a degree of correlation of lattice with mobile ions. Fig.9 shows Jonscher's plot for pure and Ag^{+} doped APB crystals and it exhibits highly dispersive region indicating the existence of A.C. conductivity only. The A.C. conductivity increases with increasing frequency for both samples. The slope and intercept of such plot gives the value of "s" and "A", the obtained value is tabulated in table no.3.

Table No. 3: "Values of 's' and 'A' "

Sample Name	s	A ($S\ m^{-1}\ rad^{-n}$) x 10^{-10}
Pure APB	0.55	0.5869
APBAG	0.65	2.050

The values of ‘s’ for both samples indicate that degree of interaction of mobile ions in the lattice is almost the same type, as shownin table 3 [6, 12]. Large difference between values of ‘A’ for both the samples indicates the effect of Ag^+ in APB crystals on its polarizability. This indicates that the dipoles per unit volume in Ag^+ doped APB crystals are comparatively more than the pure APB crystals, which further means that the polarizability strength and dielectric constant is higher for Ag^+ doped APB crystals. The physical significance of “s”in Jonscher’s equation differs for two different regimes, i.e., “$s \leq 1$”indicates that the hopping motion involved is a translational motion with a sudden hopping and “$s > 1$”suggests that the motion involved is a localized hopping of the species with a small hopping without leaving the neighborhood [10, 12].For ionic conductors, the value of “s”can lie between 0.5 and 1.00 indicating the ideal long range pathways and diffusion limited hopping [13, 14].

CONCLUSION

The pure and Ag^+ doped APB crystals were successfully grown by slow evaporation technique. From powder XRD patterns of pure APB and Ag^+ doped APB a single phase nature was observed with slight variation in the unit cell parameters and intensity. The confirmation of Ag^+ in APB crystals was obtained from EDAX and FT-IR spectrum indicated change in the values of absorption for various functional groups. The slightly decrease in dielectric constant, dielectric loss and a.c. conductivity for Ag^+ doped ABP than pure ABP is due to presence of Ag^+.

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