Sciencia Acta Xaveriana
An International Science Journal
ISSN. 0976-1152

Volume 3
No. 1
pp. 1-10
Apr 2012

Influence of Mg^{2+} on the Mechanical Properties of Ammonium Tetra Fluoro Antimonates

R. Mary Jenila[1], T. R. Rajasekaran[2] and J. Benet Charles[1]

[1] Materials Research Center, St. Xavier's College (Autonomous), Tirunelveli-627002, Tamil Nadu, India

[2] Department of Physics, Manonmaniam Sundaranar University, Tirunelveli-627012, Tamil Nadu, India

Abstract : Ammonium Tetra Fluoro Antimonate NH_4SbF_4 (ATFA) , an electro optic crystal has been grown by slow evaporation technique. Powder X-ray diffraction method has been used for structural identification and determination of lattice parameters. Micro hardness studies have been carried out using a Vicker's diamond pyramid indenter. The variation of micro hardness of pure ATFA and with the addition of metal alkali dopants such as Mg^{2+} are reported for the first time in this paper. The work hardening coefficient 'n' is 2.32 for pure ATFA and 1.822 for Mg^{2+} doped ATFA crystal. This is explained on the basis of dislocations present in the crystal. The yield strength and stiffness constant were also calculated and reported in this paper.

1. Introduction

The crystal chemistry of water soluble crystals of fluoro antimonates and their relative compounds have reported earlier in the literature [1-5]. It has also been reported that a number of fluorides have high ionic conductivity. Ammonium Fluoro Penta Antimonate $(NH_4)_2Sb_2F_5$ has shown the property of super ionic conductivity [6]. The crystal Structure of

NH_4SbF_4 was reported by Ovchinnikov et al.[7] and the dynamics of ions of ammonium and fluoride in Ammonium Fluro Antimonates was considered in [8,9] and generalized in [10]. These compounds are of interest due to the assumption that the presence of liable cations NH^{4+}in a crystal lattice is likely to lead to higher values of conductivity than in the cations of heavy alkali metals [11]. The FNMR and impedance spectroscopy investigations of NH_4SbF_4 are reported earlier [12]. Hardness measurements offer a means of determining the strength properties of a material. In this study, we report the growth, Power X-ray analysis and microhardness studies of Pure and Mg^{2+} doped ATFA for the first time.

Crystal Growth

Appropriate proportions of Ammonium Fluoride NH_4F and Antimony tri oxide Sb_2O_3 and Hydrofluoric acid, HF were mixed together to prepare the solutions of ATFA. The reaction can be represented as

$$2NH_4F \quad + \quad Sb_2O_3 + \quad 6\,HF \;\rightarrow\; 2\,NH_4SbF_4 \;+ 3\,H_2O$$

The crystals were grown by slow evaporation technique at a constant temperature. The crystals were obtained by spontaneous nucleation. Single crystals of AFTA are obtained in a period of one month. To grow the alkali metal doped ATFA, 2 mol % of MgF_2 is added with the solution of ATFA and the doped crystals are obtained in above said Procedure. Fig.1. shows the photograph of the grown crystals.

Fig. 1a. Photograph of as grown pure ATFA Crystals

Fig.1b. Photograph of grown Mg^{2+} doped ATFA single crystals

3. Results and Discussions

3.1. XRD analysis

X-Ray diffraction technique is used to investigate the inner arrangements of atoms or molecules in a crystalline material. The lattice parameters are identified by X-ray diffraction technique

.From the single X-rd data, it is found that the pure and doped AFTA crystals belongs to monoclinic structure with a = 8.165Å, b= 6.951Å, c = 16.392Å, $\alpha = \gamma = 90°$, $\beta = 104.32$ °, Volume = 901.4Å for pure ATFA and a=8.180Å, b= 6.950Å, c =16.410Å, $\alpha = \gamma = 90°$, $\beta = 104.27°$, Volume = 904.1Å for Mg^{2+} doped ATFA. The diffractogram of the pure and doped ATFA is taken by XPERT-PRO diffractometer. The range of 2θ is scanned from 10 to 80 degrees Intensity versus 2θ is recorded and shown in Fig.2.

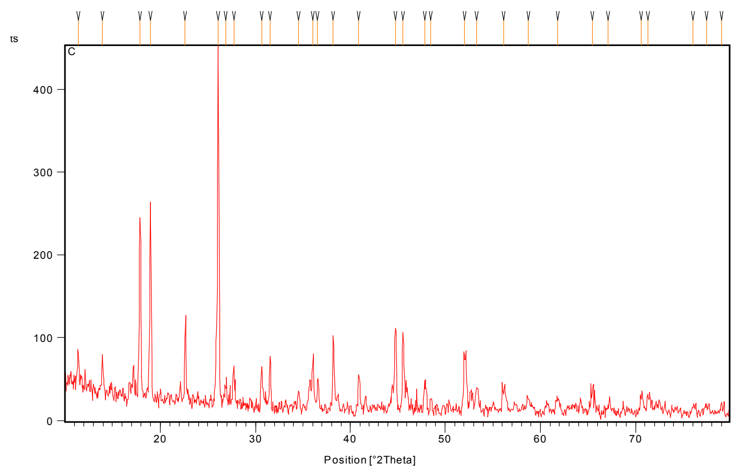

Fig 2.a. X-Ray diffractogram of pure ATFA

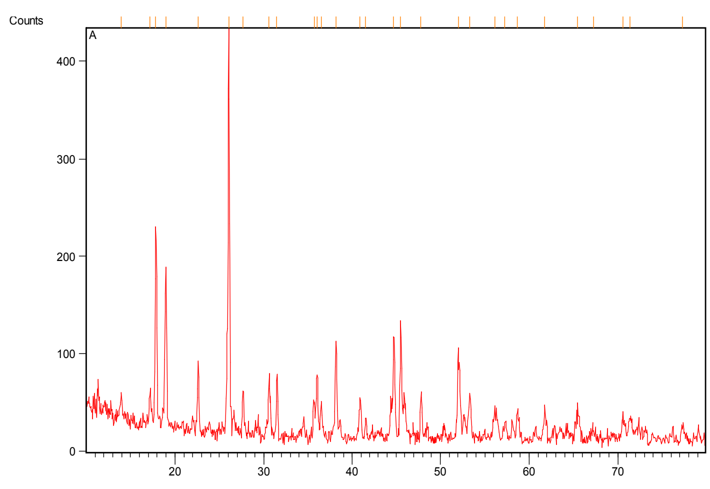

Fig. 2b. X-Ray diffractogram of Mg^{2+} doped AFTA

3.2 Indentation Tests

Hardness is defined as the resistance offered by a material to external mechanical action endeavoring to scratch, abrade, indent or any other way affect its structure. Microhardness measurement method is non destructive in most practical cases. Vickers's method is applicable to both hard and soft materials, plastic and brittle [13]. The microhardness studies of Potassium flour antimonates were reported by Besky Job et al [14] and $NH_4Sb_3F_{10}$ was reported by Rani Christu Dhas et al [15]. A Leitz microhardness tester with a diamond pyramidal indenter was used for microhardness measurements. The apical angle between the opposite pyramid planes is 136° .The load is varied from 10 to 80 gm .The indentation duration was approximately 10 secs. For each load an average of at least six imperfections were recorded for measuring the diagonal length (d) of impression. The Vickers's Hardness was determined using the formula

$$Hv = 1.8544 \, P / d^2 \qquad (1)$$

Where P is the applied load expressed in kg and Hv in kg / m2 .The variation of hardness number with load is given in Fig.3.

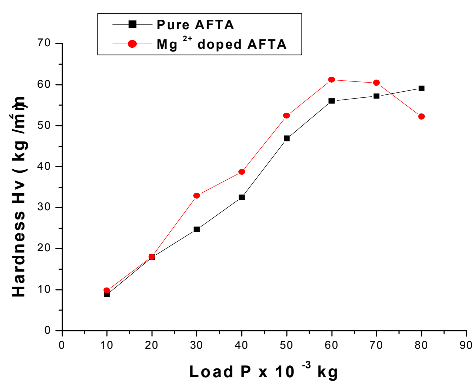

Fig 3. Plot of load P versus Hv for Pure and doped ATFA single crystals

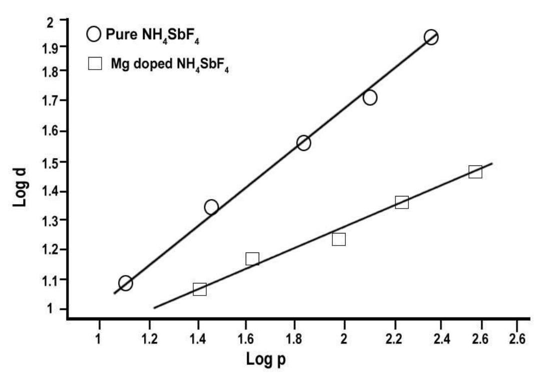

Fig 4. Plots of log P vs Log d for pure and Mg^{2+} doped ATFA crystals

The following observations are made from Fig.3.The microhardness value increases with load upto 80 gm and then decreases by increasing the load showing a maximum hump at 80 gm. While indentation is made, the crystal planes slip away from the indentation. The resistance experienced by these slips planes during the indenting and the reaction of the planes to this resistance at the removal of the indenter will depend upon the dislocation densities, dislocation interactions, dislocation intersections and also interplanar spacing. A hard or soft obstacle for the slip planes may be produced depending on the interplanar spacing and the nature of the dislocation interactions and intersections. In the case of hard obstacle, the slip planes may rebound as soon as the indenter is removed, thus decreasing the length of the indentation diagonal. In the case soft obstacle, the slip planes may be easily pushed away from the indentation and the momentum required by them may take them further away from the indentation. This will give a larger length for the indentation diagonal. Hence the real length of the diagonal will be either less or greater than the observed indentation diagonal of the ATFA crystals plots of log p versus log d were drawn by least square fit method as given in Fig.4. The value of 'n' for pure ATFA is 2.32 and that of Mg^{2+} doped ATFA is 1.822. The value of 'n' is greater than 2 for pure ATFA crystals and less than 2 for Mg^{2+} doped ATFA crystals which shows that Mg^{2+} doped crystals are more harder than the pure ATFA crystals .

Using the Meyer's relation

$$P = k_1 d^n \qquad (2)$$

Substituting Eq. (2) in (1) gives

$$Hv = b P (n - 2) / n \qquad (3)$$

We have applied a correction to the observed'd' value so that the Kick's law is satisfied as

$$P = k_2 (d + x) 2 \qquad (4)$$

Substuting the Fq. (2) in the above eq. we get

$$d^{n/2} =(k_2/k_1)^{½} d + (k_2 / k_1)^{½} x \qquad (5)$$

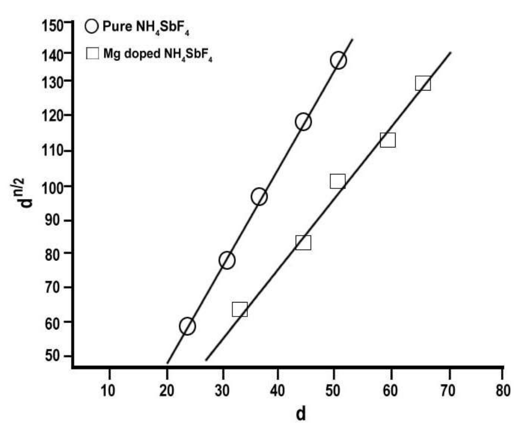

Fig .5 .Plots of d vs. $d^{n/2}$ for pure and Mg^{2+} doped ATFA crystals

As shown in Fig.5, the plots of d versus $d^{n/2}$ are straight lines for both the crystals yield the slope K_2 / k_1 and the intercept of the straight line, 'x' is calculated. The values of k_1 from Fig.6 and the values of k_2 from Fig.7 are given in Table 1.

Crystal	n	x ($\times 10^{-6}$m)	$k_1 \times 10^{-3}$	$k_2 \times 10^{-6}$	$(k_2 / k_1)^{1/2}$
Pure ATFA	2.32	24	264.8	0.0942	45.07
Mg doped ATFA	1.822	20	10.53	0.23387	1.4934

The value of 'x' is positive for both the crystals. The Meyer's index n, which is the work hardening coefficient 'n', is an important factor in studying the strength properties of materials. Work hardening is caused by the dislocations present in the crystal. When 'n' is large, the effect of the dislocation present is also large and hence the slip planes experience a large resistance to slip and they rebound at the removal of the indentation causing a positive 'x'.

Hence we propose

$$x \ \alpha \ (2 - n) \qquad (6)$$

$$\text{i.e.} \quad x = R\,(2-n)$$

where R is a constant which must be characteristic of the crystal. Plots of P versus d^n are shown in Fig.7. The slope yields the value of k_1.

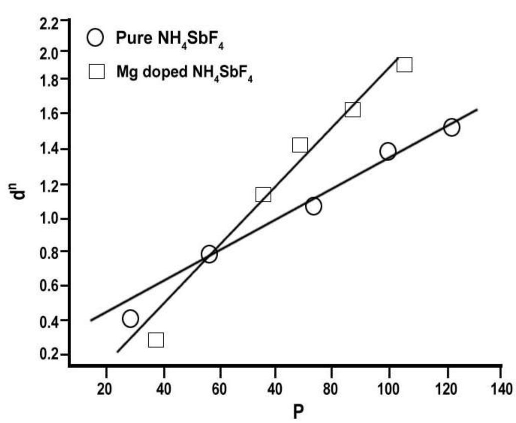

Fig. 6. Plots of P versus d^n for pure and Mg^{2+} doped ATFA crystals

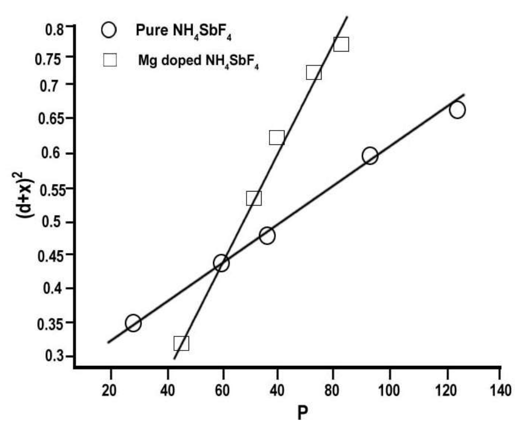

Fig.7. Plots of P versus $(d+x)^2$ for pure and Mg^{2+} doped ATFA crystals

Also the effect of the dislocations may be neglected at higher loads when the energy associated with the indenter is large. Hence as reported by many authors, the microhardness number becomes independent of the load at higher loads.[14]. The approach towards the independence of microhardness with load was reported by various authors [15-17]. The increase and then decrease of hardness at low loads were reported by various authors [18-19]. When the load is small, the energy associated with the indenter is low and hence the dislocations at the point of indentation will not allow the indenter to penetrate further. The resistance offered by the dislocations for indentation increases with load and it may have a limiting value which is independent of factors like nature of the crystal structure, dislocation interactions, dislocation intersection etc. when the load has a value more than what this resistance can with stand, the dislocations move away allowing the indenter to penetrate further and hence the hardness decreases.

A plot drawn between (d+ x) and $d^{n/2}$ is shown in Fig.8. The slope of the plot gives the ratio of $(k_2 / k_1)^{½}$.

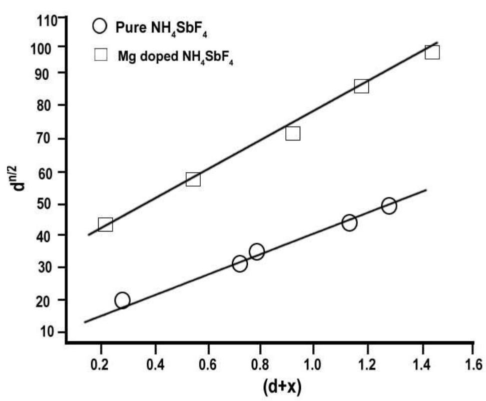

Fig .8. Plots of (d+x) versus d $^{n/2}$ for pure load P and Mg^{2+} doped ATFA crystals

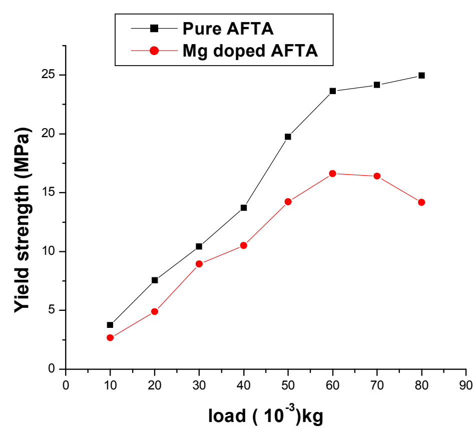

Fig.9. Plot of Yield strength versus for pure and Mg^{2+} doped ATFA crystals

The microhardness value correlates with other mechanical properties such as elastic constants and Yield strength (σ_v) is one of the property for device fabrication. The Yield strength of the material can be calculated using the relation

$$\sigma_v = Hv / 2.9 \{1 - (2 - n) [12.5 (2\text{-}n)/1\text{-}(2\text{-}n)]^{2-n} \} \qquad (7)$$

where Hv is the hardness value and n is the micro hardening index . A plot between load and yield strength is shown in Fig.9. The yield strength increases with increase in load for both the crystals. The elastic stiffness constant (C_{11}) gives an idea about tightness of bonding between neighbouring atoms. The stiffness constant for different loads has been calculated using Wooster's formula (20)

$$C_{11} = (Hv)^{7} / 4 \qquad (8)$$

A plot drawn between load and stiffness constant is shown in Fig.10.

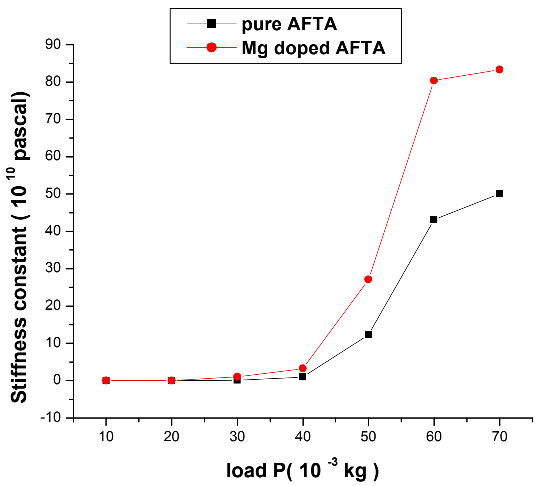

Fig 10. Variation of stiffness constant versus load for pure and Mg doped ATFA crystals

The stiffness constant increases with increase in load and its value is higher in Mg^{2+} doped crystals than that of the pure ATFA crystals. The yield strength and the Stiffness constant of both the crystals are given in Table 2.

Load P x 10^{-3} Kg	Yield strength σ_v (MPa)		Stiffness constant C_{11} (Pascal)	
	Pure AFTA	Mg doped AFTA	Pure AFTA	Mg doped AFTA
10	3.754	2.661	0.00010	0.0000217
20	7.558	4.887	0.014720	0.015306
30	10.428	8.934	0.1402	1.0430
40	13.721	10.509	0.9575	3.250
50	19.759	14.229	12.29	27.118
60	23.643	16.618	43.177	80.38
70	24.150	16.401	50.086	73.315
80	24.952	14.175	62.958	27.850

Conclusion

Single crystals of Pure and Mg^{2+} doped Ammonium Tetra Fluoro Antimonates ATFA is grown by slow evaporation technique. Both the crystals crystallize into monoclinic structure. The microhardness study shows that the hardness steadily increases and then decreases for higher loads. The hardness values are higher for Mg^{2+} doped crystals and this shows the Mg^{2+} atoms makes the ATFA lattice harder than the pure AFTA. The work hardening coefficient 'n' is found to be 2.32 for pure ATFA and 1.822 for Mg doped ATFA which shows that the addition of alkali impurity hardens the lattice of ATFA crystals. k_1, k_2 values were calculated. Yield strength and stiffness constant of both the crystals were also calculated and reported.

Acknowledgement

The author thanks Dr.K.Shivaji and Mr. M.Soundararajan,Department of Nuclear physics, Madras University, Chennai for their valuable help in doing the microhardness studies.

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