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Growth and comparison of physicochemical properties of pure, Ca^{2+} and Sr^{2+} doped $NH_4Sb_3F_{10}$ single crystals for electro optic applications

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ABSTRACT

Single crystals of pure, Ca^{2+} and Sr^{2+} doped $NH_4Sb_3F_{10}$ are grown by slow evaporation technique. The effect of dopants on the growth and physicochemical properties also have been investigated and reported for the first time. The grown crystals are characterized with the aid of single crystal X-ray diffractometry to confirm the crystal structure. EDAX studies are done to confirm the presence of dopants in the crystal lattice. The vibrational frequencies of various group ligands in the crystals have been derived from the Fourier transform infrared (FT-IR) spectrum. From the optical absorption spectrum the band gap energy was calculated and it was found to be 5.76, 6.29 and 6.35 eV for pure, Ca^{2+} and Sr^{2+} doped $NH_4Sb_3F_{10}$ crystals respectively. Thermal stability of the sample has been analysed using TG-DTA analysis. The activation energy of pure, Ca^{2+} and Sr^{2+} doped $NH_4Sb_3F_{10}$ crystals were calculated from the *dc* conductivity measurements and it is found to be 0.2728, 0.2816 and 0.3622 eV Experimental results shows improved physicochemical properties when the dopant is added to the pure material.

1. Introduction

Single crystals are the backbone of the modern technological revolution. The impact of single crystals is clearly visible in industries like semi conductors, optics, etc. Most of the high performance optoelectronic devices are made from crystalline materials [1]. The optical properties of most of the crystals are related to the non stoichiometry of crystals. The electro optic and non linear optical properties such as the change in the refractive indices are also dependent on the concentration of the intrinsic defects [2]. The various stoichiometric compounds of fluoro antimonates possess various unusual electro physical characteristics [3]. Among the extensive class of fluro antimonates, internal motions have been studied inside the fluro antimonates of alkali metals and ammonium [4,5]. Ammonium fluoro antimonates are of interest due to the presence of liable cations NH^{4+} in a crystal lattice leads to higher electrical conductivity and behave as good ionic conductors [6]. The structure, phase transitions and other characteristics of the various combinations of ammonium fluoro antimonates have been investigated by Kavun et al. [7,8]. Super ionic conductivity and phase transition has been reported by Avkhustkii et al. [9]. The growth and microhardness properties of various combinations of ammonium fluro antimonates are studied in detail by Rani Christu Dhas et al. [10,11]. The physicochemical properties of sodium fluoro antimoantes are studied and reported by Benet Charles and Gnanam [12] and Benet Charles et al. [13]. Moreover it is quiet interesting to note that small amount of impurities inhibit the growth of crystals for their inhibition, impurity species are considered to act as obstacles on the surface of the crystal during the displacement of growth steps [14]. Therefore an attempt has been taken for the first time and succeeded to add up Ca^{2+} and Sr^{2+} as dopants with $NH_4Sb_3F_{10}$ single crystals and the effect of dopants on optical, thermal, mechanical and electrical behaviour of the grown crystals are studied and reported for the first time.

2. Experimental procedure

2.1. Growth of pure and doped $NH_4Sb_3F_{10}$ crystals

$NH_4Sb_3F_{10}$ crystals are synthesized by dissolving NH_4F and Sb_2O_3 in the mixture of HF and double distilled water. The required quantity is estimated from the following reaction.

$$NH_4F + 1.5Sb_2O_3 + 9HF \rightarrow NH_4Sb_3F_{10} + 4.5H_2O$$

The calculated amount of salt is dissolved in de-ionized water. The solution is stirred well using a magnetic stirrer. And this solution is kept at a slightly higher temperature and then allowed to

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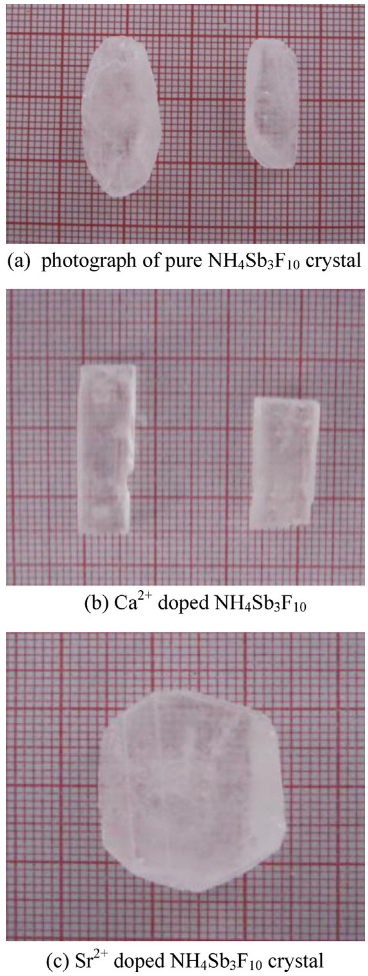

Fig. 1. Photograph of as grown single crystals of pure, Ca^{2+} and Sr^{2+} doped $NH_4Sb_3F_{10}$ single crystals: (a) photograph of pure $NH_4Sb_3F_{10}$ crystal; (b) Ca^{2+} doped $NH_4Sb_3F_{10}$ and (c) Sr^{2+} doped $NH_4Sb_3F_{10}$ crystal.

cool to the room temperature. The crystal is grown by slow and controlled evaporation of the solvent in the constant temperature bath. Clear and transparent single crystals have been grown in a period of one month. For the growth of doped crystals, CaF_2 and SrF_2 are used as dopand material. The growth of metal substituted crystal is achieved by adding dopants of 2% of CaF_2 and SrF_2 to the pure solution of $NH_4Sb_3F_{10}$ respectively. The saturated solution with dopants also prepared as mentioned above and allowed to evaporate. Colourless optically good quality single crystals are grown and shown in Fig. 1.

2.2. Characterization

The single crystal XRD data of the pure and Ca^{2+} and Sr^{2+} doped $NH_4Sb_3F_{10}$ single crystals are obtained to find the lattice dimensions using ENRAF NIUS CAD-4 X-ray diffractometer. In order to confirm the presence of Ca^{2+} present in the crystal lattice, the grown samples are subjected to Energy dispersive X-ray analysis using JOEL-6360 Scanning Electron Microscope. The various functional groups are identified from FT-IR analysis. The powdered specimen of pure and Ca^{2+} and Sr^{2+} doped $NH_4Sb_3F_{10}$ crystals was subjected to FT-IR analysis by using Perkin Elmer RX9 Fourier Infrared Spectrometer. The optical behaviour of the grown crystals is studied by optical absorption studies using Shimadzu UV-1800 UV-VIS-NIR spectrophotometer. The mechanical properties of the grown crystals are studied using a SHIMADZU HMV-2000 micro harness tester fitted with a Vickers diamond pyramidal indenter. The hardness number (H_ν) of the material is determined by the relation, $H_\nu = 1.8544p/d^2$ kg/mm^2, where p is the load applied in kg and d is the diagonal length of the indentation impression in mm. Thermal behaviour of the pure and doped $NH_4Sb_3F_{10}$ crystals are studied by analysing the TGA and DTA using the instrument Perkin Elmer Thermal Analyzer in nitrogen atmosphere at a heating rate of 5 °C/min from 5 °C to 600 °C. Electrical conductivity of the samples is studied by measuring *dc* current from the sample using an HIOKI 3532 LCR Hitester with a conventional two terminal sample holder.

Table 1
Lattice parameters of pure Ca^{2+} and Sr^{2+} doped $NH_4Sb_3F_{10}$ crystals.

Sample name	*a* (Å)	*b* (Å)	*c* (Å)	Volume
Pure $NH_4Sb_3F_{10}$	7.952	13.830	8.789	956.2
Ca^{2+} doped $NH_4Sb_3F_{10}$	7.912	13.778	8.751	945.4
Sr^{2+} doped $NH_4Sb_3F_{10}$	7.931	13.762	8.764	949.0

3. Results and discussions

3.1. Single crystal X-ray diffraction study

The crystallographic data obtained from the single crystal XRD are given in Table 1. From the data, it is confirmed that the pure and doped $NH_4Sb_3F_{10}$ single crystals belong to monoclinic crystal system and the space group is $P2_1/c$. The obtained crystallographic data reveals that there is small change in lattice parameters which indicates the influence of the dopants in the crystal lattice.

3.2. Energy dispersive X-ray analysis

Fig. 2 shows the Energy Dispersive spectrum of Ca^{2+} and Sr^{2+} doped $NH_4Sb_3F_{10}$ single crystal. From the spectrum, the characteristics X-ray peaks of Ca^{2+} is obtained for the input energy value

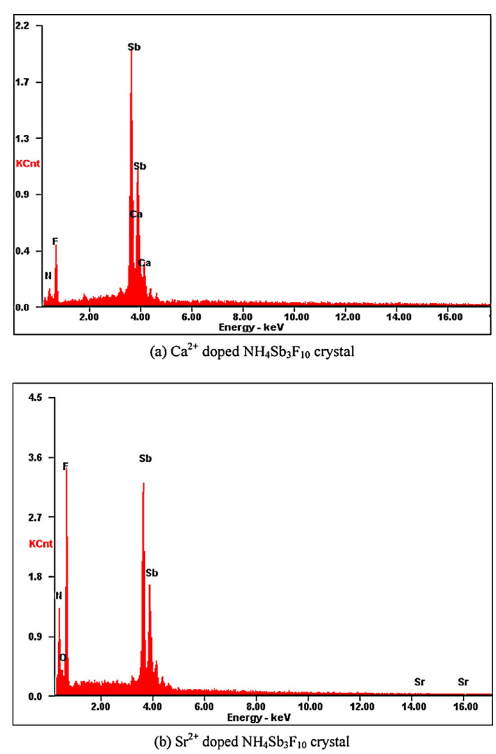

Fig. 2. EDAX spectrum of Ca^{2+} and Sr^{2+} doped $NH_4Sb_3F_{10}$ crystal: (a) Ca^{2+} doped $NH_4Sb_3F_{10}$ crystal and (b) Sr^{2+} doped $NH_4Sb_3F_{10}$ crystal.