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Short Communication

GROWTH IMPEDENCE AND SHG STUDIES OF ALUMINIUM FLOURIDE DOPED SODIUM FLUORO ANTIMONATE CRYSTALS

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ABSTRACT

Single crystals of sodium fluoro antimonate and aluminium fluoride doped sodium fluoro antimonate were grown by solution method with slow evaporation technique. Complex impedance has real part of impedance (Z') and imaginary part of impedance (Z'') and these values have been measured using an impedance analyzer at different frequencies and temperatures. Variations of real and imaginary part of impedance (Z') and (Z'') with frequency for ASFA13 crystal at different temperatures are plotted. Nyquist plots have been drawn between Z' and Z'' and these plots are presented. From plots the grain boundary resistance for the sample are obtained to be 50 x10^3 Ω at 30°C, 10x10^3 Ω at 50°C, 5x10^7 Ω at 70°C and 1.3x10^8 Ω at 90°C. The relative second harmonic generation (SHG) efficiency was measured by Kurtz powder technique using an Nd: YAG laser operating at 1064 nm. The relative SHG efficiency value of ASFA13 sample found to be 0.65 times that of KDP.

Keywords: Solution method, Impedance, SHG efficiency

1. INTRODUCTION

Antimony fluoride complexes are the inorganic compounds which exhibit interesting superionic, electrical and optical properties and it has been reported that a number of these complexes has high ionic conductivity [1-3]. These complexes may produce different purpose materials which include piezoelectric, ferroelectric and biologically active materials [4-6]. Ammonium penta fluoro diantimonate has shown superionic conductivity and it is reported that the phase transitions are at 257 K and 398 K and these successive phase transitions are due to the reorientations of NH_4^+ and $[SbF_5]^{2-}$ groups [7]. The potassium fluoro antimonate such as $KSbF_4$ and $K_3Sb_4F_{15}$ are also observed to be showing high ionic conductivity [8]. Growth and microhardness studies of $NaSbF_4$, $NaSbF_5$, $NaSb_2F_7$ and $Na_3Sb_2F_9$ have been reported in the literature. Microhardness and correction to the diagonal length of the indentation impression of $Na_2Sb_2F_8$ crystals have been reported by Benet Charles *et al*. [9, 10]. Many attempts have been made to find new ultraviolet (UV) and deep ultraviolet (DUV) nonlinear optical crystals. Compared with oxide crystals, fluoride complex crystals have larger band gap, therefore they are suitable for DUV harmonic generation. However, they have small second harmonic coefficients, which is unfavorable for obtaining high power output at the harmonic frequencies [11]. Some of the antimony fluoride compounds can be prepared and studied are $MSbF_4$, M_2SbF_5, MSb_2F_7, MSb_3F_{10}, MSb_4F_{13}, $M_2Sb_3F_{11}$ and $M_3Sb_4F_{15}$ (where M = Na, K, NH_4, Tl, Cs, Rb) [12]. Single crystals of undoped sodium fluoro antimonate ($Na_3Sb_4F_{15}$) and copper chloride doped $Na_3Sb_4F_{15}$ were recently grown and various studies have been carried out by Kumuthini *et al.* [13]. In this work, crystals of undoped and aluminium fluoride doped $NaSb_4F_{13}$ were grown by solution method and the grown crystals were subjected to different studies and the results are discussed.

2. SAMPLE PREPARATION

The precursor chemicals such as sodium fluoride, antimony trioxide and hydrofluoric acid were used for the preparation of $NaSb_4F_{13}$ sample. The reactants were dissolved in double distilled water as per the chemical equation given below and the solution was obtained.

$$2Sb_2O_3 + NaF + 12HF \rightarrow NaSb_4F_{13} + 6H_2O$$

To obtain the aluminium fluoride doped sodium fluoro antimonate (ASFA13) crystals, 3 mole% of aluminium fluoride was added as the dopant into the solution of SFA13. The reactant materials were dissolved in double distilled water and solution was stirred well using a hot plate magnetic stirrer at 35°C. The saturated solution was kept in a growth vessel and the crystals were grown by slow and controlled evaporation using a constant temperature bath. Transparent and colourless crystals of ASFA13 were obtained and a harvested crystal is shown in the figure1. The growth period was 35 days and seed immersion technique was also used to grow the crystals of ASFA13.

Fig.1: A grown crystal of aluminium fluoride doped sodium fluoro antimonate

3. IMPEDANCE ANALYSIS

Complex impedance has real part of impedance (Z') and imaginary part of impedance (Z") and these values have been measured using an impedance analyzer at different frequencies and temperatures. Generally, the impedance properties of materials arise due to intra-grain, inter-grain, and electrode processes. The motion of the charge carriers could affect dipole reorientation, space charge formation and charge displacement. Thus, the complex impedance formalism allows for a direct separation of the bulk, grain boundary and the electrode phenomena. Therefore complex impedance spectroscopy is a non-destructive but powerful technique to investigate the electrical properties of material over a wide range of frequency and temperature. Usually, equations like (1) complex impedance $Z(\omega)=Z' + jZ''$, (2)complex modulus $M(\omega) = 1/\epsilon(\omega) = M' + jM'' = j\omega C_o Z$, (3)complex admittance $Y^*=Y' + jY'' = j\omega C_o \epsilon^*$, (4)complex permittivity, $\epsilon^* = \epsilon' + j\epsilon''$ are used in the impedance spectroscopy. Here angular frequency $\omega=2\pi f$, geometrical capacitance $C_o=\epsilon_o A/t$ where t is thickness and A is the area of the sample. All the four above equations have real and imaginary parts [14, 15]. Variations of real part impedance (Z') with frequencies for ASFA13 crystal at different temperatures are shown in the figures 2 (a), (b). The frequency dependence of imaginary part of impedance for the sample is shown in the figures 3 (a), (b). The results show that both real part and imaginary part of impedance decrease with increase of frequency. From the figures it is noticed that the impedance values decrease upto 50°C and then these values increase as the temperature of the sample increases and this indicates there is a phase transition between 50°C and 70°C. Nyquist plots have been drawn between Z' and Z" and these plots are presented in the figures 4 (a), (b) and 5 From plots the grain boundary resistance for the sample are obtained to be 50 x10^3 Ω at 30°C, 10x10^3 Ω at 50°C, 5x10^7 Ω at 70°C and 1.3x10^8 Ω at 90°C.

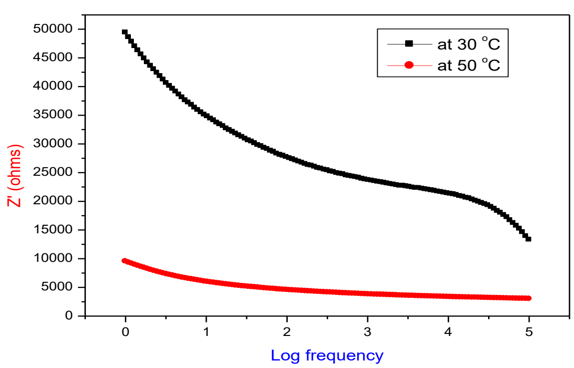

Fig.2 (a)

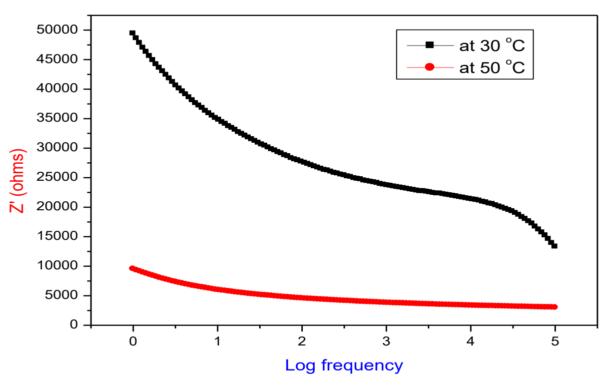

Fig.2 (b)

Fig. 2: Variation of real part impedance (Z') with frequency for ASFA13 crystal at (a) 30°C and 50°C, (b) 70°C and 90°C.

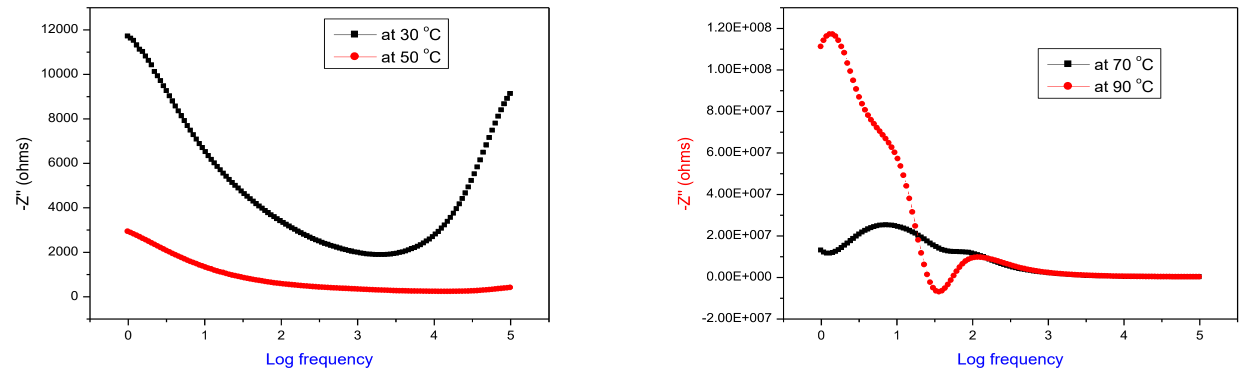

Fig.3 (a) **Fig. 3 (b)**

Fig.3: Variation of imaginary part impedance (Z'') with frequency for ASFA13 crystal at (a) 30°C and 50°C, (b) 70°C and 90°C.

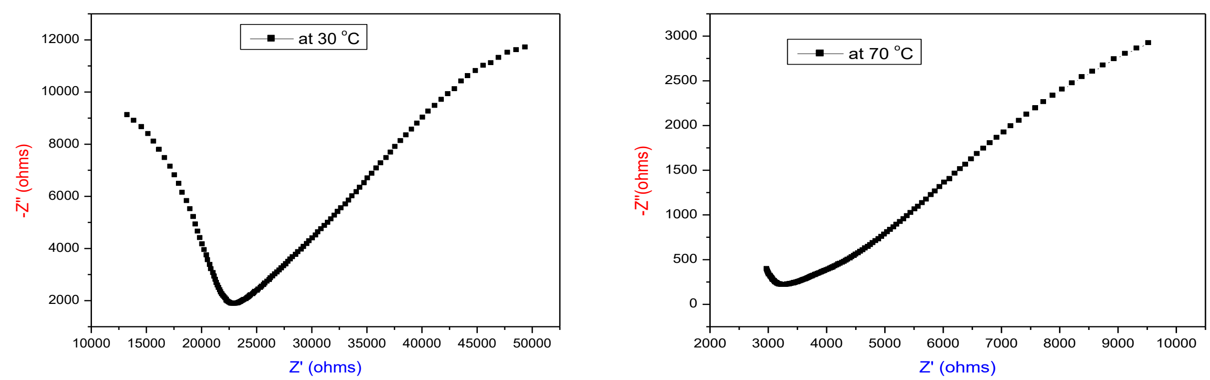

Fig. 4 (a) **Fig. 4 (b)**

Fig. 4: Nyquist plot for aluminium fluoride doped SFA13 crystal at (a) 30°C (b) 50°C

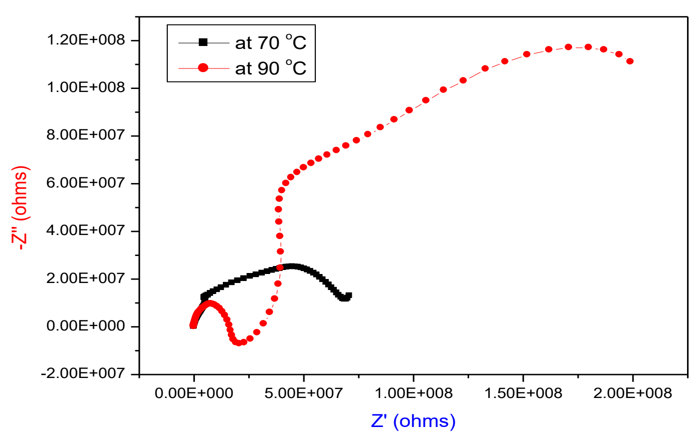

Fig. 5: Nyquist plots for aluminium fluoride doped SFA13 crystal at 70°C and 90°C

4. SHG studies

The relative second harmonic generation (SHG) efficiency was measured by Kurtz powder technique using an Nd: YAG laser operating at 1064 nm. The generation of second harmonics was confirmed as the sample is found to produce green light. The powdered material of KDP was used as the reference material. The relative SHG efficiency value of ASFA13 sample found to be 0.65 times that of KDP.

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