Analysis of the x-ray diffraction, etching, luminescence, photoconductivity, thermal and dielectric properties of an ADP crystal influenced by the bimetallic additive sodium metasilicate (Na_2SiO_3)

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Abstract

The present communication is focused on an investigation of the structural, optical, electrical and thermal properties of a sodium metasilicate (SMS)-doped ammonium dihydrogen phosphate (ADP) crystal. The slow evaporation solution technique has been adopted to grow the crystal with an optimum size of $(10 \times 6 \times 4)$ mm^3. The powder x-ray diffraction (PXRD) technique has been employed to confirm the crystalline nature, crystal structure and cell parameters of the crystal ($a = b = 7.53\,(\pm 0.01)$ Å, $c = 7.59\,(\pm 0.03)$ Å). The color-centered photoluminescence nature of the SMS-doped ADP crystal has been examined in the visible region of interest at an emission wavelength of 375 nm. Its frequency-dependent dielectric response has been investigated with reference to a pure ADP crystal to explore optoelectronic device applications. The thermal stability of the crystal has been examined by means of simultaneous thermogravimetric and differential thermal analysis, and its surface quality has been investigated by means of etching studies. Finally, photoconductivity studies have been employed to determine the nature of photoconductivity in the crystal.

1. Introduction

Ammonium dihydrogen phosphate (ADP) is a technologically vital nonlinear optical (NLO) crystal in great demand for frontier industrial applications involving the design of optical modulation, optical switching, optical data storage, telecommunication accessories and integrated photonic devices [1, 2]. The booming demand for high-performance, efficient and durable crystals for industrial applications has established a culture of constant research in order to obtain the high-quality materials desired for device fabrication. ADP is a potential crystal with tetragonal symmetry (I42d space group) that exhibits high optical homogeneity, large nonlinearity, low dielectric response and appealing physico-chemical traits. Recent research has been intensely focused on achieving improvements in the properties of the ADP crystal, and this has been accomplished either by using different growth techniques or by adding selected ratios of organic/inorganic impurities. Recently, the influence of glycine on the structural, optical, dielectric and thermal properties of the ADP crystal has been reported [3]. The UV–visible, SHG efficiency and third order nonlinear optical response of an $_L$-lysine-doped ADP crystal has been explored [4]. A detailed comparative study of the different mole concentration of $_L$-proline- and $_L$-tartaric-acid-doped ADP crystals has recently been achieved by a group of researchers [5, 6]. A keen survey of the literature reveals that metallic dopants have an influential effect on the structural, electrical, optical and physical properties of the host material. More precisely, the doping of metallic additives largely favors improvements in the physical properties of the ADP crystal. A large variety of metallic additives such as Na^+ [7], K^+ [8], Ni^{2+}

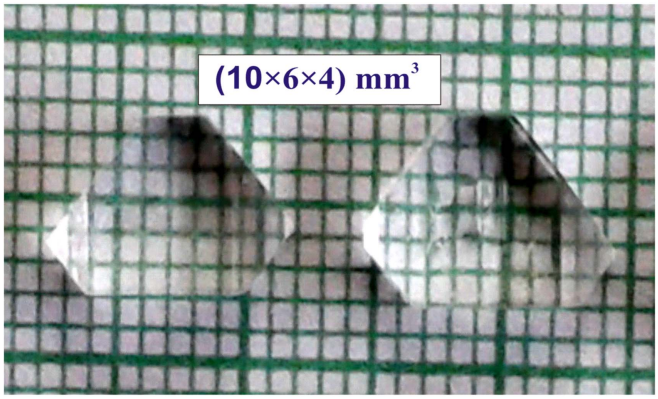

Figure 1. As-grown SMS-ADP crystals.

[9, 10] and Co^{2+} [11, 12] have been used to modify the distinct properties of the ADP crystal. As significant results have been observed in single-metal-ion-doped ADP crystals, our group first reported the doping of the bimetallic impurity sodium metasilicate (SMS) in ADP crystals and observed a large improvement in optical transparency, SHG efficiency, dielectric response and mechanical properties [13]. However, investigations into powder x-ray diffraction, color-centered photoluminescence emission, photoconductivity and the thermal stability of SMS-doped ADP crystals has not been reported in the literature. Hence, this communication reports on the extended work that has been done regarding the properties of SMS-doped ADP crystals, work which has been accomplished by means of powder x-ray diffraction (PXRD), TG/DTA, photoconductivity, dielectric and photoluminescence characterization studies.

2. Experimental procedure

A supersaturated solution of ADP was prepared at room temperature by dissolving the Merck made AR grade ADP salt in double deionized water stirring at constant speed. A precisely measured quantity of 0.1 mole% of SMS was added to the supersaturated solution of ADP in steps. This solution was agitated for six hours by continuous stirring at a uniform speed. The homogeneous SMS-doped ADP solution was filtered in a rinsed beaker using Whatman filter paper and kept for evaporation in a dust-free and isothermal environment to facilitate the growth of a crystal with fewer defects and an enriched optical quality. Figure 1 shows good quality SMS-doped ADP (SMS-ADP) crystals grown in a period of two weeks. The doping of the additive in a specific quantity shows its direct effect on the physical parameters (cell dimension, morphology and crystalline quality) of the host crystal. In the case of the ADP crystal, a slight change in morphology due to the addition of several additives is the more common phenomenon, as reported earlier [11, 14]. This is identical to what is observed in an SMS-ADP crystal.

3. Results and discussion

3.1. Powder x-ray diffraction (PXRD) analysis

PXRD analysis is a crucial tool, as the plane wave dynamical theory of x-ray diffraction helps to identify the defect-centered crystalline nature and structural purity of the material [15, 16]. Hence, for the PXRD pattern of the SMS-ADP crystal, material has been recorded in the 2θ range of 8°–55° using a Rigaku Miniflex II powder x-ray diffractometer, as shown in figure 2(a). The indexing of the identified major peaks has been done using PowderX software. The materials grown at lower temperatures possess ample structural grain boundaries, which actively affect the diffraction pattern, in particular the crystalline purity of the grown crystal. The sharper and fewer full width half maxima diffraction peaks of the SMS-ADP crystal material might have been expressed due to the lesser grain boundaries, and this is the most desirable parameter for enhancing the crystalline nature of a grown crystal [17]. Analysis of the PXRD pattern revealed that the grown SMS-ADP crystal has a tetragonal crystal structure oriented in the I42d space group. The evaluated cell parameters of the SMS-ADP crystal are in good agreement with the reported values [13], as discussed in table 1.

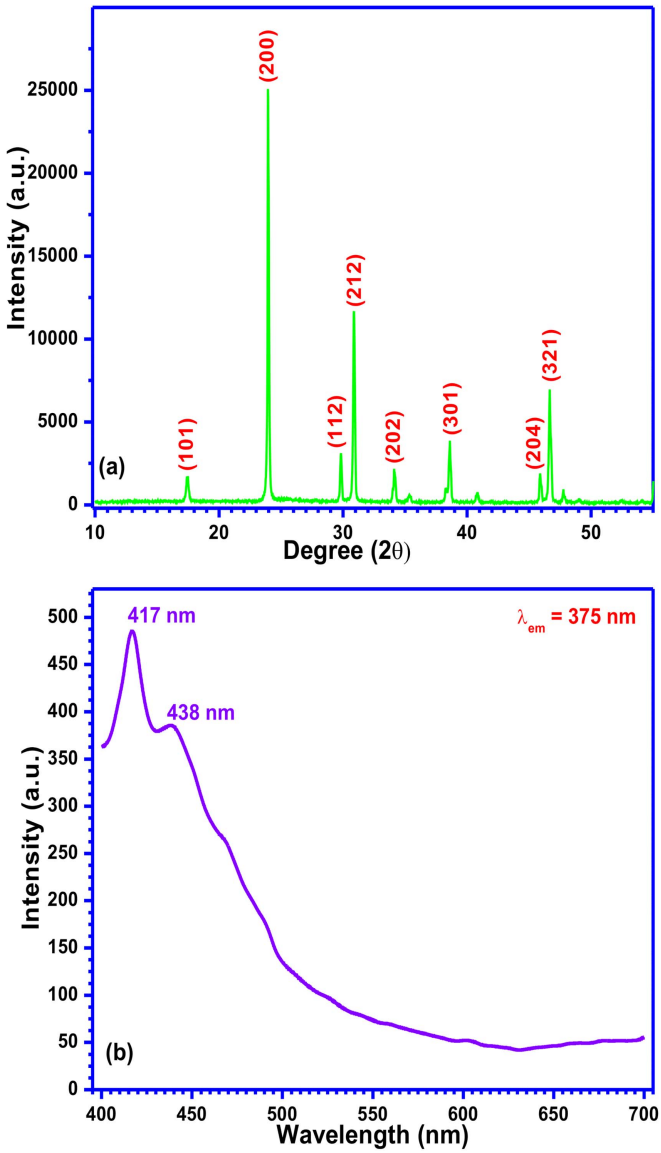

Figure 2. (a) The PXRD pattern of the SMS-ADP crystal; (b) the PL emission spectrum of the SMS-ADP crystal.

Table 1. Crystallographic data.

Crystal	Crystal system	Cell parameters (Å)	Volume (Å)^3	Reference
ADP	Tetragonal	a = b = 7.51, c = 7.56	426	[13]
SMS-ADP	Tetragonal	a = b = 7.52, c = 7.61	430	[13]
SMS-ADP	Tetragonal	a = b = 7.53 (±0.01), c = 7.59 (±0.03)	430	Present study

3.2. Photoluminescence (PL) study

The later occurrence of specific radiative relaxation to the optical excitation of the material demonstrates the promising feature of photoluminescence. A PL emission study at a selected wavelength is a potential technique for unveiling the quality of the material, the associated impurities and the recombination of the electron transition [18], which play a crucial role in photonics, biomedical and chemical applications [19]. In the present analysis, the SMS-ADP crystal sample was photo-excited with an energy wavelength of 216 nm (5.75 eV) and the emission spectrum (figure 2(b)) was recorded in the range of 400–700 nm at 375 nm. The observed major intensity peak centered at 417 nm corresponding to the photon energy of 2.97 eV confirms the prominent violet-colored radiative relaxation emission in the SMS-ADP crystal. The shoulder peak at 438 nm might have occurred due to a recombination of the transition occurring due to defects and active electronic impurities. A single-colored emission with a relatively high intensity is the ideal quality of SMS-ADP crystal for device applications.

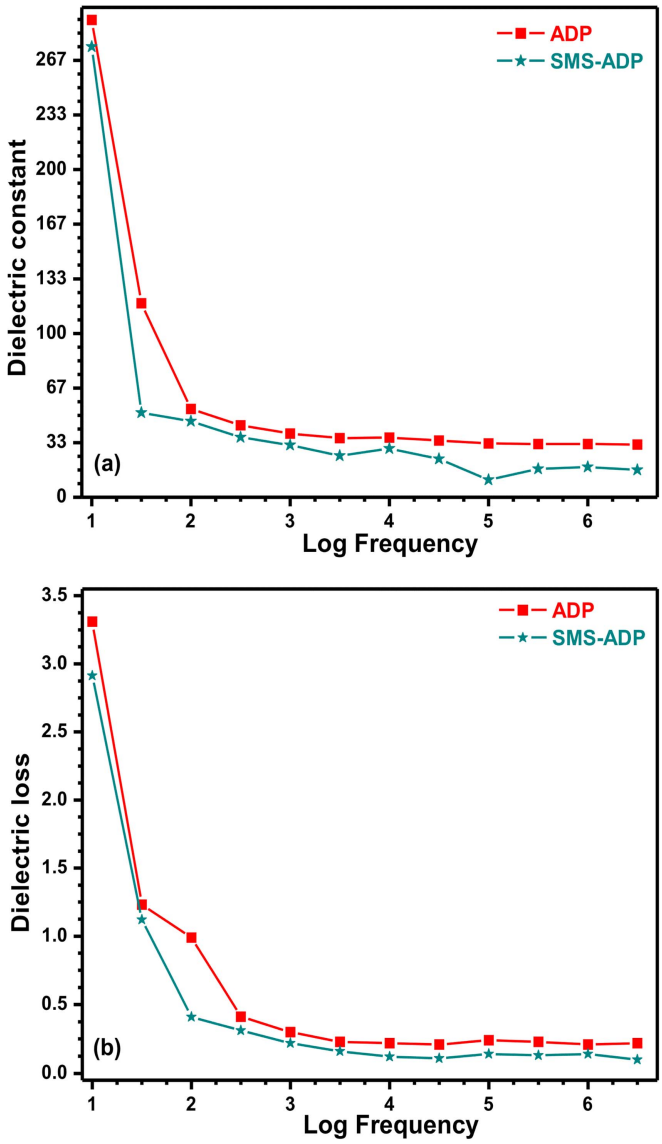

Figure 3. Frequency-dependent (a) dielectric constant, and (b) dielectric loss.

3.3. Dielectric measurements

The pure and the SMS-ADP crystal sample were subjected to dielectric measurement at room temperature using a Gwinstek-819 LCR cubemeter. In order to measure the dielectric constant, the plane and smoothly faced single crystals were coated with a silver paste to ensure accuracy in the data accumulation. The dielectric properties of the material give collective information about the loss of electromagnetic power in the material medium facilitated by the defect centers associated with crystals, and thus serve a vital role. The dielectric constant originates from a change in the relaxation time of the molecular dipoles, governed by the electronic, ionic, dipolar and space charge polarization mechanism [20]. The dielectric constant of the pure and SMS-ADP crystal shown in figure 3(a) reveal a high magnitude of dielectric constant at lower frequencies and a lower magnitude of dielectric constant at higher frequencies. The dielectric constant at higher frequencies is lower due to low polarization activity in the higher frequency domain [21]. It is noticeable that the dielectric constant of the SMS-ADP crystal is significantly lower than the ADP crystal. The lower dielectric constant is a vital parameter for designing microelectronics, electro-optic modulators, field detectors, terahertz wave generators and photonic devices [22, 23]. The lower dielectric constant is a favorable parameter for procuring enhanced SHG efficiency in materials, as demonstrated by Miller's study [24, 25]. The frequency response of dielectric loss is shown in figure 3(b). It reveals that the dielectric constant of both the crystals decreases with an increase in frequency. However, the dielectric loss of the SMS-ADP crystal is found to be significantly lower than the ADP crystal. The relatively lower dielectric loss confirms the presence of a minimum defect density and the enhanced optical quality of the SMS-ADP crystal [26, 27].

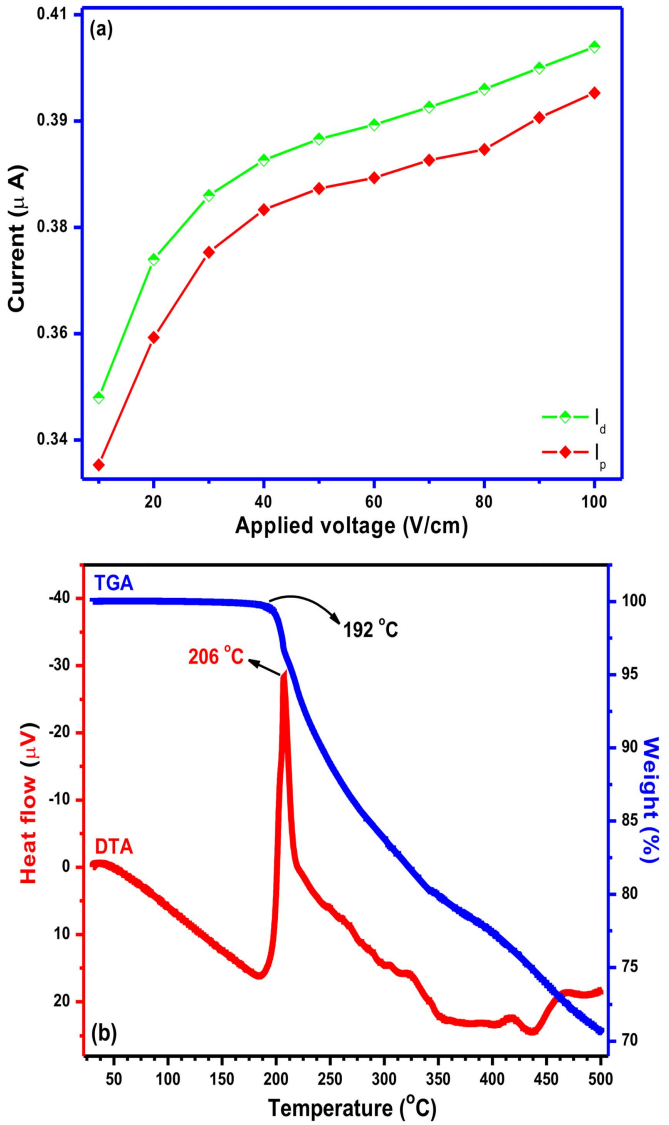

Figure 4. (a) Photoconductivity in the SMS-ADP crystal; (b) a TG-DTA thermogram.

3.4. Photoconductivity study

The nature of photoconductivity in the SMS-ADP crystal was investigated by looping the crystal in series with a high tension power supply and a Kiethley-480 picoammeter. Electrical probes were systematically connected to the crystal surface and a voltage was applied in steps up to 100 V. The voltage was applied in steps of 10 V and the behavior of the dark and photo current was recorded, respectively. The dark current (I_d) was recorded by enclosing the crystal sample in a radiation-free cavity, whereas the same crystal sample was irradiated by a halogen lamp of 100 W to study the behavior of the photo current (I_p). The nature of I_d and I_p in the studied voltage range is shown in figure 4(a). This reveals that the magnitude of dark current is higher with reference to the photo current, confirming the existence of negative photoconductivity in the SMS-ADP crystal. The energy state with a large seizing cross section close to the valence band traps electrons from the conduction band and holes from the valence band, and decreases the mobility of the charge carriers, which is the principle factor responsible for negative photoconductivity [28, 29].

3.5. Thermal studies

The thermal studies of the SMS-ADP crystal material were carried out by employing simultaneous thermogravimetric and differential thermal analysis (TG/DTA) constrained in a homogeneous nitrogen atmosphere. The TG/DTA thermogram of the grown crystal was recorded in the range of 23 °C–500 °C using an SQT-600 thermal analyzer by increasing the temperature at a specific rate (20 °C min^{-1}). The TG/DTA thermogram of the SMS-ADP crystal is shown in figure 4(b). Analysis of the TGA curve reveals that decomposition is stable up to 192 °C. It is noteworthy that an increase in temperature above 192 °C results in a

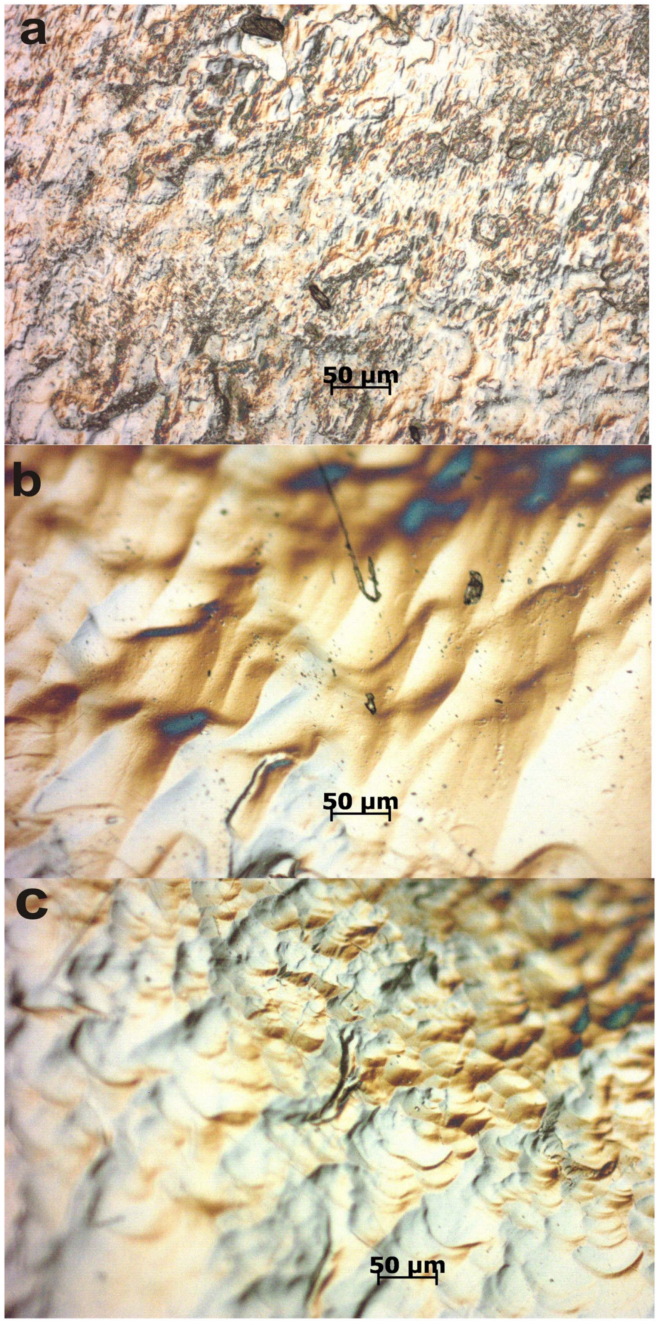

Figure 5. The etch pattern of the SMS-ADP crystal (a) with the surface as grown (b) after 10 s (c) after 20 s.

single stage decomposition up to 500 °C. The DTA curve shows that the SMS-ADP crystal has a sharp endothermic peak centered at 206 °C, which corresponds to the melting point of the SMS-ADP crystal. The absence of an endothermic peak below 100 °C and the sharpness of the peak at 206 °C confirm that the grown crystal is free from solvent inclusions/impurities, and that the crystal is of good quality.

3.6. Etching study

The etch pattern recorded after a regular time interval helps to examine the crystal defects, growth hillocks, etch patterns and reciprocity along the crystal surface [30, 31]. In the present analysis, the micrograph shown in figure 5(a) reveals the presence of a number of inclusions of nonsymmetrical shape and size. The growth of crystals at low temperatures causes the segregation of impurities and solvent inclusions, which appear in the form of irregularly shaped grain boundaries, spiral etch patterns and flat-bottomed etch pits [26, 32]. After etching the crystal surface with water for 10 s, a uniformly layered SMS-ADP crystal growth habit was observed with the absence of etch pits and solvent inclusions. In crystals grown at low temperatures, the change in temperature of the growth medium and the supersaturation density of the solution causes the growth habit to

change, i.e. the etch pattern of the crystal surface [33]. However, 20 s of etching (figure 5(c)) unfolds the evenly ordered growth pattern throughout the crystal surface and the absence of any solvent inclusion confirms the two dimensional nucleation growth habit of the SMS-ADP crystal.

4. Conclusion

Optical quality SMS-ADP crystals have been grown by a slow evaporation solution growth technique at ambient temperature. The observed sharp and high-intensity diffraction peaks in the PXRD analysis confirm the good crystalline nature and high purity of the tetragonal-structured SMS-ADP crystal. In a photoluminescence study of the crystal, the emission spectrum recorded at 375 nm reveals the prominence of a violet-colored emission with peak maxima centered at 417 nm. The dielectric measurement results reveal a decrease in the dielectric parameters with an increase in the frequency. Furthermore, the relatively lesser magnitude of the dielectric constant and the dielectric loss suggest the suitability of the SMS-ADP crystal for optoelectronic device applications. The SMS-ADP crystal is found to exhibit negative photoconductivity in the range of 10–100 V. TG/DTA analysis reveals that it is thermally stable up to 192 °C and its preliminary melting point goes up to 206 °C; an etching study confirmed the two-dimensional growth habit of the crystal. The good crystalline nature, high optical transparency, sufficient thermal stability and lower dielectric constant are highly promising regarding the use of SMS-ADP crystals in microelectronics, photonics and NLO device applications.

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