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Electron irradiation effects on optical properties of semiorganic antimony thiourea bromide monohydrate single crystals

K. Mahesha Upadhya *, N.K. Udayashankar

Department of Physics, National Institute of Technology Karnataka, Surathkal, P.O. Srinivasnagar, Karnataka 575025, India

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ABSTRACT

Antimony thiourea bromide monohydrate (ATBM) single crystals were grown by solution growth technique at room temperature for the first time. The UV–vis, FT-IR and fluorescence spectra were recorded and electron irradiation effects on these properties were studied. The optical absorption edge of the UV–vis spectrum shifts towards lower wavelength with the increase of irradiation. The fluorescence quantum yield is increased for electron irradiated ATBM crystals. The FT-IR analysis shows that the water of crystallization is weakly bonded in as-grown and electron irradiated ATBM crystals.

1. Introduction

In recent years, the interest for practical application of MeV electron bombardment is due to its potential in tuning the various properties of the materials. The irradiation of crystals by MeV electron beam introduces defects in crystals [1–3]. This produces changes in electrical conductivity and optical properties depending upon the extent of damage caused and their penetration depth of electrons which varies with both energy of the electron and the atomic number of the material under consideration [4–6].

Single crystals of some inorganic complexes of thiourea are gaining importance in recent years because of their unique optical properties [7–9]. The knowledge of electron irradiation effects on these crystals is important from the viewpoint of their optical efficacy. The thiourea molecule is an interesting inorganic matrix modifier due to its large dipole moment [10] and its ability to form an extensive network of hydrogen bonds. In the work of growing semiorganic crystals of antimony thiourea bromide monohydrate (ATBM), thiourea which is a typical polar molecule, was selected to combine with antimony bromide. Bhat and Dharmaprakash [11] have grown single crystals of ATBM in sodium meta silicate gel at ambient temperature. Upadhya and Udayashankar [12] have grown single crystals of ATBM by solution growth technique at room temperature and studied its structure by X-ray single crystal diffraction. Up to the present no studies have been addressed to electron irradiation effects on ATBM single crystals. Hence the present investigation is aimed at the electron irradiation effects on optical properties of these single crystals. The authors wanted to confirm the expected change in the crystallinity of the sample, absorption in the UV–vis region, fluorescence quantum yield and position as well as intensity of the peaks in FT-IR spectra after irradiation.

2. Experimental

ATBM crystals were prepared according to the following reaction scheme:

$$Sb_2O_3 + HBr \rightarrow SbBr_3 \xrightarrow{CS(NH_2)_2} Sb[CS(NH_2)_2]_2Br_3 \cdot H_2O$$

For 100 ml concentrated hydrobromic acid, 7 g of antimony oxide was mixed, stirred well and filtered to get antimony bromide solution. This solution is thoroughly mixed with 14 g of thiourea dissolved in 300 ml of distilled water, filtered and kept at room temperature to get yellow coloured ATBM crystals. These crystals were irradiated by pulsed and tangentially accelerated electrons with electron beam energy of 8 MeV produced in Microtron by an alternating radio frequency electric field of constant frequency, in a constant uniform magnetic field [13]. The irradiation is carried out for graded doses of 1, 1.5 and 2 kGy.

The powder X-ray diffraction patterns for as-grown and electron irradiated ATBM crystals were obtained using Rigaku X-ray diffractometer with CuKα radiation ($\lambda = 1.540562$ Å) in the range 10°–50° at 2 °/min. The as-grown and electron irradiated samples were subjected to UV–vis studies in the spectral range

* Corresponding author. Tel.: +91 9900800618; fax: +91 8242474033.
E-mail address: mahesh.upadhya@yahoo.com (K. Mahesha Upadhya).

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190–1100 nm using UV-1800 UV–vis spectrophotometer and the absorption spectra were recorded at the room temperature. The fluorescence spectra were recorded using JASCO FP-6200 spectro-flourometer in the wavelength range 220–700 nm. The FT-IR spectra of as-grown and electron irradiated ATBM crystals were recorded in Nicolet Avatar 330 FT-IR spectrometer in the wavelength range 500–4000 cm^{-1} by KBr pellet technique.

3. Results and discussion

3.1. Structural response

Powder X-ray diffraction patterns of as-grown and electron irradiated (2 kGy) ATBM samples are shown in Fig. 1(a) and (b); 2θ and *d*-spacing values for each peak are shown in Table 1. A truly significant change in the diffraction pattern is observed in the case of sample irradiated at 2 kGy with only two sharp peaks. The disappearance of four X-ray peaks for irradiated sample indicates that the sample starts to amorphize after electron irradiation at this dosage [14–16].

3.2. UV–vis spectra

The results of optical absorption study [17] with UV–vis spectrophotometer carried out on as-grown and electron irradiated ATBM crystals are shown in Fig. 2. From the plot it is observed that the optical absorption edge of the spectrum shifts towards lower wavelength with the increase of irradiation.

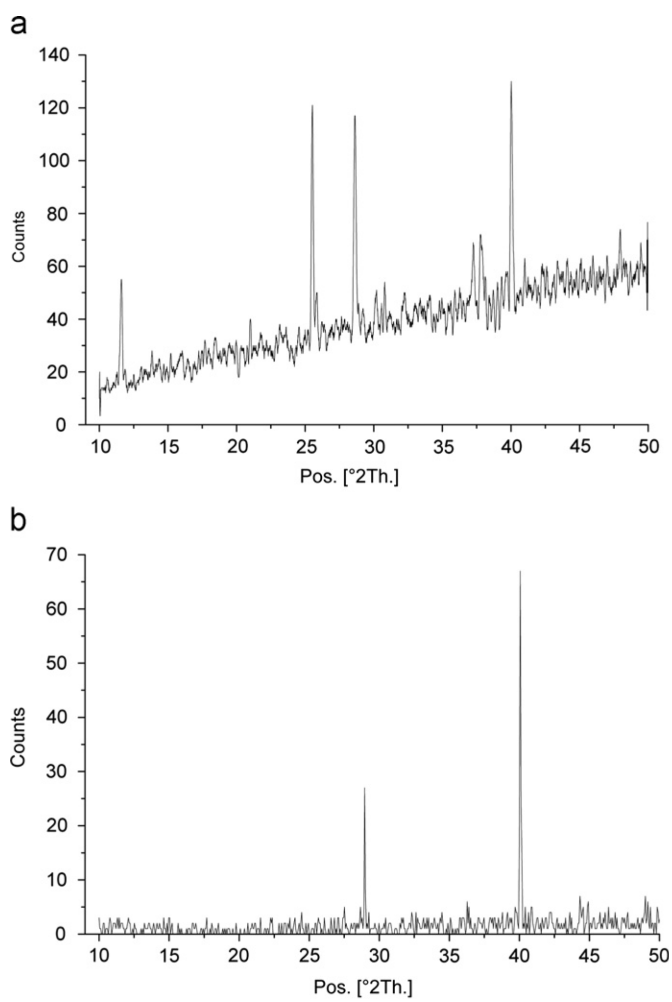

Fig. 1. X-ray diffraction patterns of (a) as-grown and (b) electron irradiated ATBM at 2 kGy.

Table 1
Powder X-ray diffraction data for as-grown and electron irradiated ATBM at 2 kGy.

Peak no.	As-grown ATBM		Electron irradiated ATBM (2 kGy)	
	2θ	*d*-spacing (Å)	2θ	*d*-spacing (Å)
1	11.6076	7.6238	–	–
2	25.5229	3.4901	–	–
3	28.6239	3.1187	28.9413	3.085
4	37.2465	2.4141	–	–
5	37.8483	2.3771	–	–
6	40.0163	2.2513	40.0821	2.2495

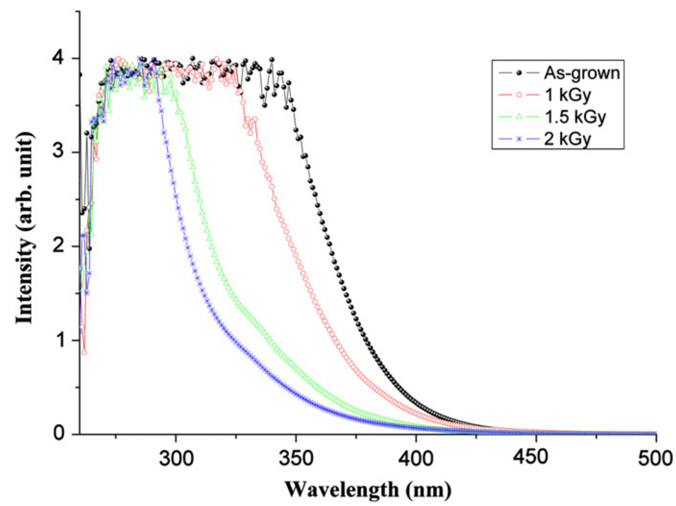

Fig. 2. UV–vis spectra of as-grown and electron irradiated ATBM at 1, 1.5 and 2 kGy.

3.3. Fluorescence spectra

The fluorescence spectra [18–20] of as-grown and electron irradiated ATBM crystals dissolved in N, N-dimethylformamide with a concentration 5.642×10^{-3} M are shown Fig. 3(a)–(d). One can observe in the fluorescence spectra of as-grown ATBM that there is no noticeable change in the position of the fluorescence maxima corresponding to a change in excitation wavelength. But in the fluorescence spectra of irradiated ATBM, there is a change in the position of the fluorescence maxima corresponding to a variation in excitation wavelength. The fluorescence quantum yield of a sample in solution is determined relative to a standard sample of known quantum yield using the equation [21–23]

$$\Phi_S \equiv \Phi_r \left[\frac{A_r \times I_S}{A_S \times I_r}\right]$$

Here Φ_S=quantum yield of luminescence of the sample, A_S=absorbance at the excitation wavelength of the sample, I_S=relative integrated fluorescence intensity of the sample and the subscript *r* denotes the respective values of the reference substance. Quinine sulfate in 0.5 M H_2SO_4 [24,25] is taken as the reference substance to calculate the quantum yield. The fluorescence quantum yield for as-grown and electron irradiated ATBM crystals were given in Table 2. The fluorescence quantum yield is low for as-grown ATBM crystals when compared to electron irradiated ATBM crystals. This is due to the exponential dependence of the nonradiative decay rate constant on the energy gap between singlet and ground states,

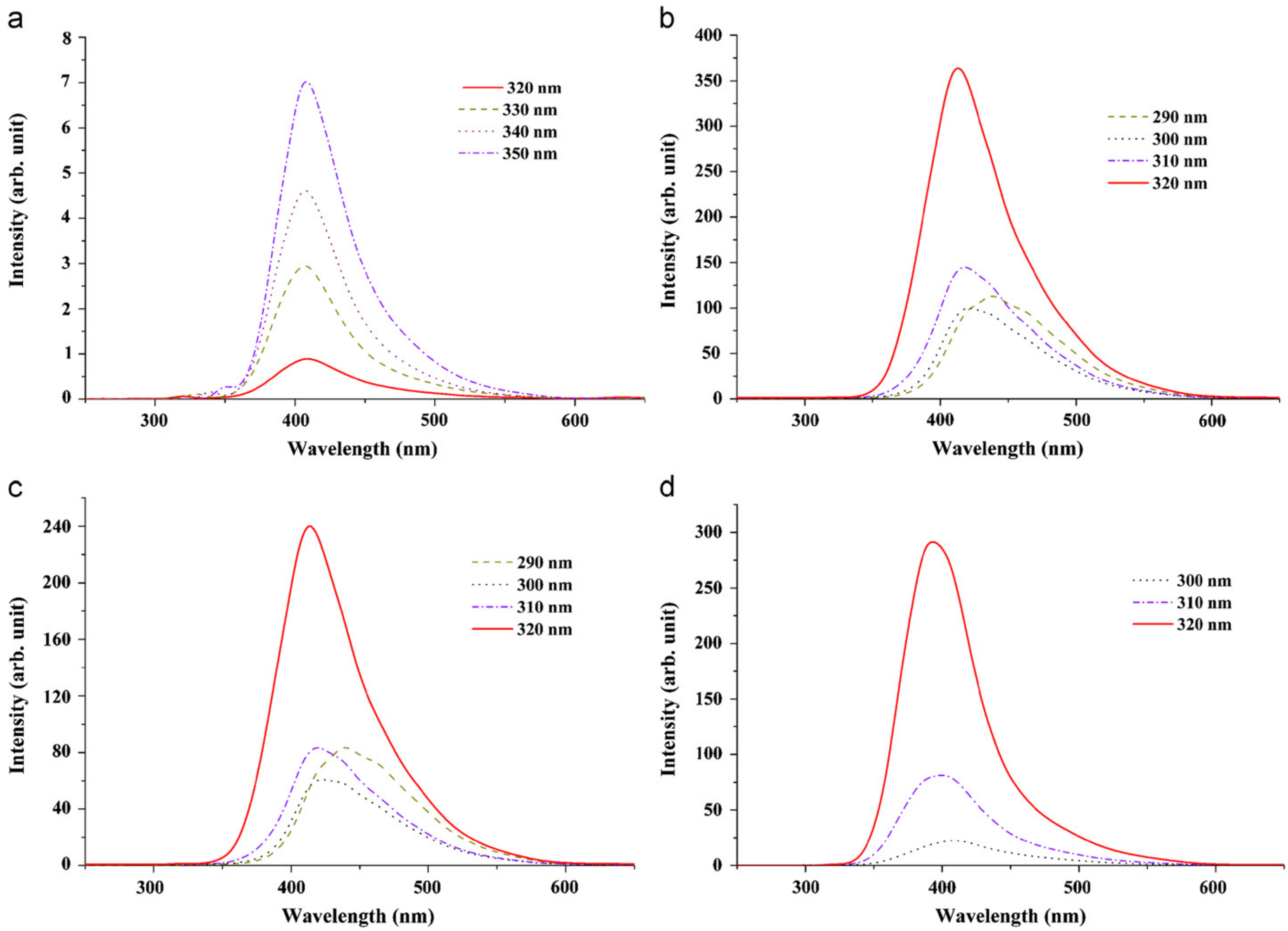

Fig. 3. Fluorescence spectra of (a) as-grown and electron irradiated ATBM at (b) 1 kGy (c) 1.5 kGy and (d) 2 kGy.

Table 2
Fluorescence quantum yield for as-grown and electron irradiated ATBM crystals.

Sample		Excitation wavelength (nm)	Wavelength of fluorescence emission peak (nm)	Quantum yield[a] ($\times 10^{-6}$)
As-grown ATBM		320	409	0.0475
		330	407	0.1407
		340	407	0.1974
		350	408	0.3797
Electron irradiated ATBM	1 kGy	290	438	7.0452
		300	421	5.8574
		310	418	8.2939
		320	413	19.3935
	1.5 kGy	290	439	5.3203
		300	423	3.9071
		310	419	7.4725
		320	414	30.2689
	2 kGy	300	408	2.0210
		310	400	10.6718
		320	393	49.3336

[a] Quinine sulfate in 0.5 M H_2SO_4 is taken as the reference substance to calculate the quantum yield.

which is known as optical energy gap law [26,27]. It can also be noted that as the excitation wavelength is increased, the intensity of the fluorescence maxima is also increased in case of both as-grown and electron irradiated samples.

3.4. FT-infrared spectra

The FT-IR spectra of as-grown and electron irradiated [28] ATBM crystals are represented in Fig. 4(a)–(d). Few peaks were found to be shifted slightly when compared with the spectrum of thiourea [29,30] due to the following reason. The structure of ATBM reveals that antimony bonds with sulphur [12], as most of the metals form complexes via sulphur [31]. Hence the C–S stretching frequency should decrease and that of C–N should increase on complex formation [31]. The absorption at 1618 cm^{-1} due to NH_2 deformation mode is not affected indicating the absence of nitrogen metal bond. Absorption at 1086 cm^{-1} due to NH_2 rocking mode is not affected by the formation of metal–sulphur bond alone. Thus the metal–sulphur bond is assumed to be responsible for the shifting of the vibration at 1412 and 730 cm^{-1} to a lower frequency [31]. Comparison of vibrations of thiourea with as-grown and electron irradiated ATBM crystals are shown in Table 3. Fig. 4(a)–(d) shows clearly the general decrease in intensity of these characteristic peaks of irradiated samples compared to the as-grown crystal. Absorption at 1086 cm^{-1} due to NH_2 rocking mode is not present in irradiated samples.

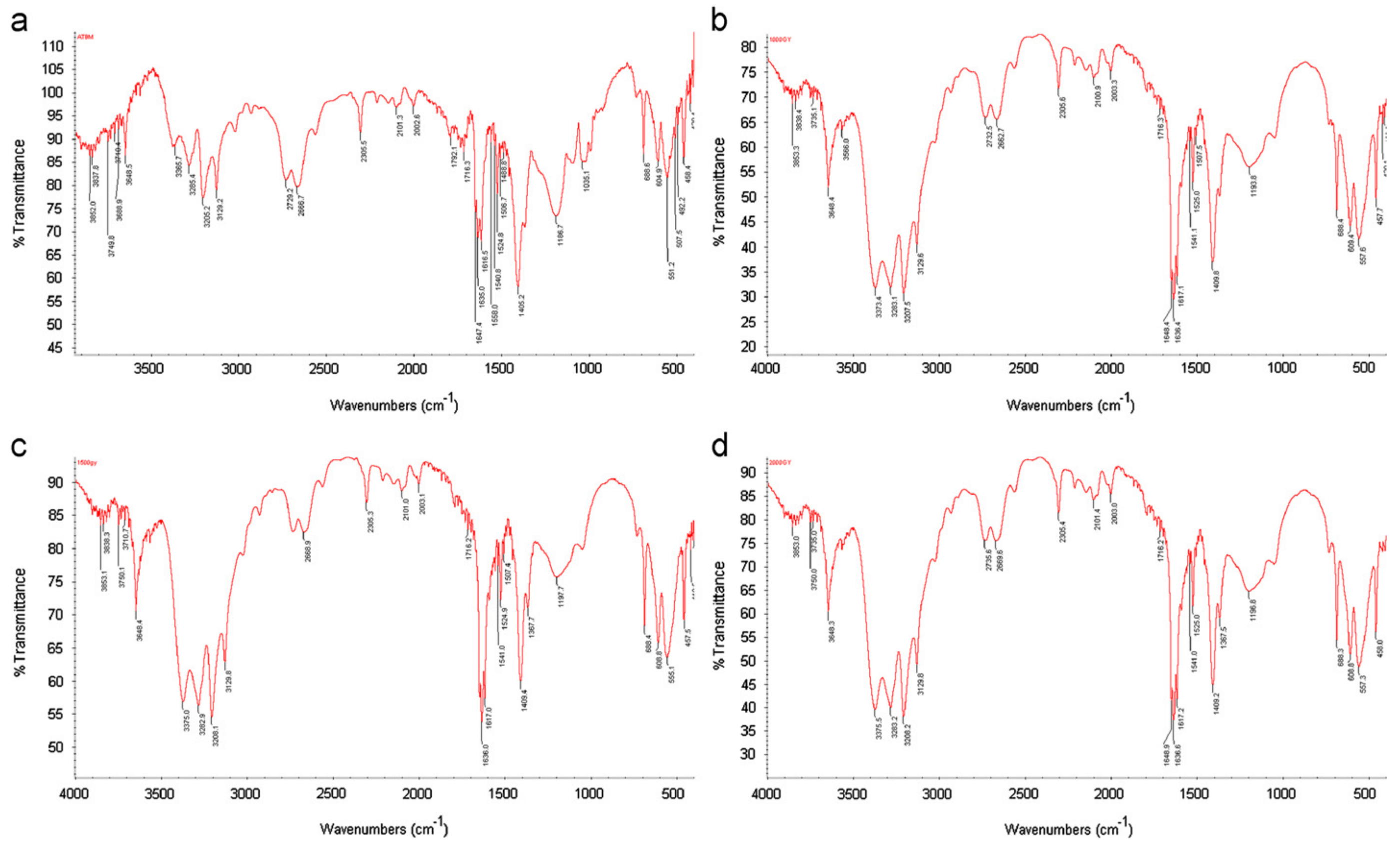

Fig. 4. FT-IR spectra of (a) as-grown and electron irradiated ATBM at (b) 1 kGy (c) 1.5 kGy and (d) 2 kGy.

Table 3
Assignment of IR band frequencies (cm^{-1}) in as-grown and electron irradiated ATBM crystals.

Thiourea	As-grown ATBM	Electron irradiated ATBM			Assignment[a]
		1 kGy	1.5 kGy	2 kGy	
3375	3365.7	3373.4	3375.0	3375.5	ν(N–H)
3280	3285.4	3283.1	3282.9	3283.2	ν(N–H)
1618	1616.5	1617.1	1617.0	1617.2	$\delta(NH_2)$
1471	1524.8	1525.0	1524.9	1525.0	ν_{as}(C–N)
1412	1405.2	1409.8	1409.4	1409.2	ν_s(C–S)
1086	1035.1	absent	absent	absent	$\rho(NH_2)$
730	688.6	688.4	688.4	688.3	ν_s(C–S)

[a] δ—Deformation; ν—band stretching; ρ—rocking; s—symmetric; as—asymmetric.

Table 4
Comparison of H_2O mode vibrations in as-grown and electron irradiated ATBM crystals with isolated water molecule.

Isolated water molecule vibrations (cm^{-1})	H_2O mode vibrations (cm^{-1})				Assignments[a]
	As-grown ATBM	Electron irradiated ATBM			
		1 kGy	1.5 kGy	2 kGy	
500–800	458.4	457.7	457.5	458.0	Wagging of H_2O (ν_L)
	551.2	557.6	555.1	557.3	Rocking H_2O (ν_L)
	604.9	609.4	608.8	608.8	
1643.5	1635.0	1636.4	1636.0	1636.6	ν_2 H_2O
2127.5	2101.3	2100.9	2101.0	2101.4	Combination of ($\nu_L+\nu_2$) H_2O
3404	3648.5	3566.0 3648.4	3648.4	3648.3	ν_1 and ν_3 H_2O

[a] ν_L—librations; ν_1—symmetrical stretching vibration; ν_3—asymmetrical stretching vibration; ν_2—bending vibration [32].

Librational modes viz, rocking, twisting and wagging modes of water molecule can be expected in the 500–800 cm^{-1} region [32–34]. The appearance of stretching modes at wave numbers higher than those of a free water molecule and the bending mode at lower wave number confirm that water of crystallization is weakly bonded in ATBM [33] which is in agreement with the structural analysis [12]. Comparison of H_2O mode vibrations in as-grown and electron irradiated ATBM crystals with isolated water molecule is shown in Table 4.

4. Conclusions

The growth of antimony thiourea bromide monohydrate (ATBM) single crystals is reported. The solution growth technique at room temperature is found suitable for growing ATBM single crystals. The presence of only two X-ray peaks in the diffractogram of sample irradiated at 2 kGy indicates variation in degree of crystallinity of as-grown and electron irradiated samples. From the plot of UV–vis spectra, it is observed that the optical absorption edge of the spectrum shifts towards lower wavelength with the increase of irradiation. It is also observed that fluorescence quantum yield is low for as-grown ATBM crystals when compared to electron irradiated ATBM crystals. FT-IR analysis reveals that electron irradiation results in decrease of intensity of characteristic peaks without causing significant changes in their position. Absorption at 1086 cm^{-1} due to NH_2 rocking mode is not present in the FT-IR spectra of irradiated samples.

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