

## X-ray excited optical luminescence studies on the system $BaXY$ ( $X, Y = F, Cl, Br, I$ )

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**Abstract.** The present paper reports the experimental observations on the x-ray excited optical luminescence (XEOL) along with the afterglow and colour center features found for the barium salts, represented by the formula,  $BaXY$ , where  $X$  and  $Y$  are the halides. The system thus consists of four dihalides ( $BaF_2, \dots, BaI_2$ ) and six mixed halides ( $BaFCl, \dots, BaBrI$ ). To start with, it was found that on two of the binary halides of barium,  $BaClI$  and  $BaBrI$ , no literature exists, and so these were prepared for the first time and their crystal structures were determined. An x-ray generator of 3-kW rating was next coupled to a spectrometer via a high throughput fiberoptic sensor for recording the luminescence spectra under x-irradiation. Also presented in this paper are the observations on the  $BaXY$  compounds in which about 0.1 mole% of  $Eu^{2+}$  was doped, in order to study the efficiency between the prompt luminescence and the photostimulated luminescence in these compounds. The crystal structure varies from fluorite ( $BaF_2$ ), to matlockite ( $BaFX$ ) and finally to orthorhombic ( $BaCl_2, \dots, BaBrI$ ) for these compounds. Hence searching for systematics and empirical relations in the observed XEOL behaviour of these compounds is still a challenging problem.

**Keywords.** X-ray excited optical luminescence; colour centers; barium mixed halides.

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### 1. Introduction

When x-rays interact with matter, all the analogous processes known in geometrical and physical optics have been found to occur. The physical effects are classified as absorption, elastic scattering (diffraction) and inelastic scattering. We are concerned with the absorption of x-rays by the solid and the resulting phenomena. Basically, the absorbed energy is returned by the solid as x-ray fluorescence and optical luminescence, or is stored in the form of colour centers and other defects or is dissipated as heat through a complex process. The phenomenon of light emission is therefore appropriately called x-ray induced optical luminescence, or XEOL for

short, and in the literature on solid-state luminescence, XEOL is considered as a special case of the radioluminescence phenomenon [1-4].

Compared to the x-ray fluorescence method, the XEOL technique is far more sensitive, and was originally intensively developed for application in the study of rare earths. Realising the great potential of the rare earth compounds, it became necessary to measure their (small) concentration in various matrices. X-ray excited optical luminescence resulting from the electronic transitions from the various 4f manifolds of the rare earths proved to be an extremely sensitive method [5,6]. The same effect was also being investigated by high-energy physicists for their applications as scintillators to record fast and ultrafast events. Now, XEOL can be observed even in a pure substance containing no dopant. The luminescence from the pristine material is called *intrinsic luminescence*, and that shown by the dopant is called *impurity luminescence*. Curiously, the rare earth researchers find the intrinsic luminescence to be an interference, and try to eliminate it by heating the sample [7]. In spite of their great practical value, the efficiency with which the phosphors convert x-rays into visible light is quite small ( $\sim 15\%$ ). The physical processes that are responsible for the luminescence in the solid state are only now being understood, and in this context, the simplest type of solids, viz., the alkali halides have served as a testing ground for the various models [8].

There are at least three broad stages, which are now believed to be responsible for the conversion of an x-ray photon into visible light. The first stage consists of the absorption of x-rays by the solid, primarily by the photoelectric effect taking place in about  $10^{-15}$  s. The next stage, occurring in the time interval between  $10^{-15}$  and  $10^{-9}$  s results in the evolution of the x-ray induced electron hole pairs, into bewildering types of defect species. The ability to dislodge lattice ions and create vacancies and interstitials by x-ray photons possessing negligibly small momentum is an intriguing aspect in the radiolysis of halides [9,10]. During this second stage, excitons, colour centers and other defect aggregates are formed. In the third and final stage ( $10^{-9}$  s onwards), the radiation induced defects choose one of the three channels: recombine to produce prompt luminescence, remain as metastable colour centers or decay by a non-radiative process producing only heat. The first process, resulting in XEOL, can occur in two different wavelengths and time-scales for the same material. For example in  $\text{BaF}_2$  the values are (220 nm, 0.8 ns) and (330 nm,  $0.6\mu\text{s}$ ). Another intriguing feature of the XEOL is the persistence of luminescence well after the x-ray beam has been cut off. This phenomenon is termed 'afterglow'. While this effect is undesirable in x-ray imaging as it would produce 'ghost' images due to previous exposure, the 'persistent luminescence' is of practical value if it is induced by the abundant ultraviolet region of the solar energy [11].

Observation of x-ray induced colouration in ionic and insulating crystals and identification of the various colour centers constitutes one of the triumphs in the physics of solids [12]. It was shown that the energy stored in the colour centers could be retrieved by stimulating the solid by the light which is absorbed by the colour centers. The luminescence thus produced is called photostimulated luminescence (PSL). If a dopant, whose excitation wavelength matches with the exciton recombination energy due to the optical absorption by the colour centers is present in the matrix, then the PSL efficiency is highly enhanced. The 4f levels of the rare earths are ideally suited for this purpose. In particular, with europium ions

(occupying the barium sites), the  $4f^7$  levels are excited efficiently by the energy released due to the optical absorption by the halide colour centers. Intense activity in pursuing this field has resulted in achievements such as imaging plate [13–15], colour center lasers [16] and high density storage devices [17].

From the brief description of the present status of the XEOL field given above, it is evident that any study aimed at understanding the first two stages requires advanced and sophisticated equipment as well as single crystal samples [18]. The present paper therefore is concerned with the third stage. The motivation was to choose a representative system such as an alkaline earth halide and study the XEOL, afterglow and colour center behaviour in the entire family of compounds. As there is an ongoing programme in our laboratory to develop an imaging plate reader (based on barium fluorobromide phosphor) for laboratory and industrial applications, barium halides were chosen for this study and the observations made on this system are reported in detail below. It is hoped that this study will stimulate the search for identifying systematics, functional relationships and empirical laws governing these effects.

## **2. Experimental aspects**

### *2.1 Preparation and characterisation of the phosphors*

The four dihalides of barium were procured from reputed firms and standard powder XRD runs were made to ascertain the phase purity. With  $\text{BaCl}_2$  and  $\text{BaBr}_2$ , prior heat treatment is necessary to remove water. The mixed halides were prepared by the solid-state reaction. For europium doping, required quantity of europium halide was added and the procedure adopted for the preparation of the pristine salts was followed. In order to ensure that europium replaces the barium sites in the divalent state, all runs were made in a reducing atmosphere. All the salts could be prepared in high purity alumina crucibles, in an atmosphere of argon+hydrogen, at temperatures around  $800^\circ\text{C}$  and running the synthesis for about 20 h.

Powder x-ray diffraction data were generated using a STOE-make X-ray diffractometer. The XRD patterns taken on 20 samples (10 pristine and 10 doped with  $\text{Eu}^{2+}$ ) to ensure the phase purity, as well as the XPS and photoluminescence checks to confirm the 2+ valence state of europium, can be found in ref. [19]. The crystal structure data for the new compounds  $\text{BaClI}$  and  $\text{BaBrI}$ , which have been prepared for the first time, are available in ref. [20].

The crystal structure data on all the 10 compounds are presented in table 1.

### *2.2 Description of the XEOL spectrometer*

For obtaining the x-ray excited optical spectra on all the samples, the apparatus shown schematically in figure 1 was used. An x-ray generator rated for 60 kV and 50 mA to excite a commercial sealed x-ray tube rated for 1.5 kW, was first built (Metronics Industries, Chennai). A radiation-safe, sample chamber was next designed incorporating a number of features, such as multiple windows for

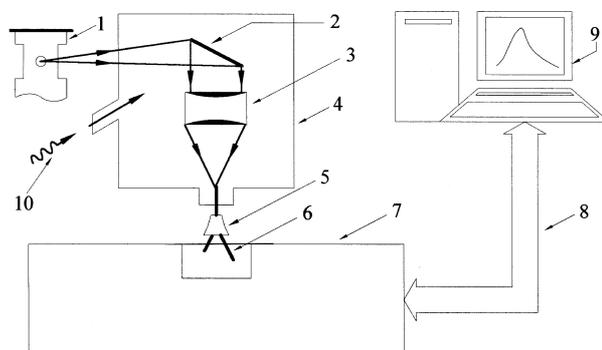
**Table 1.** Crystal structure data on all the 10 compounds of the BaXY system ( $X, Y = \text{F, Cl, Br, I}$ ).

Compound	Crystal structure	Space group	Lattice parameters (Å) at 300 K			Reference
			a	b	c	
BaF <sub>2</sub>	Cubic (fluorite)	Fm3m	6.2001	–	–	(a)
BaCl <sub>2</sub>	Cubic (fluorite)	Fm3m	7.340	–	–	(b)
		Pbnm	9.333	7.823	4.705	(a)
BaBr <sub>2</sub>	Orthorhombic (PbCl <sub>2</sub> )	Pbnm	9.838	8.247	4.948	(a)
		Pbnm	10.566	8.862	5.268	(a)
BaFCl	Tetragonal (PbFCl)	P4/nmm	4.478	–	7.303	(c)
BaFBr	Tetragonal (PbFCl)	P4/nmm	4.503	–	7.435	(d)
BaFI	Tetragonal (PbFCl)	P4/nmm	4.654	–	7.962	(e)
BaClBr	Orthorhombic	Pnma	8.167	4.825	7.498	(f)
BaClI	Orthorhombic	Pbam	17.841	8.441	5.642	(g)
BaBrI	Orthorhombic	P222 <sub>1</sub>	13.667	12.012	10.871	(g)

<sup>a</sup>Wyckoff, R.G., Crystal Structures, 2nd Edition, Vol. 1, Interscience, 1965; <sup>b</sup>International Committee on Powder Diffraction Data, PDF No. 70-1076; <sup>c</sup>ICDD – PDF No. 84-0636; <sup>d</sup>ICDD – PDF No. 76-1288; <sup>e</sup>ICDD – PDF No. 76-0481; <sup>f</sup>ICDD – PDF No. 76-1344; <sup>g</sup>Jestin *et al* [20].

sending and receiving radiation of different types in order to examine photo- and photostimulated- and thermostimulated luminescence from the sample. The light emission from the sample was collected and focussed on to the fiberoptic bundle, which transmitted the light output to a Jobin-Yvon Fluoromax-3 spectrofluorometer.

A fairly large number of parameters are available to the experimenter for setting and monitoring, some of them being, the kV and mA settings of the x-ray tube which govern the quality and the quantity of the x-rays falling on the sample, irradiation time and temperature, the wavelength regions scanned, scanning speed and the polarization of the light emitted when single crystals are used as samples. In this work, all samples were polycrystalline powders and the spectra were recorded at 300 K.



**Figure 1.** Schematic of the apparatus used to record the x-ray excited optical luminescence. (1) X-ray source of a 3 kW x-ray generator, (2) sample holder receiving x-ray beam, (3) lenses to focus the luminescence emission on the fiberoptic sensor, (4) sample chamber with adequate shielding to absorb the unused x-rays and to prevent any stray light from outside reaching the sample, (5) fiberoptic sensor with two arms linked to the excitation and emission monochromators of the spectrometer and the third arm to send and receive light from the sample, (6) light-tight compartment linking the fiberoptic sensor to the entrance and exit slits of the spectrometer, (7) Jobin-Yvon Fluoromax-3 spectrometer, (8) command input and data output link between the spectrometer, (9) PC system and (10) additional port(s) for sending a laser beam to record any photostimulated luminescence from the sample, even while the x-ray beam is ON.

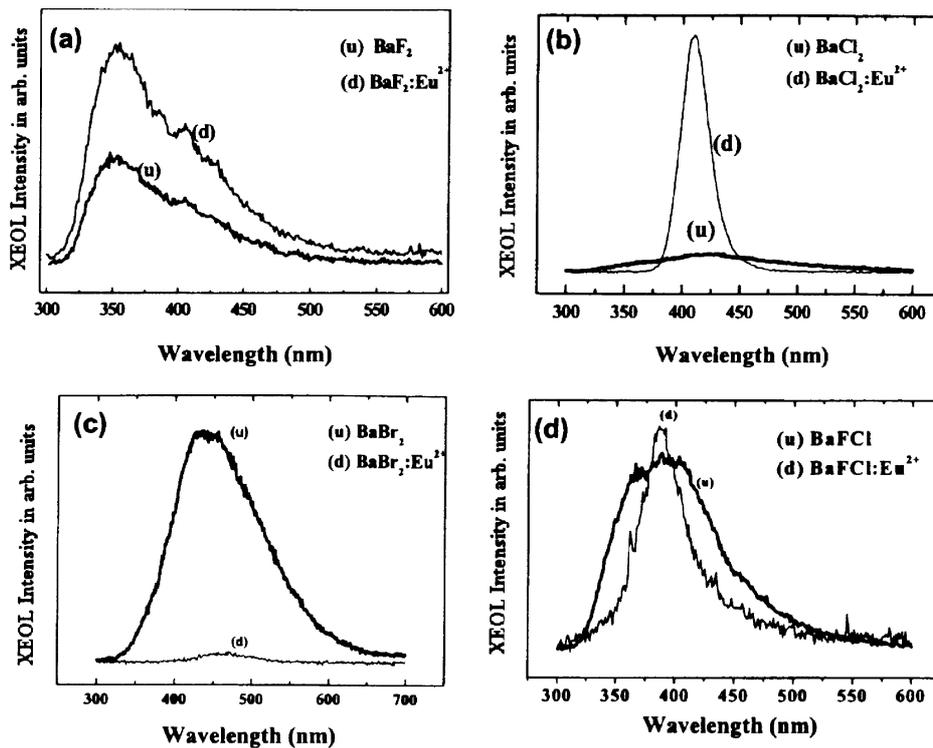
### 3. Observed luminescence spectra for the barium halides

In this section, the x-ray excited optical luminescence spectra of all the 20 compounds obtained at room temperature and for the typical settings of 30 kV and 25 mA of the copper target x-ray tube are presented. The x-ray  $K\alpha$  absorption edges for the five elements are (in keV): 37.4 (Ba), 0.686 (F), 2.823 (Cl), 13.474 (Br) and 33.17 (I). For Ba, Br and I the L-edge absorption will also occur. This aspect can be expected to influence the intensity but not the qualitative features of the luminescence spectra. Conflicting reports can be seen in the literature, but exhaustive studies on the spectral dependence of defect production by x-rays in alkali halides have settled the absorption edge issue by showing that there is no discernible effect [21]. The situation in alkaline earth halides may be assumed to be similar. However, Naftel *et al* [21] find that the XEOL in  $\text{CaF}_2$  reflects the x-ray absorption behaviour of the Ca L-edge. Further studies are needed to examine this aspect. Care was taken to perform a large number of runs by varying the slit width (bandpass) and integration time settings in the spectrometer so as to ascertain reproducibility and to identify and eliminate artifacts. The spectra are reproduced in figure 2 and the panels are designated as 2a to 2i for the compounds. It may be mentioned that except for the fluorine-based salts, to the authors' knowledge, there are no previous reports on the XEOL of these compounds and hence the present

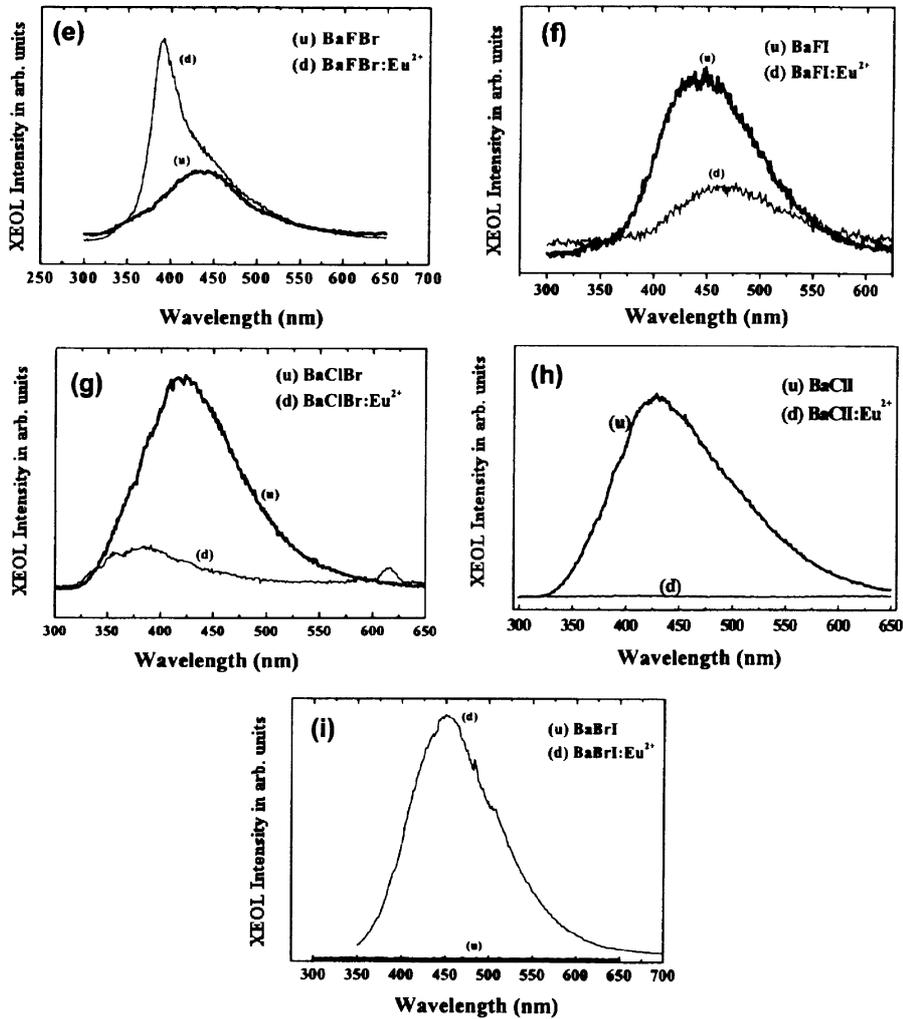
paper reports the first observations. A detailed description for each compound is given below.

### 3.1 $BaF_2$

Figure 2a shows the XEOL spectra for the pristine and doped salts. Pure barium fluoride crystals are known to be fast scintillators [22]. There is a fast component in the UV region at 220 nm with a lifetime of 0.8 ns and hence a PMT with a fast response and having a quartz window can only detect this. This mode of luminescence occurs in insulators in which the core to valence energy separation is smaller than the bandgap. In  $BaF_2$ , the fast component is due to the electronic transition from the  $F^-(2p)$  valence band to the  $5p$   $Ba^{2+}$  core band. With the PMT provided in the spectrometer, only the other XEOL component appearing at 340 nm could be detected. The lifetime of this component is reported to be  $0.6 \mu s$ , and the emission is from the decay of the self-trapped exciton produced by the x-rays. For the doped salt, the same emission could be observed. As the excited states of  $Eu^{2+}$  in  $BaF_2$  lie above the conduction band, the characteristic Eu luminescence does not occur. For detecting ultrafast processes, the presence of the



Figures 2a–d.



**Figure 2.** The observed luminescence spectra of the binary halides of barium excited by x-rays (30 kV, 25 mA). The panels, designated 2a through 2i, contain the spectra for the undoped (symbol u) and  $\text{Eu}^{2+}$  doped (d) samples. The spectra for  $\text{BaI}_2$  are not shown as its XEOL was low and no clear peak could be identified.

slow component needs to be suppressed. It is reported that  $\text{Ce}^{3+}$  doped in  $\text{BaF}_2$  reduces the 340 nm peak [23]. But in the present work, doping with  $\text{Eu}^{2+}$  is seen to enhance the 340 nm peak (figure 2a), and the mechanism is yet to be understood.

The peak observed near 420 nm in the doped sample appears to be caused by traces of oxygen [24] and is therefore not discussed further.

Neither sample showed any detectable afterglow, but they acquired a pale blue colour after prolonged x-irradiation [25].

### 3.2 $BaCl_2$

Anhydrous barium chloride is known to exist in two temperature-dependent structural modifications: the high-temperature cubic beta form crystallising in Fm3m symmetry and the low-temperature alpha form, which is thermodynamically stable at room temperature, crystallises in the Pnam symmetry [26]. Care was taken to ensure that no cubic phase was retained after the dehydration runs, and that the sample was in the orthorhombic structure. Panel 2b reproduces the observed spectra. The pristine sample shows a broad peak around 430 nm but with a low intensity. It appears that in  $BaCl_2$  the excitons decay via a nonradiative channel to the lattice. Upon  $Eu^{2+}$  doping the luminescence peak shifts to 410 nm with a large increase in intensity. Unlike in  $BaF_2$ , the excited states of  $Eu^{2+}$  lie within the forbidden gap. This XEOL emission in  $BaCl_2:Eu^{2+}$  appears in its photoluminescence spectrum, when the excitation wavelength is set at 275 nm, and the emission is from the excited  $4f^65d$  to  $4f^7$  ground state of  $Eu^{2+}$ . The photoluminescence observations were found to be in good agreement with the work of Secu *et al* [27].

The undoped sample showed a more prolonged afterglow and appeared grey after irradiation. In contrast, the doped sample showed no afterglow and looked pale yellow.

### 3.3 $BaBr_2$

Barium bromide crystallises in the  $PbCl_2$ -type orthorhombic structure. The XEOL behaviour of the bromide (figure 2c), in contrast to the chloride, showed that the pristine sample yielded a higher luminescence. The peaks appear at 440 nm and 470 nm respectively for the undoped and doped salts. When excited with a 275 nm radiation, the doped sample gives a good luminescence peaking around 420 nm, confirming that the XEOL is indeed to be associated with europium [27]. There was no afterglow in either sample and both samples turned pale yellow after irradiation.

### 3.4 $BaI_2$

The XEOL intensity for the undoped or the doped  $BaI_2$  for the x-ray tube operated at 30 kV and 15 mA was low and it was difficult to identify any 'peak' in the spectrum. However, when the x-ray tube parameters were raised to 40 kV and 25 mA, a faint blue luminescence could be seen in both the cases. It may be pertinent to add that the difficulty in obtaining a reliable XEOL spectrum could be partly due to the fact that the iodide samples undergo fast photodecomposition when irradiated with x-rays. This effect is quite pronounced when the sample is in the powder form [28]. The samples turned brown and traces of moisture also accelerated these processes, rendering the XEOL observation difficult.

In contrast, for  $BaI_2:Eu^{2+}$ , good photoluminescence spectra could be obtained. Two excitation wavelengths at 270 and 360 nm respectively excited the  $Eu^{2+}$  to  $4f^65d$  ( $t_{2g}$ ) and  $4f^65d$  ( $e_g$ ) configurations; which reach nonradiatively to the same relaxed excited state, and the subsequent transition to the ground state results in the luminescence appearing around 420 nm.

### 3.5 *BaFCl*

The mixed halides of the alkaline earths, with two different halogen ions in the lattice, can develop two types of F-centers and can therefore show more interesting excitonic states compared to the dihalides [29–31]. The fluorine-based mixed halides crystallise in the matlockite (PbFCl) type structure. It can be seen from figure 2d, that both the undoped and doped samples gave comparable luminescence intensity centered at 385 nm. The doped salt shows an additional narrow peak at 363 nm. The 385 nm peak is due to the electronic transition from the  $4f^65d$  state of  $\text{Eu}^{2+}$  to the  $4f^7$  ground state. The narrow peak is ascribed to the intraband transition  ${}^6\text{P}_{7/2} \rightarrow {}^8\text{S}_{7/2}$ . These assignments are again made from the photoluminescence excitation spectra of  $\text{BaFCl:Eu}^{2+}$ . For the  $\text{BaXY}$  system the intraband transition of  $\text{Eu}^{2+}$  is seen only in  $\text{BaFCl}$ . Both the samples showed a substantial afterglow and turned to a pink colour after the irradiation.

### 3.6 *BaFBr*

For the fluorobromide, the undoped salt gave a broad luminescence peak located at 440 nm, while the europium-doped sample showed a pattern which could be decomposed into two Gaussians located at 390 nm and 440 nm (figure 2e). These are ascribed to the electronic transitions from the  $4f^65d$  manifold split by the crystal field to the  $4f^7$  ground state. A photoluminescence run with an excitation of 275 nm resulted only in the 390 nm peak, and the reason for the absence of 440 nm emission in the PL run is not clear.

The literature on  $\text{BaFBr}$  and  $\text{BaFCl}$  is extensive, as both these are materials of practical importance (see refs [13–15]). An aspect worth mentioning is the following: it is well-known that a serious problem in luminescence work is posed by the role played by the unintentional/unavoidable impurities present in the sample under investigation. The effects caused by the impurities may be misinterpreted as an intrinsic mechanism. In this connection, the pioneering work done by Spaeth's group [32] has shown by a variety of magnetic resonance techniques that the luminescence and storage properties of, for example,  $\text{BaFBr}$ , can be ascribed to the presence of  $\text{O}^{2-}$  substituting the halide site. The present authors have also investigated the role of oxygen in the charge compensating mechanism in the intensifying phosphor  $\text{BaFBr:Eu}$  [33].

The undoped  $\text{BaFBr}$  acquired a bluish pink colour, and the doped salt displayed a pink colour after the irradiation. The former showed a short lasting afterglow, while the latter showed a long lasting afterglow.

### 3.7 *BaFI*

Figure 2f displays the XEOL spectra observed for this compound. The peak positions found were at 450 nm and 480 nm respectively for the pristine and doped  $\text{BaFI}$ . The undoped sample showed a substantially higher intensity than the europium-doped compound.

The strong excitonic luminescence in pure BaFI does not seem to transfer its energy when  $\text{Eu}^{2+}$  is doped. Instead, colour center formation is enhanced and the doped salt may be expected to show photostimulated luminescence.  $\text{BaFI}:\text{Eu}^{2+}$ , similar to the other mixed halides, shows a broad peak PL at 450 nm when excited again at 275 nm. The present observation on the doped BaFI is in agreement with the work of Nakano's group [34].

Both the salts displayed an afterglow lasting over several seconds, and both appeared a striking turquoise blue after irradiation.

### 3.8 *BaClBr*

The XEOL spectra of the two compounds are shown in figure 2g. The undoped sample gave a higher luminescence than the doped one. The peaks are located at 410 nm for the undoped and at 390 and 610 nm for the europium-doped samples. The 610 nm peak is unexpected and indicates the possible formation of  $\text{Eu}^{3+}$  during x-irradiation. However, a PL run with an excitation wavelength of 250 nm gave both the 390 and 610 nm peaks in  $\text{BaClBr}:\text{Eu}^{2+}$  indicating the presence of  $\text{Eu}^{3+}$  during the compound formation. Attempts to eliminate the  $\text{Eu}^{3+}$  by synthesising the sample in a strongly reducing atmosphere are in progress. A faint afterglow was observed in BaClBr and no colour centers were formed. In contrast, the europium-doped compound showed no afterglow, but turned grey.

### 3.9 *BaClI*

It was mentioned that BaClI and BaBrI (next section) have been synthesised for the first time. From powder XRD the lattice parameters could be determined. However, as the single crystals are yet to be grown, the actual ionic positions in the unit cell are not known. The XEOL spectra of the pristine and doped BaClI are shown in figure 2h. There was rich XEOL from the undoped sample, while the europium-doped BaClI did not yield any luminescence. The excitonic emission occurs in the undoped specimen at 420 nm. What is remarkable is that while under x-ray irradiation  $\text{BaClI}:\text{Eu}^{2+}$  showed no luminescence, its photoluminescence spectra showed that there are four emission peaks at 409, 425, 433 and 448 nm. It is thus clear that the physical processes governing the XEOL are different from photoluminescence.

The BaClI had a substantial afterglow, lasting over several minutes, while the doped sample showed no afterglow. The former became dark yellow, resembling the appearance of colour centers in NaCl, while the doped salt turned pale yellow.

### 3.10 *BaBrI*

This is the last of the  $\text{BaXY}$  system. The XEOL spectra in figure 2i show a feature in sharp contrast to what was reported for BaClI in the previous section. While the undoped sample showed only a feeble emission even under high power x-irradiation, the doped sample gave a strong luminescence around 450 nm. As the doped samples permit photoluminescence studies, these were performed on  $\text{BaBrI}:\text{Eu}^{2+}$  so as to arrive at the assignments to the emission peaks. The PL runs showed that there

are four emission peaks located at 411, 429, 439 and 458 nm which could be excited by a 270 nm radiation. The XEOL peak shows only a broad emission. Further discussion on the photoluminescence spectra of BaClI and BaBrI can be found in ref. [35]. The samples showed no afterglow features and both turned brown after x-irradiation.

#### **4. Observations of colour center formation in the BaXY compounds**

Formation of colour centers in wide-gap inorganic solids under x- or  $\gamma$ -irradiation, a study of their physical properties and their applications to (colour center) lasers and optical data storage are well-reported in the literature. Single crystals play a vital role in investigating the physics of colour centers in solids.

In the present study, all the samples were in the form of polycrystalline powders. Hence the desirable procedure of measuring the optical absorption after x-irradiation to reveal the features of colour centers features could not be performed. Nevertheless, it was felt that reporting the visual observations on the colour center formation in the BaXY compounds will be useful for two reasons. Firstly one can understand the differences found in the XEOL behaviour between the undoped and doped samples of a given compound as well as that between the different compounds in the BaXY family. The basis for doing this is the anticorrelation between the propensity of colour center formation and the luminescence observed in alkali halides [36,37]. During irradiation, if the colour center formation is high, the XEOL intensity is low and vice versa. Table 2 summarises the visually observed colouration caused by x-rays for all the BaXY compounds and shows that the patterns observed in the XEOL can be qualitatively interpreted.

The second reason why the observations on the colour centers is important stems from the fact that the energy stores in the phosphor can be subsequently photo-stimulated by shining light whose wavelength matches that of the colour center absorption. As mentioned earlier, this is possible only with single crystals. If one does not have single crystals, is there a possibility of identifying the optical absorption by performing thermostimulated luminescence (TSL) measurements? The assumptions made are that the electrons responsible for the colour center will give thermoluminescence and that there is a reliable formula to determine the optical absorption from the temperature at which the glow peaks occur. The relation  $E_{OA}(eV) = 5.16 \times 10^{-3} (K)$  where  $T_g$  is the glow peak temperature is used in [38]. Thermostimulated luminescence runs after the x-ray and also  $\gamma$ -ray exposures are therefore being done on all the BaXY compounds. It is also hoped that the TSL studies will help in understanding the ‘afterglow’ effects observed in barium halides.

#### **5. Discussion**

It has been pointed out that the XEOL in ionic solids arises from three processes, which occur simultaneously: ultrafast core-valence or Auger-free transitions (picosec), slow self-trapped exciton luminescence (microsec) and fast activator (Eu, Ce etc.) luminescence (nanosec). The necessary condition for the first type to

**Table 2.** Summary of the various properties observed during the investigation on the XEOL of barium halides. The symbols u and d stand for the undoped and the doped samples respectively. NAG means, there was no noticeable afterglow from the sample after the x-ray irradiation was stopped. Where available the bandgap values have been shown. The theoretical estimates generally give an underestimate of the actual bandgap.

Compound	$\lambda$ XEOL (nm)	Afterglow	Appearance of colour center	XEOL intensity	$E_{\text{Gap}}$ (eV)
BaF <sub>2</sub>	350	NAG	Dark blue	$I_u < I_d$	10.48
BaF <sub>2</sub> :Eu	350	NAG	Bluish pink		
BaCl <sub>2</sub>	430	Faint	Dirty white	$I_u < I_d$	
BaCl <sub>2</sub> :Eu	410	NAG	Pale yellow		
BaBr <sub>2</sub>	440	NAG	Sandalwood	$I_u > I_d$	
BaBr <sub>2</sub> :Eu	470	NAG	Pale yellow		
BaI <sub>2</sub>	No clearly seen peak	NAG	Pale yellow	$I_u$ and $I_d$	7.75
BaI <sub>2</sub> :Eu		Faint	yellow	Both very low	
BaFCl	385	Substantial	Pink	$I_u \approx I_d$	6.28
BaFCl:Eu	385	Substantial	Pink		
BaFBr	450	Medium	Bluish pink	$I_u < I_d$	8.3
BaFBr:Eu	390, 440	Substantial	Pink		
BaFI	450	Medium	Turquoise blue	$I_u > I_d$	5.1
BaFI:Eu	480	Medium	Turquoise blue		
BaClBr	410	Faint	No change	$I_u \gg I_d$	
BaClBr:Eu	390, 610	NAG	Grey		
BaClI	420	Very long	Dark yellow	$I_u > I_d$	
BaClI:Eu	Low XEOL	NAG	Pale yellow		
BaBrI	Low XEOL	NAG	Brown	$I_u < I_d$	
BaBrI:Eu	450	NAG	Brown		

**Note:** The values indicated in italics for the bandgap are the theoretical values reported by Kalpana *et al* [46] and Hassan *et al* [47].

occur in halides is that the bandgap must be larger than the valence-core energy separation. This is satisfied only for BaF<sub>2</sub> in the BaXY system (the values are 10.5 eV and 6.8 eV respectively).

It is therefore not surprising that intensive research has gone on to use this luminescence for fast scintillator applications [39]. The exciton mode of XEOL, with a decay time of the order of microsec, occurs after a lapse of nine orders of magnitude in time-scale reckoned from the absorption of the primary x-ray photon. As many events take place during this time, the excitonic mechanism is more difficult to interpret. It is now established that the incident photon energy is passed on to the lattice in two ways, one of which gives luminescence and the other produces displacements, and that there is an anti-correlation between their rates. Assuming that the essential entity in the energy conversion is the molecular halide ion which undergoes excitation to form a bound electron-hole pair or an exciton, the long-

lived excited state, before decay, allows momentum conservation by the interaction with the lattice, so that the negligible momentum of the photon is unimportant in the movement of ions. After the absorption of the x-ray photon and production of excited states in the solid, the two competing processes start operating: luminescence or production of colour centers. In alkali halides it is now well-established that at low temperatures XEOL dominates, but above 200 K, the colour center formation takes over.

An important finding concerning the excitons in alkali halides [37], and for BaFBr:Eu<sup>2+</sup>, in particular [40] is that they could be created in the ( $V_k + e$ ) state by ultraviolet photons and that they relax to form F+H pairs. Here,  $V_k$  represents the  $X_2^-$  ion, F, the electron trapped in an  $X$  vacancy and H, the  $V_k$  residing in an interstitial position. Recombination of the F and H center restores the perfect lattice. The threshold energy needed to create excitons of the various halide species has been determined by careful experiments using VUV synchrotron beams, and the data show a decrease in the threshold energy from F to I, for a given cation.

The peak value of the XEOL wavelength,  $\lambda_m$ , is given by  $hc/[E_g - E_b]$ , where  $E_g$  is the bandgap energy and  $E_b$  is the binding energy of the exciton. For the BaXY compounds the  $\lambda_m$  values observed in the present study are gathered in table 2. The bandgap values, wherever available have also been indicated. For the pristine dihalides, the peak of XEOL increases as we go from BaF<sub>2</sub> to BaI<sub>2</sub>, in accordance with the decreasing energy needed to create the exciton from fluorine to iodine.

Another aspect arises due to the orthorhombic structure of the chloride, bromide and iodide. Here, the halogen ion can occupy either of the two sites, designated F<sub>1</sub> and F<sub>2</sub>. The former has four barium ions as close neighbours, forming a distorted tetrahedron and the latter has five barium ions as nearest neighbours, forming an irregular pyramid. But the present XEOL results and the earlier work of Houlier [41] seem to indicate that only the F<sub>1</sub> center seems to be preferentially formed.

For the mixed halides, one would have expected two XEOL bands, corresponding to the two excitons associated with the halides. However, we could observe only one broad band for all the six dihalides. For the fluorine-based dihalides, BaFCl and BaFBr, it has been reported in the literature that the absence of fluorine-related exciton emission is probably due to an efficient Auger-type decay ion which the hole transfers from the fluorine to either chlorine or bromine rather than evolve into the fluorine exciton creation [42]. In this reference, while the XEOL found for BaFCl (375 nm) is close to the present value (385 nm), the wavelength reported for BaFBr (295 nm) does not match with our value (450 nm). The reason is not clear. For the other dihalides, the present observation of a single broad XEOL peak raises the question whether the individual excitonic peaks can be resolved by a more detailed study.

The fluorine-based barium salts show an interesting sequence in their crystal structure as the fluorine content decreases. The fluoride, BaF<sub>2</sub>, has the cubic fluorite structure. When half the number of F ions are replaced by  $X$  (Cl, Br or I), the compound BaFX, changes over to the tetragonal matlockite structure. Finally when F is replaced fully by  $X$ , the compound BaX<sub>2</sub>, adopts the orthorhombic structure. It is interesting to inquire whether there is a critical F/ $X$  ratio, at which these structural transitions occur, and whether the XEOL behaviour will show the corresponding changes. The only study made so far on the phase diagram of the

system  $\text{BaF}_2 + \text{BaBr}_2$  by Kolb *et al* [43] shows that there is no detectable deviation from stoichiometry in the  $\text{BaFX}$  system. In other words, the compound  $\text{BaF}_{2-\delta}\text{X}_\delta$  ( $0 \leq \delta \leq 2$ ) shows only three sharp phases for  $\delta = 0$  (cubic), 1 (tetragonal) and 2 (orthorhombic). For other values of  $\delta$ , the system is a mixture of two (c, t or o) phases, governed by the lever rule.

A significant finding in this study is that amongst all the barium halides,  $\text{BaClI}$  has the highest luminescence yield with a peak at 420 nm. This is of practical value, provided the afterglow problem is overcome. The vulnerability of  $\text{BaClI}$  to moisture attack is another problem. Turning now to the colour center formation, as mentioned earlier, we have reported only the visual observations in these compounds (table 2). Generally, the colour of appearance is due to the optical absorption of the complementary colour. For example,  $\text{BaFBr}$ , appearing blue/violet after irradiation, has a strong absorption in the red region. Thus, by shining light matching the wavelength of colour center absorption, the  $\text{F} + \text{H}$  pair can be made to radiatively decay. If the dopant ion has electronic levels matching this decay energy, then a strong photostimulated luminescence will result. This is the basis of imaging phosphors, and at present  $\text{BaFBr}$  doped with  $\text{Eu}^{2+}$  is widely used in computed radiography. To determine the exact positions of the absorption bands, measurements have to be performed on single crystals. The colour centers therefore also contain important information about the excitons, apart from the practical applications. In this connection, it is interesting to read that the technique of photostimulated luminescence was first used by Schulman in the fifties, to develop an x-ray dosimeter for the US Navy purposes [44]. The first material was silver-doped lithium aluminium phosphate glass, which has the colour center absorption band at 320 nm, and a photostimulated luminescence due to the silver ion at 640 nm. This is in contrast with  $\text{BaFBr}:\text{Eu}^{2+}$ , in which, the colour center absorption is around 600 nm, and the PSL emission, due to  $\text{Eu}$  is at 390 nm.

From the spectra appearing in figure 2, one can speculate that the europium-doped halides which show lower XEOL than the pristine salt are likely to show the PSL property. This aspect forms a separate study and will be reported later.

One of the remarkable systematics in colour center phenomena, in particular for the alkali halides, is the discovery of the Mollwo-Ivy law, which is now a text book topic in solid-state physics. The law simply states that the colour center absorption peak wavelength,  $\lambda_m = c/d^n$ , where  $d$  is the lattice parameter of the alkali halide and  $c$  and  $n$  are constants. A plot of  $\lambda_m$  vs.  $\ln d$  is a linear relation and a set of lines for the various centers (F, M, and R) in alkali halides have been obtained [12]. The index  $n$  is related to the depth and width of the potential well in which the F-center electron is trapped. The question naturally arises whether a similar Mollwo-Ivey law exists for the alkaline earth compounds. Townsend and Kelly [12] have shown that for the F-center absorption in Ca, Sr and Ba fluorides, for which the structure is characterised by a single lattice parameter, the Mollwo-Ivey law is roughly obeyed, with  $n$  close to 2. For the other barium halides possessing the matlockite and orthorhombic structure, appropriate parameters have to be identified. In this context, the paper by Cywinski and Damm [45], where they have tried to formulate a generalised Mollwo-Ivey law for the alkali halides, to include intrinsic luminescence, may be of interest.

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