Summary

The investigation of the information storage and read-out processes in the X-ray storage phosphor BaFBr:Eu^{2+} showed that it is necessary to distinguish between stoichiometric and non-stoichiometric BaFBr. It turned out that the stoichiometric material is always contaminated with oxygen whereas no oxygen contamination was found in the non-stoichiometric one.

For stoichiometric as well as for non-stoichiometric BaFBr, the PSL active electron trap centres are F(Br$^-$) and F(F$^-$) centres. In stoichiometric BaFBr, “impurity” sites (e.g. oxygen or the activator) are preferred sites for the radiation-induced electron-hole centre generation. The F centre (electron trap) generation is significantly influenced by the incorporated oxygen impurities which provide the necessary anion vacancies for the F centres. The electron-hole pairs are obviously not created via a F-H process. In spite of thorough research by optically-detected magnetic resonance techniques no H centres ($(\text{halogen})_2^-$ molecules occupying single halide sites) have been observed. The F centre generation seems thus to be impurity-limited. The hole centre taking part in the photostimulated luminescence process is still unknown.

It was shown by magic angle spinning nuclear magnetic resonance that in non-stoichiometric BaFBr, 10% fluorine “antisites” (fluorines on bromine sites) are present. The F centre generation occurs via a F-H process between the F$^-$ and Br$^-$ sublattices whereas no F-H process within one sublattice was observed. This is in agreement with the observations in stoichiometric BaFBr where no H centres have been found either. The existence of fluorine antisites enables the F centre generation. In non-stoichiometric BaFBr it is thus not impurity limited as in stoichiometric BaFBr. This feature is very promising for the use of non-stoichiometric BaFBr as X-ray storage phosphors for very high doses.

The spatial resolution of X-ray storage phosphor screens based on the optically anisotropic BaFBr is limited by the scattering of the read-out light. The scattering can probably be reduced by using optically isotropic crystal systems instead. The search for such X-ray storage phosphors, which have also comparable figures of merit as Eu^{2+}-doped BaFBr, yielded the alkali halides $RbBr:Ga^+$ and $CsBr:Ga^+$ as best candidates, as well as $CsBr:Eu^{2+}$. The elpasolite $Cs_2NaYF_6:Ce^{3+}$ is also very promising whereas $KBr:In^+$ and $RbI:Tl^+$ are not so interesting for the practical applications.

The information storage and read-out process in $RbBr:Ga^+$ and $CsBr:Ga^+$ can be explained by a simple pair mechanism: Upon X-irradiation F centres are generated as electron trap centres and Ga^{2+} centres as complementary hole trap centres. Two different types of Ga^{2+} hole trap centres were observed: $(Ga^{2+})^I$ and $(Ga^{2+})^{II}$ centres. Type I is an isolated Ga^{2+} on a Rb^+ or Cs^+ site, whereas type II is a complex between Ga^{2+} on Rb^+ or Cs^+ site and a nearest neighbouring cation vacancy. Only the type I Ga^{2+} centres are taking part in the PSL process. In $RbBr:Ga^+$ a sufficient high Ga^+ concentration suppresses the $(Ga^{2+})^{II}$ generation. In $CsBr:Ga^+$ the $(Ga^{2+})^I$ centres clearly dominate over the PSL-inactive $(Ga^{2+})^{II}$ centres for all Ga^+ doping levels.

For practical use, it is advantageous to red-shift the PSL-excitation to the near-infrared in order to use low cost, but high intensity laser diodes as stimulation light sources in the read-out process. $BaFBr:Eu^{2+}$ as well as the two alkali halides $RbBr:Ga^+$ and $CsBr:Ga^+$ can be co-doped with smaller cations, leading to the formation of perturbed electron trap centres (F_A centres) the absorption bands of which are clearly red-shifted. It turned out that these sites are preferred sites for the electron-hole centre generation. Especially for low X-ray doses the ratio between the perturbed F_A and unperturbed F centres is clearly in favour of the perturbed one. This is in analogy to the red-shift of the PSL excitation in $BaFBr:Eu^{2+}$: The PSL excitation can be made sensitive to stimulation further into the infrared by additional Ca^{2+} or Sr^{2+} doping. Upon X-irradiation $F_A(Br^-, Ca^{2+}$ or $Sr^{2+})$ centres are formed preferentially as photostimulable centres electron traps.

The energy storage and read-out processes in the alkali halides $KBr:In^+$ and $RbI:Tl^+$ and in the elpasolites $Cs_2NaYF_6:Ce^{3+}$ and $Cs_2NaYF_6:Pr^{3+}$ are completely understood assuming a simple pair model of an F centre as electron trap centre and the activator itself as complementary hole trap centre.

The observation that upon X-irradiation the electron and hole trap centres are always created with a spatial correlation to the activator is of particular interest for the functioning of the corresponding materials as storage phosphors. The reason for this spatial correlation is still an open question. A possible explanation for this phenomenon could be a lattice distortion around the activator due to an ionic radius misfit. However, an electron nuclear double resonance investigation of Eu^{2+} in BaFBr yielded that such a lattice distortion would only be very small (below 2%).

Another approach to reduce the scattering of the read-out would be a phosphor based on a glass. It was shown that a fluorozirconate glass ceramic doped with Eu^{2+} or Ce^{3+} shows a significant PSL effect after X-irradiation at RT. The application of such glass ceramics as X-ray storage phosphors will depend upon optimising the crystallite size and dopant concentration so as to maximise efficiency and minimise scattering. The development of such systems is still at its beginning.