ANION AND CATION EXCITATIONS IN HEXAFLUOROGERMANATES

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The development of novel Si-PMs, with higher sensitivity in the UV-VUV region, has sparked new interest towards materials with cross-luminescence (CL). CL arises from an intrinsic radiative recombination of core holes with valence electrons resulting in ultrafast emission (decay time $\tau < 1$ ns) [1]. Powder samples of ternary hexafluorogermanates K_2GeF_6 and $BaGeF_6$ were synthesized. According to band structure calculations (AFLOW [2]), both compounds host complex valence band structures, due to sub-bands of Ge 4s,4p states, resulting in radiative transitions covering the VUV-UV-Vis range (Fig. 1a). The samples were investigated by means of cathodoluminescence (Tartu, Estonia) and time-resolved luminescence spectroscopy under synchrotron radiation excitation at 10 K (FinEstBeAMS beamline, MAX IV, Lund, Sweden). Our studies revealed several fast emission bands ($\tau \sim 400$ ps) in the spectral range of 8 – 2.4 eV (Fig. 1b) assigned to CL (K 3p → Ge 4s,4p, F 2p) and intraband luminescence (Ge 4s,4p → Ge 4p, F 2p), overlapping well with the sensitivity range of novel Si-PMs. Based on the experimental results and calculated electronic band structure, relaxation processes of anion and cation electronic excitations in hexafluorogermanates will be discussed and prospects of their implementation as scintillators for fast timing applications evaluated.

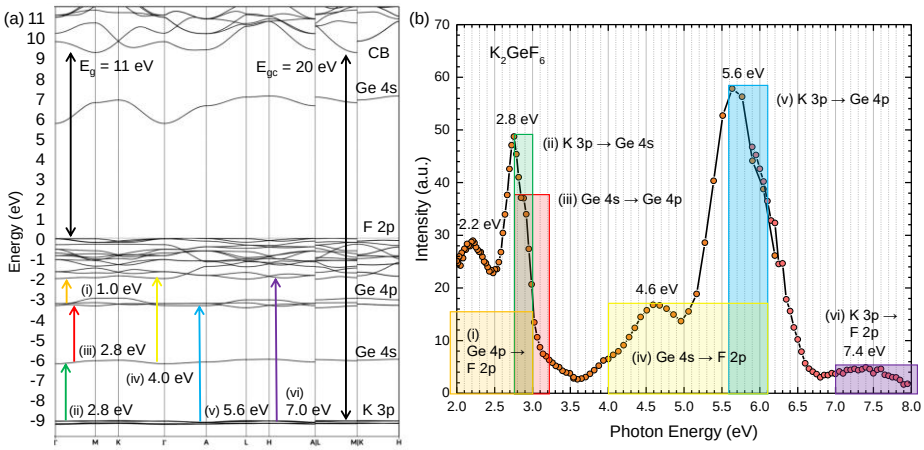

Fig. 1. (a) Computed band structure of K_2GeF_6, with the experimental values of anion (E_g) and cation energy gap (E_{gc});(b) Combined luminescence spectra in the fast time window (Vis-UV) and time-integrated in VUV. The boxes indicate the energy range of transitions between the core- and valence bands shown in (a).

References

1. V.N. Makhov, 2014, Physica Scripta **89**, 044010.
2. O. Isayev, *et al.*, 2017, *Nature Comm.*, **8**, 15679.

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