Supplementary information

On the relations between the band gap, structure and composition of the M-Si-N (M = alkali, alkaline earth or rare-earth metal) nitridosilicates

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Determination of the bandgap

The values of the bandgap, as used for the article, have been derived from experimental data from literature. In literature, different types of experiments have been performed from which a bandgap can be derived, including soft X-ray spectroscopy, diffuse reflectance, optical absorption, and photoluminescence excitation (PLE) measurements. In addition, different methods are used to obtain a bandgap from the experimental data, and the bandgap can also be defined in different ways (e.g. the optical bandgap and the electronic bandgap) leading to different values reported in literature. In order to make the data comparable, we have therefore reanalyzed the data from literature.

In the excitation spectra of the 5d-4f emission of (low concentrated) Eu^{2+} or Ce^{3+} doped samples an absorption feature can sometimes be observed that corresponds to the energy of exciton creation (E_{ex}).[1] E_{ex} can also be estimated from the diffuse reflectance spectra of an undoped sample by extrapolating the linear part of the slope to the energy where the reflectance would be zero. This usually leads to similar values for E_{ex} (within 0.2 eV). If the absorption spectrum of the compound is known, one can calculate the onset of fundamental absorption E_{fa} or optical bandgap via a so-called Tauc plot where $(\alpha h\nu)^{1/n}$ is plotted against $h\nu$. Here, $h\nu$ is the photon energy, α the absorbance, and n = 2 in case of an indirect allowed transition. E_{fa} is about 0.3-0.5 eV lower in energy than E_{ex}.[2] The onset of fundamental absorption is sometimes also determined from a diffuse reflectance measurement, by converting the reflectance in an absorbance, using the Kubelka-Munk (KM) relation.

Once E_{ex} is known, the (electrical) bandgap energy E_{VC}, i.e. the energy between the top of the valence band and the bottom of the conduction band, can then be estimated by including the exciton binding energy, using the equation:[3]

$$E_{VC} = E_{ex} + 0.008(E_{ex})^2$$

Note that in earlier work[1] the exciton binding energy was estimated as 8% of E_{ex}, leading to slightly different values for E_{VC}.

The experimentally determined bandgaps collected from literature are summarized in Table S1. From these values, E_{VC} is estimated, based on the information given above. It is realized that this procedure may induce an error of several tenths of an electronvolt (up to about 10%), but that is still small enough in order to establish the general trends discussed in the manuscript.

Table S1. Bandgaps of the nitridosilicates.

Compound	E_{VC}	X-ray	Absorption	Diffuse reflectance	PLE
α-Si_3N_4	**5.9**			5.6[4]	
γ-Si_3N_4	**5.1**	4.8[5]			5.1[6] (undoped)
Li_8SiN_4	**2.7**		2.4[7] (Tauc)		
Li_5SiN_3	**2.8**		2.5[8] (Tauc)		
$LiSi_2N_3$	**6.9**			6.4[9]	6.2[10] (Eu)
Li_2SiN_2	**> 6.9**			>6.4[11]	
$MgSiN_2$	**5.5**	5.6[12]		5.3[13, 14]	
α-$CaSiN_2$	**5.0**			4.8[15, 16]	4.8[15] (Eu)
$Ca_{16}Si_{17}N_{34}$	**4.7**		3.7[17] (Tauc)	4.6[17], 4.5[18]	
$Ca_2Si_5N_8$	**5.2**			5.0[19]	5.0[19](Eu), 5.0[20](Ce)
$SrSiN_2$	**5.0**		4.4[21] (KM)	4.8[22], 4.7[21]	4.9[22](Eu), 4.8[21] (Eu), 4.8[21](Ce)
$Sr_2Si_5N_8$	**5.1**			4.9[19], 4.7[23]	5.0[19](Eu), 4.9[20](Ce)
$SrSi_6N_8$	**3.7**			3.6[24]	3.4[25] (undoped)
$BaSiN_2$	**4.9**		4.1[21] (KM)	4.6[21]	4.7[21](Eu), 4.7[21](Ce)
$Ba_2Si_5N_8$	**5.1**		4.0[26](KM)	4.9[19]	4.8[19](Eu), 4.8[20](Ce)
$BaSi_7N_{10}$	**5.8**			5.4[27]	5.6[28](Eu)
$LaSi_3N_5$	**5.0**		4.5[29](KM)	4.6[30]	5.0[31](Eu), 4.9[30](Ce)
$CaMg_3SiN_4$	**4.1**				4.0[32](Ce)
$SrMg_3SiN_4$	**4.1**			4.0[32]	
$BaMg_3SiN_4$	**4.1**			4.0[33]	
$Li_2Ca_2Mg_2Si_2N_6$	**4.8**			4.6[34]	
$Li_4Ca_3Si_2N_6$	**4.1**		3.6[35](KM)	4.0[35]	4.0[35] (undoped)
$CaLaSiN_3$	**3.1**			3.0[36]	
$CaYSi_4N_7$	**5.2**			5.0[37]	
$SrYSi_4N_7$	**5.2**			5.0[37-39]	5.0[39](Eu)
$BaYSi_4N_7$	**5.2**			4.9[37, 38], 5.0[40]	

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