Electronic Supplementary Material (ESI) for Materials Advances.

Table SI1. Detailed atomic positions extracted considering I4/m space group for the K_3 compound.

Atoms	Wyckoff position	x(Δx)	y(Δy)	z(Δz)
In_1 [6]	*2a*	0	0	0
In_2 [6]	*2b*	0.5	0.5	0
In_3 [6]	*4c*	0.5	0	0
In_4 [6]	*8f*	0.25	0.25	0.25
K_1 [6]	*4d*	0.5	0	0.25
K_2 [6]	*4e*	0	0	0.25
K_3 [6]	*8h*	0.75	0.25	0
K_4 [12]	*16i*	0.241(1)	0.0198(9)	0.1013(4)
K_5 [12]	*16i*	0.011(1)	0.251(1)	0.3621(7)
F_1	*4e*	0.5	0.5	0.61(3)
F_2	*4e*	0	0	0.616(3)
F_3	*8h*	0.146(4)	0.889(3)	0
F_4	*8h*	0.624(4)	0.879(3)	0
F_5	*8h*	0.124(3)	0.574(3)	0.5
F_6	*8h*	0.514(4)	0.325(3)	0
F_7	*8g*	0	0.5	0.617(3)
F_8	*16i*	0.304(2)	0.086(2)	0.233(1)
F_9	*16i*	0.920(2)	0.809(2)	0.774(1)
F_{10}	*16i*	0.736(3)	0.714(2)	0.861(2)

Table SI2 : Kinetic law refinements of Ce^{3+} doped Rb_2KInF_6 and K_3InF_6 compounds.

Samples	Reaction order	A	k_1 (s^{-1})	B	k_2 (s^{-1})	R^2
$Rb_2KIn_{0.98}Ce_{0.02}F_6$	1*1	35,18	4,97E-05	/	/	86,56
	1*2	29.27	/	/	5.83E-07	91.58
	2*1	**28.13**	**1.29E-05**	**35.30**	**5.07E-04**	**98.29**
$K_3In_{0.98}Ce_{0.02}F_6$	1*1	22.09	1.88E-04	/	/	86.23
	1*2	16.30	/	/	1.88E-06	95.23
	2*1	**18.34**	**5.32E-05**	**48.00**	**5.97E-04**	**97.51**

Table SI3 : Kinetic law refinements of In^+ ions luminescence in irradiated Ce^{3+} doped Rb_2KInF_6 and K_3InF_6 compounds.

Samples	Reaction order	A	k_1 (s^{-1})	B	k_2 (s^{-1})	R^2
$Rb_2KIn_{0.98}Ce_{0.02}F_6$	1*1	7.27	1.15E-04	/	/	82.87
	1*2	**2.28**	/	/	**9.70E-07**	**96.01**
	2*1	6.52	7.61E-05	18.56	4.11E-01	88.79
$K_3In_{0.98}Ce_{0.02}F_6$	1*1	9.43	2.66E-04	/	/	77.32
	1*2	**5.80**	/	/	**2.52E-06**	**95.49**
	2*1	7.64	5.55E-05	65.52	6.38E-04	93.64

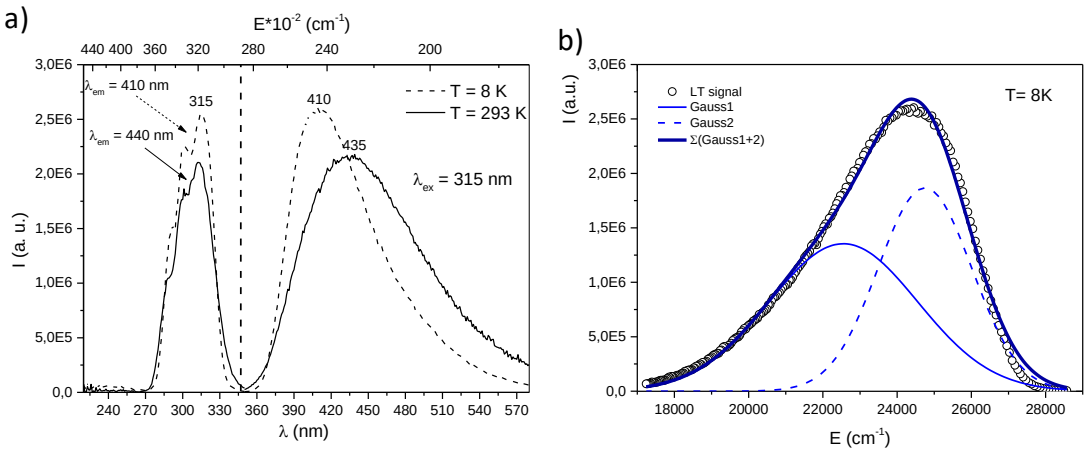

Figure SI1 : Excitation and emission spectra of Ce^{3+} -doped K_3InF_6 compound (K_3) at room (full line – T=293 K) and low temperature (dotted line- T=8 K) (a); deconvolution of the emission spectra into two 5d(T_{2g}) →$^2F_{7/2}$ and 5d(T_{2g} →$^2F_{5/2}$) bands at low temperature (b)

An increase of the highest energy component regarding the lowest one is noticeable, which affects the maximum of the global emission band. This might result in a stronger reabsorption effect of the 5d(T_{2g})→$^2F_{5/2}$ electronic transition (highest energy transition) by the 5d(T_{2g})→$^2F_{7/2}$ (lowest energy transition), in parallel to an increase of the temperature effect on the population of the vibrational energetic levels.

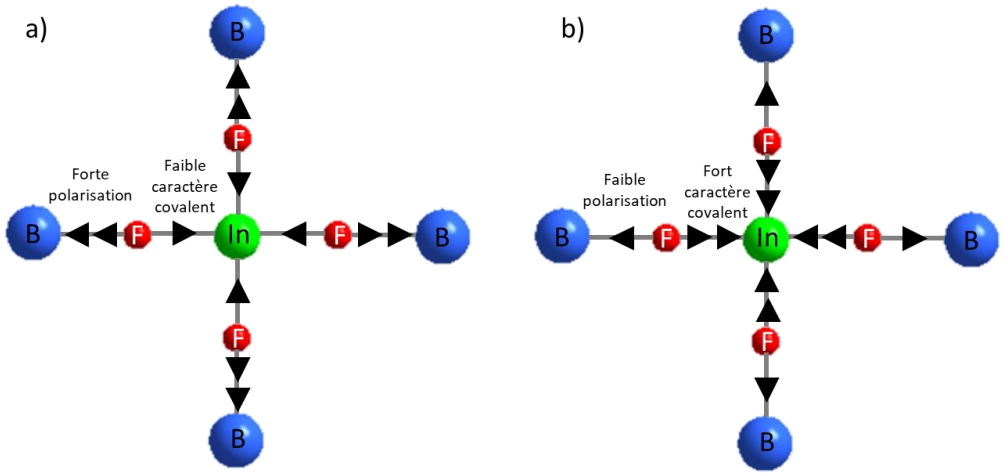

Figure SI2 : 2D representation of the B^+ cations polarization effect on the In-F chemical bonding for the elpasolite and cryolite compound. The scheme illustrates the equatorial plane of the InF_6 octahedron adn the arrow. the intensity of the dipolar momentum.