ESRF	**Experiment title:** Metal borohydrides with perovskite structure type: ionic conduction and hydrogen storage.	**Experiment number**: 01-02-1037
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Shifts: 9	**Local contact(s)**: Dr. V. Diadkin	*Received at ESRF:*

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Many different systems containing perovskite borohydrides $AB(BH_4)_3$ with A = alkali metal, B = rare-earth were studied. Two typical examples are given below:

$LiBH_4 + KBH_4 + YbCl_3$

The perovskite phase $KYb(BH_4)_3$ is formed in ball milled mixtures 12:4:3. At RT the perovskite is simple cubic, and at 95°C it transforms to the orthorhombic phase with 8 × superstructure SQRT(2) / 2 / 2SQRT(2) which was not reported among oxide perovskites [1]:

Compound	*SG*	*V* (Å^3)	*V/Z* (Å^3)	*a* (Å)	*b* (Å)	*c* (Å)	*T* / K
LT-$KYb(BH_4)_3$	*P*-43*m*	176.3	176.3	5.607			298
HT-$KYb(BH_4)_3$	*Pm*2$_1$*b*	1423.8	177.9	7.832	11.267	16.135	403

Evolution of unit cell volume and lattice parameters with temperature is shown on Figure 1. The decrease of the cell volume above 180°C is due to dissolution of chloride from LiCl in the perovskite.

Lanthanides form the basis of RGB (red-green-blue) colours in LED-based solid-state lighting with many important applications. Room temperature emission and excitation

spectra of $KYb(BH_4)_3$ were measured in our laboratory down to 10 K. The Yb^{2+} emission is centred at 520 nm, when excited in the UV at 355 nm [1].

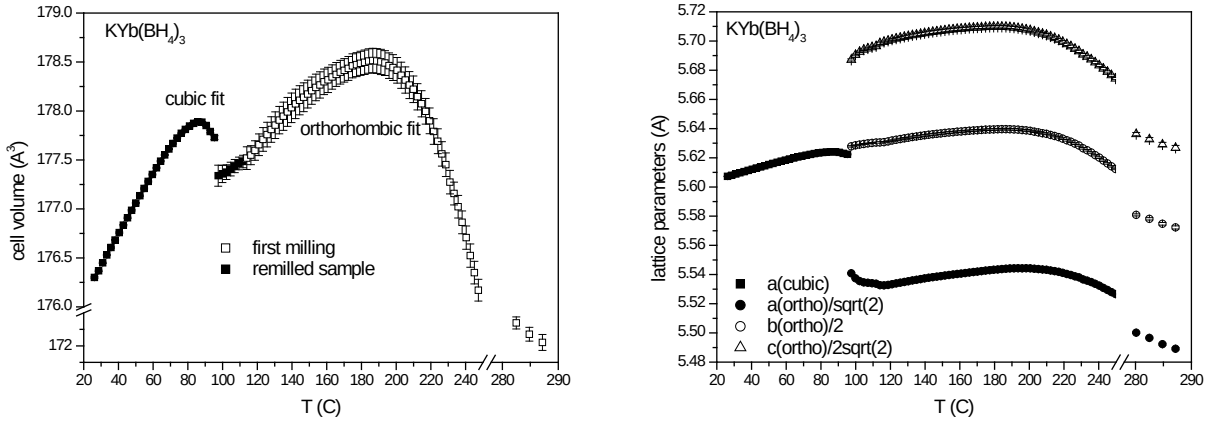

Figure 1: Evolution of unit cell volume and lattice parameters with temperature for cubic and orthorhombic perovskite $KYb(BH_4)_3$.

$LiBH_4 + KBH_4 + Gd(BH_4)_3$

Gadolinium crystals are of interest as host materials for trivalent lanthanides based phosphors. Gadolinium forms double-perovskite phases $Cs_3Gd(BH_4)_6$ and $Cs_2LiGd(BH_4)_6$ with bigger alkali metal [1]. A different phase is formed with smaller alkali metal K in the mixtures 4:3:3, but also without lithium in mixtures 0:3:2 as shown on the T-ramp of 4:3:3 mixture in Figure 2.

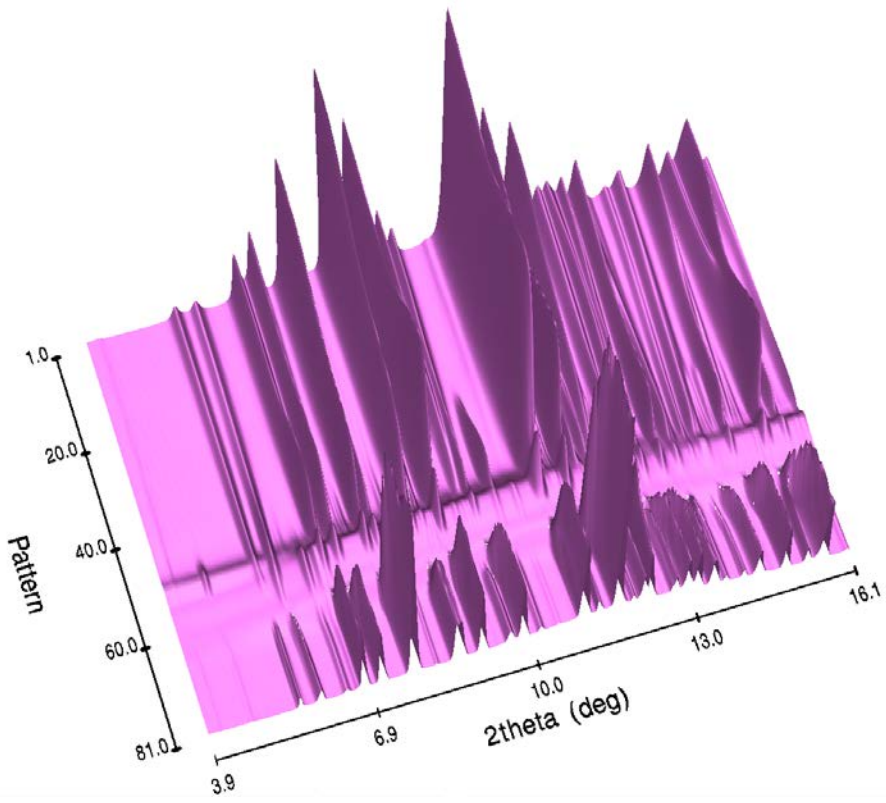

Figure 2: T-ramp of the ball-milled mixture 4 $LiBH_4$ + 3 KBH_4 + 3 $Gd(BH_4)_3$ showing a new phase formed by ball mailing at RT, and disappearing in the pattern no. 53. at T ~ 150°C.

Despite a great effort invested in its crystal structure solution, no satisfactory model has been obtained yet.

[1] Schouwink et al., *Nature Comm.*, submitted.