

Supporting Information

In the following a detailed analysis is presented in order to clarify the identity of the two side-phases occurring in the diffraction pattern of the $\text{Rb}_4\text{P}_4\text{O}_{12}$ mixture. To this end several batches were investigated by NMR and X-ray diffraction methods. These batches showed different product ratios due to a variation of the reaction temperature and duration.

A Rietveld refinement for RbH_2PO_4 was done with fixed atomic parameters given in literature² (Fig.1: blue line). This led to slightly different cell parameters: $a = 9.5424$ (13); $b = 6.1960$ (7); $c = 7.6889$ (10); $\beta = 109.028$ (7). This phase is present in the synthesis of a **mixture A** of $\text{Rb}_4\text{P}_4\text{O}_{12}$, monoclinic² RbH_2PO_4 and an unknown side-phase X (Fig. 1: green line) as well as in the synthesis of a **mixture B** of monoclinic² RbH_2PO_4 and an unknown side-phase X (Fig. 1: red line). The unknown side-phase X shows reflexes at the following 2θ values given in degree: 6.90, 8.11, 9.85, 13.15, 15.85, 19.25, 19.78, 20.06, 20.49, 20.80, 21.45, 27.87, 28.22, 28.47, 29.38, 29.96, 32.23 and 32.88. The $\text{Rb}_4\text{P}_4\text{O}_{12}$ shows only several broad reflexes consistent with an x-ray amorphous compound. From quantitative ^{31}P NMR (Fig.2) experiments on **mixture B** it is clear that it is free of any phosphates other than orthophosphates.

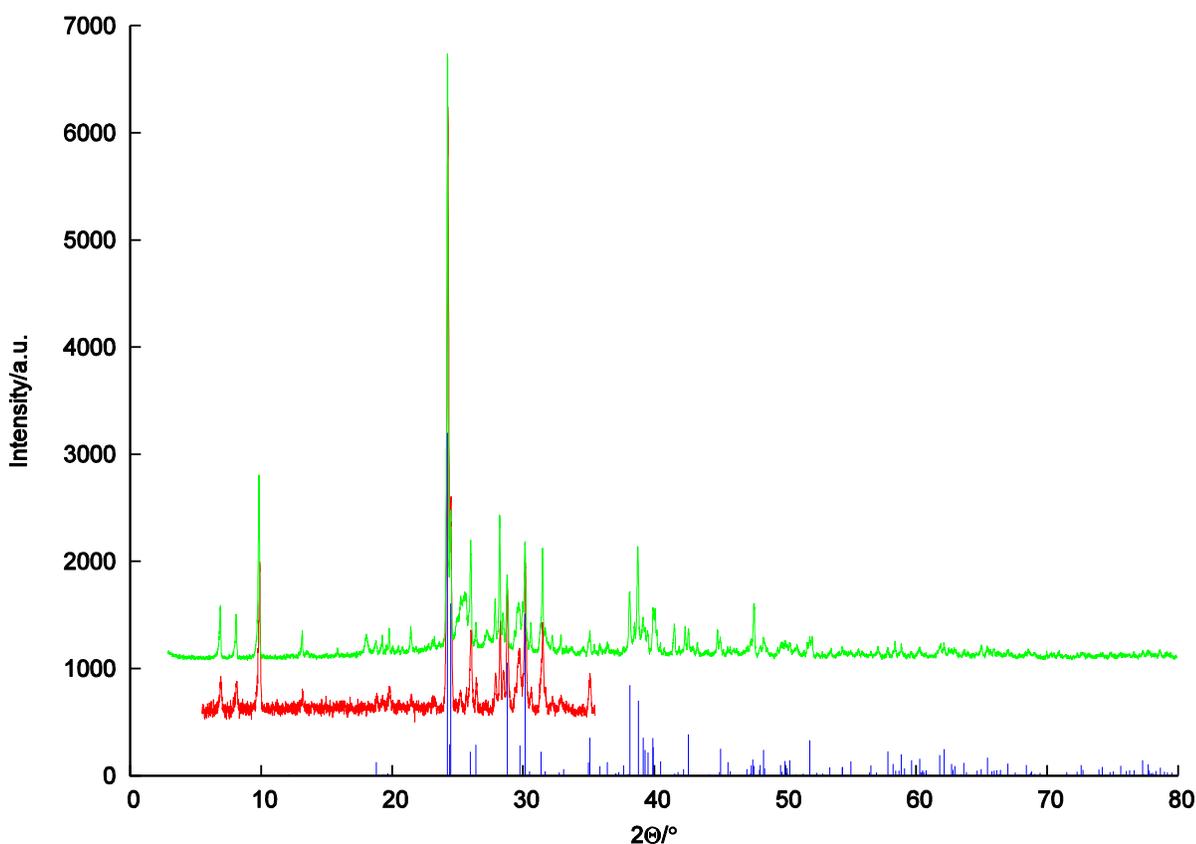


Fig. 1 Powder X-ray diffraction pattern ($\text{CuK}\alpha_1$) of a **mixture A** (green line, top) of $\text{Rb}_4\text{P}_4\text{O}_{12}$ with RbH_2PO_4 and an unknown crystalline side-phase, a **mixture B** (red line, middle) of monoclinic² RbH_2PO_4 and an unknown crystalline side-phase, however free of $\text{Rb}_4\text{P}_4\text{O}_{12}$ according to a quantitative ^{31}P NMR spectrum and the powder diffractogram (vertical blue lines, bottom) of monoclinic² RbH_2PO_4 according a Rietveld refinement of the published structure to the obtained powder diffractogram.

The NMR experiments corroborate the existence of monoclinic RbH_2PO_4 . One side phase is assigned to monoclinic RbH_2PO_4 , since the chemical shifts of the ^{31}P -MAS-NMR spectrum and the ^1H -MAS-NMR spectrum agree well with literature values.¹ The ^{31}P -MAS-NMR spectrum (Fig. 2) shows a single peak with an isotropic chemical shift of -2.7 ppm that agrees well with the literature value (Table 1). In the ^1H -MAS-NMR spectrum (Fig. 3) the sharp peaks around 0 and 2 ppm are assigned to grease, the solvent and decomposition products thereof, while the broad peaks from -10 to 10 ppm are assigned to water on the surface of the crystallites. The expected peaks of

RbH₂PO₄ at 13.8 and 14.2 ppm overlap with one another.

The question remaining is whether the sharp reflexes of the phase X refer to a phosphate compound relevant to this contribution. If phase X would consist both of H and P atoms it should be possible to disentangle the NMR spectra with the help of a ³¹P{¹H} HETCOR experiment (Fig. 4). Clearly no indication of such a crystalline nor an amorphous compound can be found down to the noise level of the experiment. The other possibility would be a hydrogen-free phosphate, which would have to be an unknown crystalline Rb₃PO₄ because of the observed ³¹P NMR chemical shift. However the presence of such a compound would require a signal which cannot be dephased as in a ³¹P{¹H} REDOR experiment (Fig. 5). Consequently both H free and H containing phosphates cannot explain for the sharp reflexes observed for phase X, which means phase X is not a phosphate.

Table 1: Chemical shifts of RbH₂PO₄ in literature and in this work after deconvolution):

	Reference [1]	This work
$\delta(^1\text{H})/\text{ppm}$ of RbH ₂ PO ₄	11.9, 13.8 and 14.2	11.9, 13.9 and 14.8
$\delta(^{31}\text{P})/\text{ppm}$ of RbH ₂ PO ₄	-3.0	-2.7

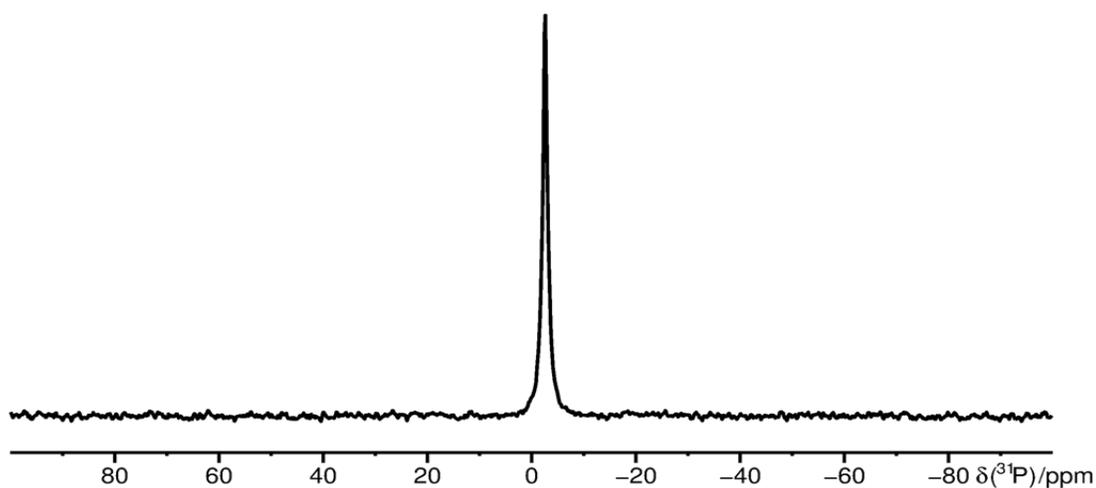


Fig. 2 ³¹P-MAS-NMR spectrum of *mixture B* containing RbH₂PO₄ and an unknown side phase X; measured at 4.7 T and 19 kHz sample rotation frequency; 4 repetitions with a delay of 3000 s after saturation combs were applied.

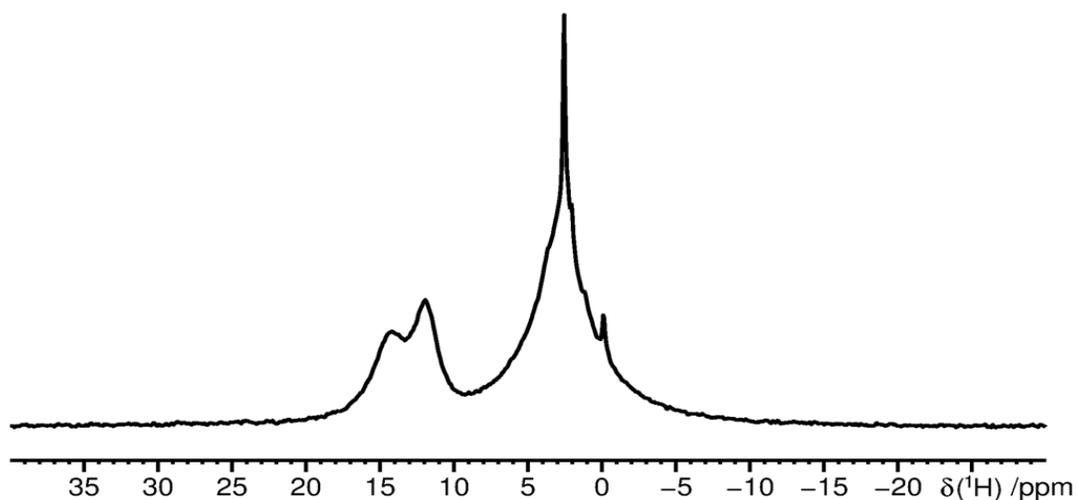


Fig. 3 Spin-echo ^1H -MAS-NMR spectrum of *mixture B* containing RbH_2PO_4 and an unknown side phase X; measured at 4.7 T and 19 kHz sample rotation frequency; 16 repetitions with a delay of 8 s after saturation combs were applied; the peak at around 0 and 2 ppm are assigned to grease, the solvent and decomposition products thereof; the broad peak from -10 to 10 ppm is assigned to water on the surface of the crystallites; the peaks above 10 ppm are assigned to RbH_2PO_4 .

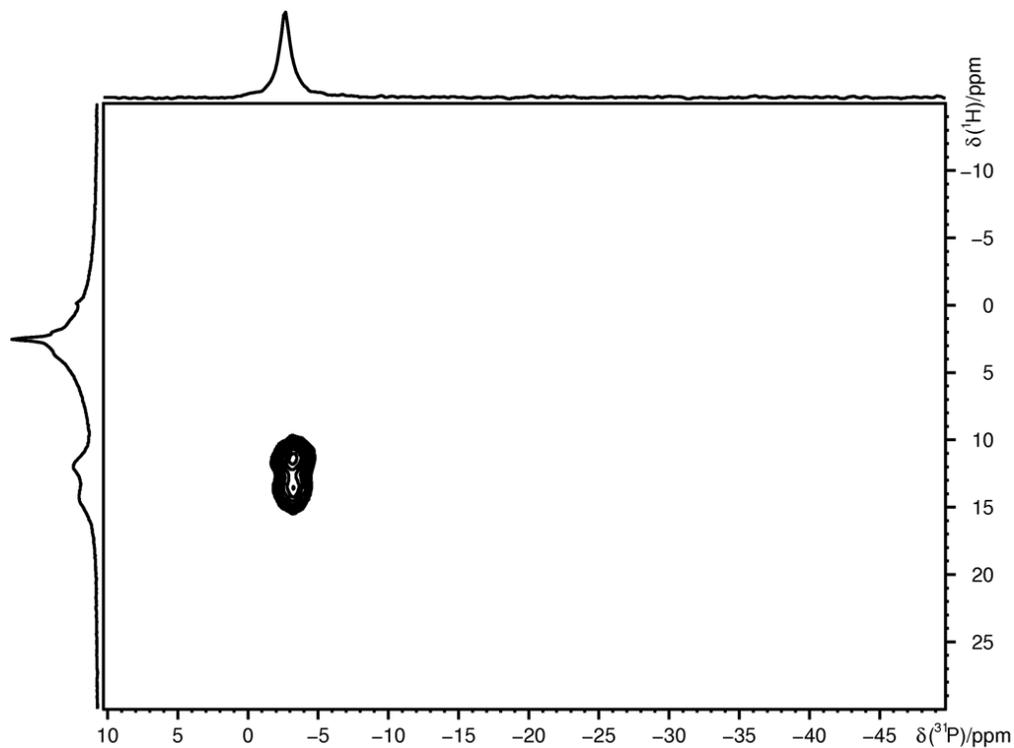


Fig. 4 $^{31}\text{P}\{^1\text{H}\}$ heteronuclear correlation spectrum of *mixture B* containing RbH_2PO_4 and an unknown side-phase X; measured at 4.7 T and 20 kHz sample rotation frequency; 16 repetitions with a delay of 3 s after saturation combs were applied and a contact time of 2 ms.

The $^{31}\text{P}\{^1\text{H}\}$ C-REDOR experiment from a sample containing RbH_2PO_4 and an unknown side-phase (Fig. 5) shows that there is spatial proximity between ^{31}P and ^1H . The $^{31}\text{P}\{^1\text{H}\}$ heteronuclear correlation spectrum (Fig. 1) shows no further correlation peaks apart from the expected ones.

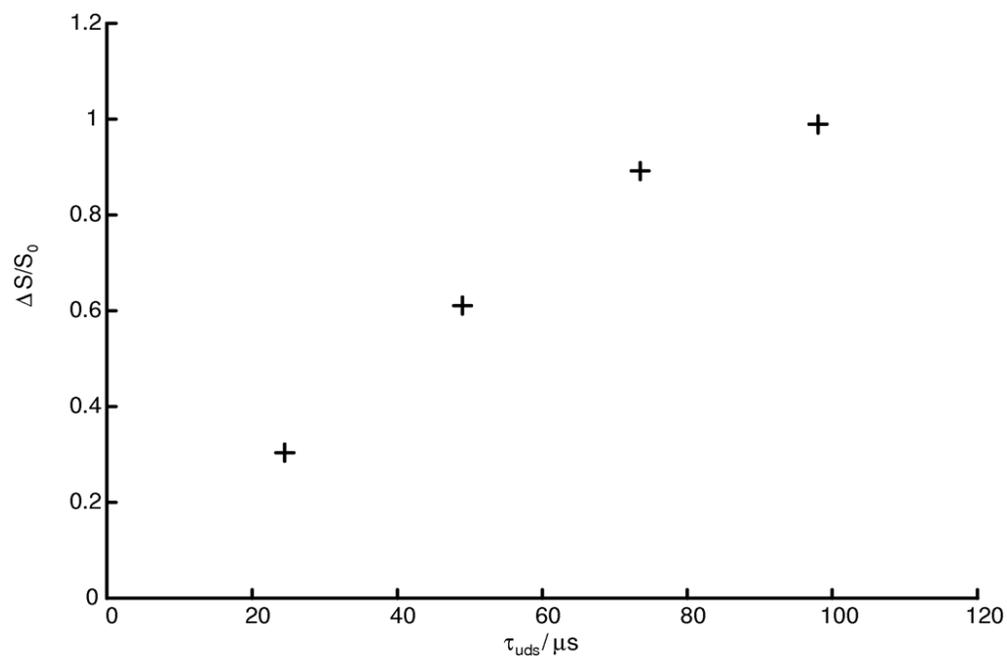


Fig. 5 $^{31}\text{P}\{^1\text{H}\}$ C-REDOR of **mixture B** containing RbH_2PO_4 and an unknown side-phase X; measured at 4.7 T and 20 kHz sample rotation frequency; 16 repetitions with a delay of 60 s after saturation combs were applied.

References

- 1 M. Vijayakumar, A.D. Bain, and G.R. Goward, *J. Phys. Chem. C*, 2009, **113**, 17950.
- 2 M. T. Averbouch-Pouchot, A. Durif, *Acta Cryst. C*, **1985**, 41, 665.