Supplementary Material to the article **“Synthesis and properties of 12442-family superconductors”**

1. **Synthesis of $RbLn_2Fe_4As_4O_2$ (Ln = Sm, Dy)**

A resent work [1] shown the possibility of synthesizing superconducting materials of the 12442 family with formula $RbLn_2Fe_4As_4O_2$ (Ln = Sm, Dy). Authors claimed that the initial components for synthesis by solid-phase reactions were: $Rb_{1.03}Fe_2As_2$, LnAs, Ln_2O_3, FeAs, Fe_2As. The precursors in stoichiometric ratio were compressed into pellets and placed in a corundum crucible. The alumina crucible was placed in a tantalum container which were sealed in a quartz ampoule. The heat treatment was in the range of 940-980 ℃, the holding time was about 40 h, and the cooling was performed by the switching off the furnace.

We used the starting components for the preparation of polycrystalline samples of $RbSm_2Fe_4As_4O_2$ (12442) by solid-phase reactions were $Rb_{1.03}Fe_2As_2$, SmAs, Fe_2O_3 and Fe, the precursor $Rb_{1.03}Fe_2As_2$ was previously synthesized from Rb with 3% excess and FeAs in a stoichiometric ratio of 1:2. In the second case we used FeO, FeAs, As and Rb with 3% excess, Sm, and in the third case: $Rb_{1.03}Fe_2As_2$, SmAs, Fe, Fe_2O_3, Rb with 5% excess. Before the annealing, the precursors were mixed and ground in a cryomill. Precursors in stoichiometric ratio were placed in corundum crucibles and welded in steel containers in high purity argon atmosphere. Next, a multi-step heat treatment was performed. Heating was carried out at a rate of 100-200 ℃/h, holding time ranged from 3 h to 168 h at various temperatures from 700 ℃ to 1200 ℃, and then cooling was carried out either in the off furnace mode or by thermal shock (quenching). No evidence of $RbSm_2Fe_4As_4O_2$ phase formation was detected by X-ray phase analysis regardless of the temperature regime of synthesis or its route (Table S1). All operations with precursors and samples were performed in an argon glove box. XRD results are presented in fig. S1, S2.

Phase 12442 is a crystallographic derivative of the two phases, formed from successive blocks of $RbFe_2As_2$ phase (122) and SmFeAsO phase (1111). Particular attention should be paid to the diffractograms of samples obtained at temperatures of 700 ℃, 750 ℃ and 800 ℃. At these temperatures, the coexistence of phases 122 and 1111 can be seen, but they do not form phase 12442, this behavior of the system may indicate a lack of energy for phase formation. It is also remarkable that regardless of the initial precursors and heating rate, the $RbFe_2As_2$ (122) phase is formed, indicating that there is no depletion of the composition by rubidium.

At all temperatures above 850 ℃, regardless of heating rate, holding temperature, holding time, cooling method or cooling rate, a number of phases formed is the same.

Rb with 3% excess of Rb, Dy_2O_3, FeAs and Dy served as starting components for the preparation of polycrystalline samples of $RbDy_2Fe_4As_4O_2$ by solid-phase reactions. The precursors were mechanically activated in a cryomill before annealing. Precursors in stoichiometric ratio were placed in corundum crucibles, welded in steel containers in high purity argon atmosphere. Next, a prolonged multi-step heat treatment was performed. Heating was carried out at a rate of 100-200 ℃/h, holding time ranged from 21 h to 168 h at various temperatures from 700 ℃ to 1100 ℃, and then cooling was carried out either in the off furnace mode or by thermal shock (quenching). No evidence of $RbDy_2Fe_4As_4O_2$ phase formation was detected by X-ray phase analysis regardless of the temperature regime of synthesis. All operations with precursors and samples after annealing were performed in an argon glove box.

In the case of $RbDy_2Fe_4As_4O_2$, the sample obtained at 700 ℃ exposure shows the coexistence of $RbFe_2As_2$ phase (122) and DyFeAsO phase (1111), but they do not form 12442 phase. At all temperatures above 900 ℃, regardless of heating rate, holding temperature, holding time, the set of phases formed is the same. Conditions and results of these syntheses are presented in Table S2, XRD results are presented in fig. S3.

1. Wang, Z. C., He, C. Y., Wu, S. Q., Tang, Z. T., Liu, Y., & Cao, G. H. (2017). Synthesis, Crystal Structure and Superconductivity in $RbLn_2Fe_4As_4O_2$ (Ln= Sm, Tb, Dy, and Ho). *Chemistry of Materials, 29*(4), 1805-1812.

Table S1. Conditions and results of syntheses of $RbSm_2Fe_4As_4O_2$

Sample number	Precursors	Holding temperature, C	Holding time, houres	Cooling type	Phases
Sm2-700	FeO, FeAs, As, Rb, Sm	700	168	Cooling at a 100 C/h rate	$RbFe_2As_2$, SmFeAsO, Sm_2O_3, FeAs
Sm4-750	$Rb_{1.03}Fe_2As_2$, SmAs, Fe, Fe_2O_3, $Rb_{изб}$	750	48	Quenching	$RbFe_2As_2$, SmFeAsO, Sm_2O_3, FeAs
Sm3-800	$Rb_{1.03}Fe_2As_2$, Sm, FeO, As	800	72	Quenching	$RbFe_2As_2$, SmFeAsO, Sm_2O_3, FeAs
Sm3-850	$Rb_{1.03}Fe_2As_2$, Sm, FeO, As	850	22	Quenching	$RbFe_2As_2$, SmFeAsO, Sm_2O_3, FeAs
Sm3-900	$Rb_{1.03}Fe_2As_2$, Sm, FeO, As	900	22	Quenching	SmFeAsO, Sm_2O_3, FeAs
Sm4-900	$Rb_{1.03}Fe_2As_2$, SmAs, Fe, Fe_2O_3, $Rb_{изб}$	900	48	Quenching	$RbFe_2As_2$, SmFeAsO, Sm_2O_3, FeAs
Sm1-930	FeO, FeAs, As, Rb, Sm	930	48	Quenching	SmFeAsO, Sm_2O_3, FeAs
Sm3-950	$Rb_{1.03}Fe_2As_2$, Sm, FeO, As	950	22	Quenching	SmFeAsO, Sm_2O_3, FeAs
Sm3-950 cold	$Rb_{1.03}Fe_2As_2$, Sm, FeO, As	950	48	Cooling at a 100 C/h rate	SmFeAsO, Sm_2O_3, FeAs
Sm1-960	FeO, FeAs, As, Rb, Sm	960	15	Quenching	SmFeAsO, Sm_2O_3, FeAs
Sm1-990	FeO, FeAs, As, Rb, Sm	990	20	Quenching	SmFeAsO, Sm_2O_3, FeAs
Sm1-1020	FeO, FeAs, As, Rb, Sm	1020	30	Quenching	SmFeAsO, Sm_2O_3, FeAs
Sm1-1050	FeO, FeAs, As, Rb, Sm	1050	21	Quenching	SmFeAsO, Sm_2O_3, FeAs
Sm5_1050_cold	$Rb_{1.03}Fe_2As_2$, SmAs, Fe, Fe_2O_3, $Rb_{изб}$	1050	3	Cooling at a 100 C/h rate	SmFeAsO, Sm_2O_3, FeAs
Sm2-1100	FeO, FeAs, As, Rb, Sm	1100	20	Quenching	SmFeAsO, Sm_2O_3, FeAs
Sm2-1200 fast	FeO, FeAs, As, Rb, Sm	1200	3	Quenching	SmFeAsO, Sm_2O_3, FeAs

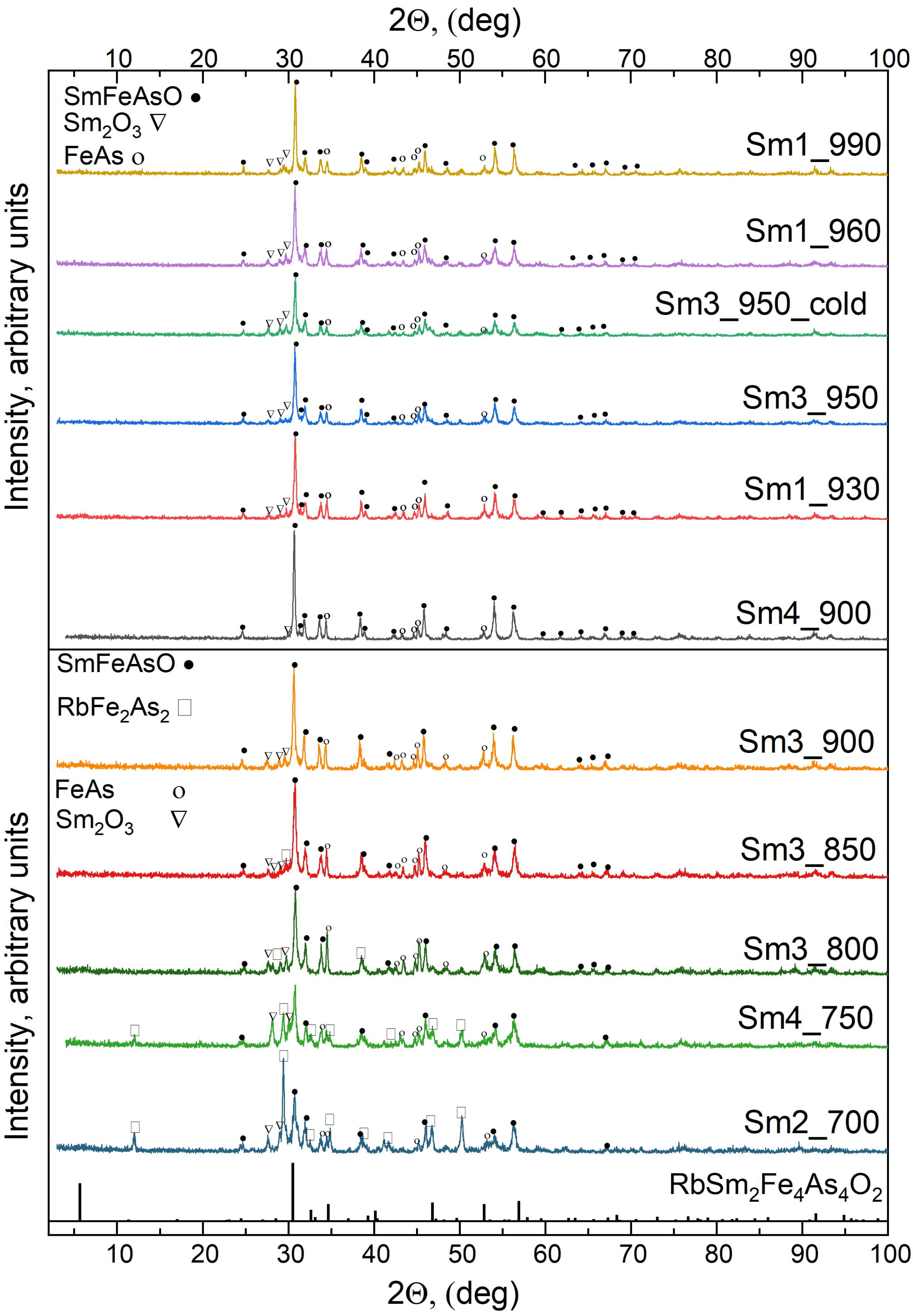

Fig. S1. XRD results of syntheses of $RbSm_2Fe_4As_4O_2$ (700 – 990 ℃)

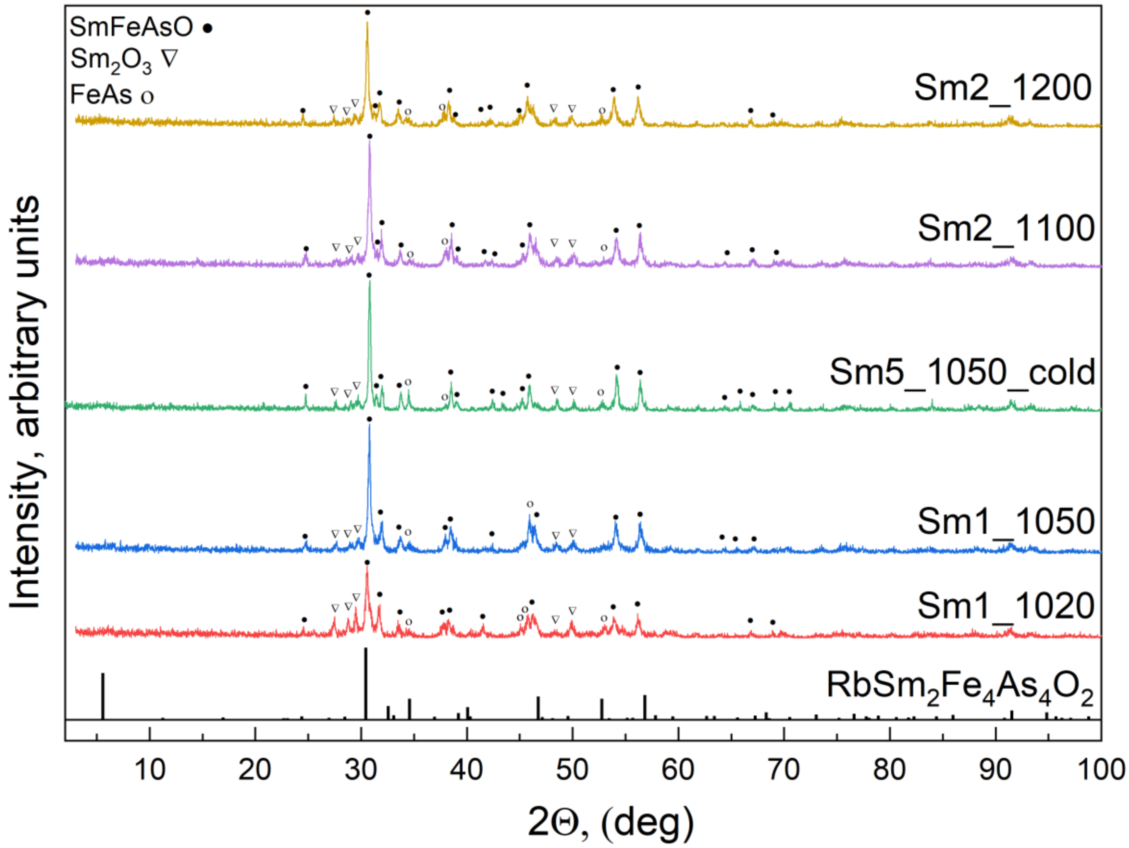

Fig. S2. XRD results of syntheses of RbSm$_2$Fe$_4$As$_4$O$_2$ (1020 – 1200 °C)

Table S2. Conditions and results of syntheses of RbDy$_2$Fe$_4$As$_4$O$_2$

Sample number	Precursors	Holding temperature, C	Holding time, houres	Cooling type	Phases
Dy2-700	Rb, FeAs, Dy$_2$O$_3$, Dy	700	168	Cooling at a 100 C/h rate	RbFe$_2$As$_2$, DyFeAsO, Dy$_2$O$_3$, Rb$_2$O, FeAs
Dy1-950	Rb, FeAs, Dy$_2$O$_3$, Dy	950	48	Quenching	DyFeAsO, Dy$_2$O$_3$, Rb$_2$O, FeAs
Dy1-975	Rb, FeAs, Dy$_2$O$_3$, Dy	975	21	Quenching	DyFeAsO, Dy$_2$O$_3$, Rb$_2$O, FeAs
Dy1-1050	Rb, FeAs, Dy$_2$O$_3$, Dy	1050	22	Quenching	DyFeAsO, Dy$_2$O$_3$, Rb$_2$O, FeAs
Dy1-1100	Rb, FeAs, Dy$_2$O$_3$, Dy	1100	22	Quenching	DyFeAsO, Dy$_2$O$_3$, Rb$_2$O, FeAs

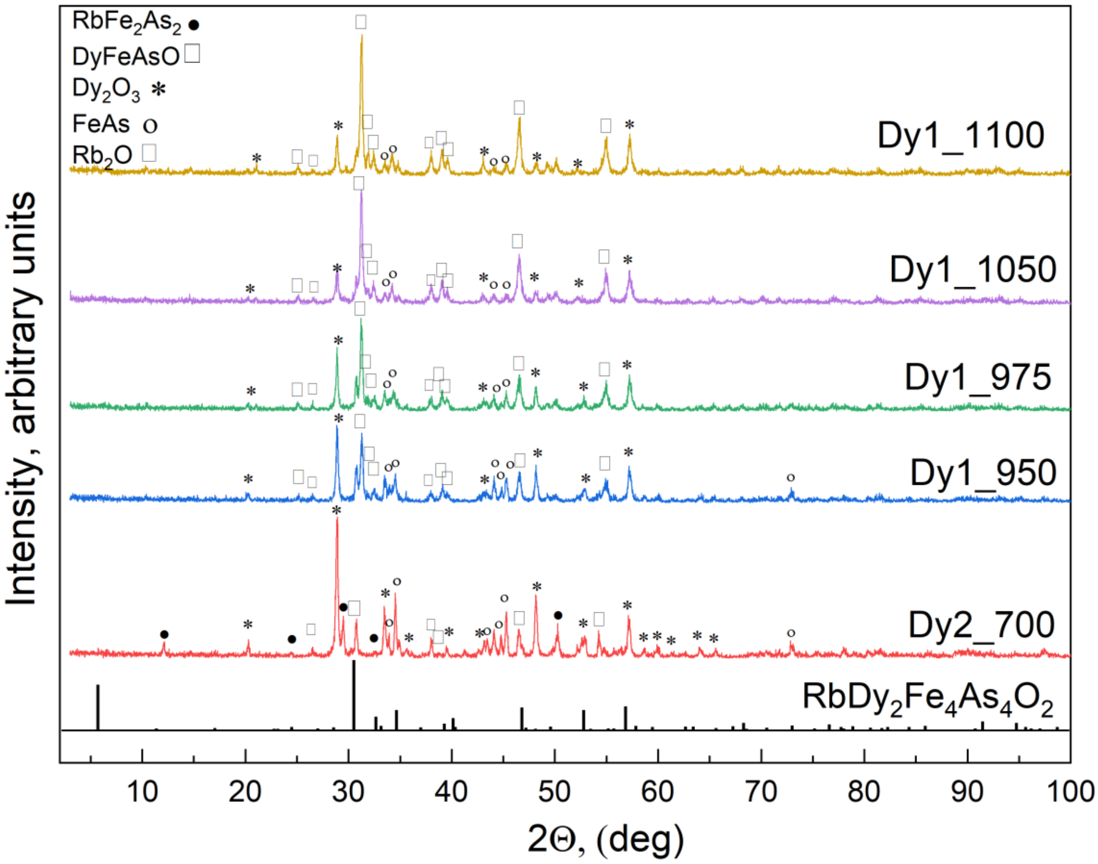

Fig. S3. XRD results of syntheses of $RbDy_2Fe_4As_4O_2$ (700 – 1100 ℃)

2. Transport data for Sample2 of $KCa_2Fe_4As_4F_2$ and activation energy H-dependence for $KCa_2Fe_4As_4F_2$ Sample1 and $RbCa_2Fe_4As_4F_2$

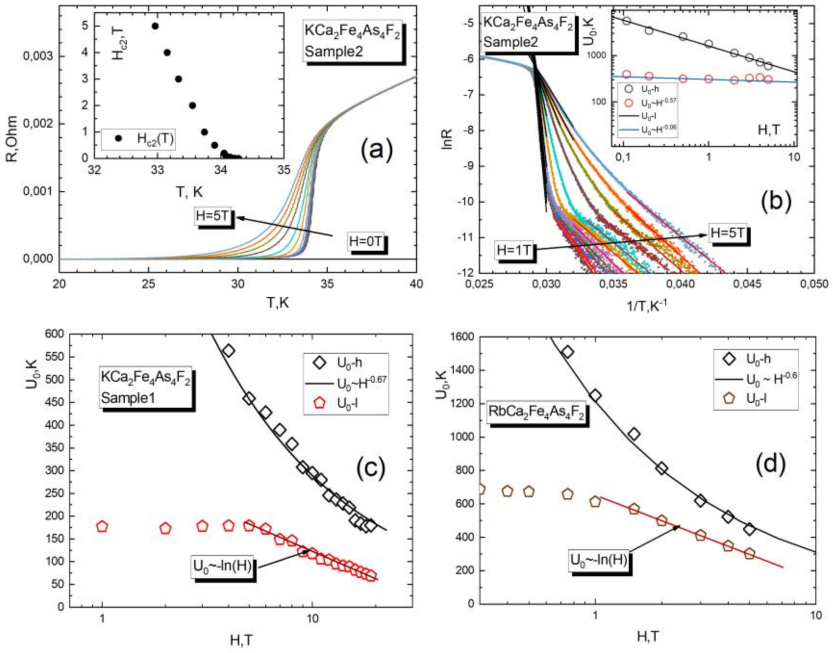

Fig. S4. Resistive transitions in different magnetic fields (inset shows the H_{c2}(T) behavior) and Arrhenius plot (inset shows activation energy U_0(H) field dependence) for $KCa_2Fe_4As_4F_2$ Sample2; Energy activation H-dependence for $KCa_2Fe_4As_4F_2$ Sample1 (c) and $RbCa_2Fe_4As_4F_2$ (d) in semi logarithmic scale.