Electronic Supplementary Information for

Design and Synthesis of Metal Hydroxide Three-Dimensional Inorganic Cationic Framework

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Table S1. Crystal data and results of the structure refinement of Dy,Fe,Cr-3D-ICF

Identification code	Dy,Fe,Cr-3D-ICF
Formula	$Dy_{14.34}FeCr_{0.66}O_{42}H_{42}NaCl_6$
Formula weight/gmol^{-1}	3369.89
Temperature/K	293(2)
Crystal size/mm^3	0.02×0.02×0.02
Lattice parameter/Å	a=b=c=13.2181(1)
Cell volume/Å^3	2309.44(3)
Crystal system	cubic
Space group	Im-3 (229)
$\rho_{calcd.}$/Mgm^{-3}	4.846
Z	2
F(000)	2958
λ/Å	0.71073
Reflections (independent)	5737 (558)
Theta range for data collection/deg.	3.08 to 29.04
Limiting indices	-17<=h<=17, -17<=k<=16, -16<=l<=16
Completeness to theta=29.04	94.7 %
Max. and min. transmission	0.6478 and 0.6478
Refinement method	Full-matrix least-squares on F^2
Data/Restraints/Parameters	558/1/36
Weighting scheme	
R_1 [I > 2σ(I)]	0.0434
R_1 (all)	0.0500
wR_2 [I > 2σ(I)]	0.0867
wR_2 (all)	0.0895
GooF (all)	1.020
Largest diff. peak and hole/eÅ^{-3}	4.129 and -5.763

Table S2. Atomic sites and equivalent isotropic displacement parameters of Dy,Fe,Cr-3D-ICF.

Atom	Wyck	Site	x/a	y/b	z/c	U(eq)[Å²]*
Dy(1)	24g	m..	0.3538	0.3314	0	0.010
Cr(1)	8c	.-3.	0.2500	0.2500	0.2500	0.058
Fe(1)	8c	.-3.	0.2500	0.2500	0.2500	0.058
Dy(2)	8c	.-3.	0.2500	0.2500	0.2500	0.058
O(1)	24g	m..	0.1885	0.3973	0	0.012
O(2)	12e	mm2..	0.3903	0.5000	0	0.039
O(3)	48h	1	0.1995	0.1104	0.3151	0.030
Cl(1)	12d	mm2..	0.5000	0.5000	-0.2633	0.030
Na(1)	2a	m-3	0.5000	0.5000	-0.5000	0.022
H(1)	24g	m..	0.1426	0.3424	0	0.015
H(2)	24g	m..	0.4575	0.5000	0.467	0.047
H(3)	48h	1	0.1389	0.0739	0.2910	0.036

*U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

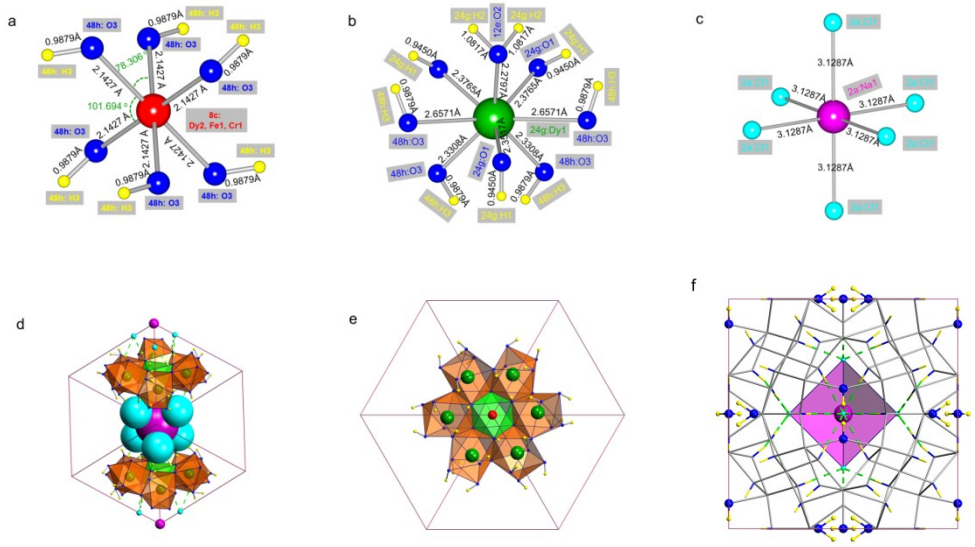

Fig. S1. Building blocks and local structure of Dy,Fe,Cr-3D-ICF. **a**, Coordination of octahedral site with the group of $(Dy_{0.58},Fe_{0.25},Cr_{0.17})(OH)_6$. **b**, Coordination of rare-earth site polyhedral group of $Dy(OH)_8$. **c**, Body-centered site of $NaCl_6$ anionic group. **d**, Similarity to layered double hydroxide in partial structure of Dy,Fe,Cr-3D-ICF. Hydrogen bond of O-H…Cl is presented as green segmented lines, space-filling atoms of Na (pink) and Cl (cyan) is presented to show the anion occupancy in the cage. **e**, Edge-sharing $Dy(OH)_8$ polyhedrons and $(Dy_{0.58},Fe_{0.25},Cr_{0.17})(OH)_6$ octahedrons, yellow H atoms linked with O are pointed to the inside of cage. **f**, Unit cell structure of Dy,Fe,Cr-3D-ICF view from <001> direction.

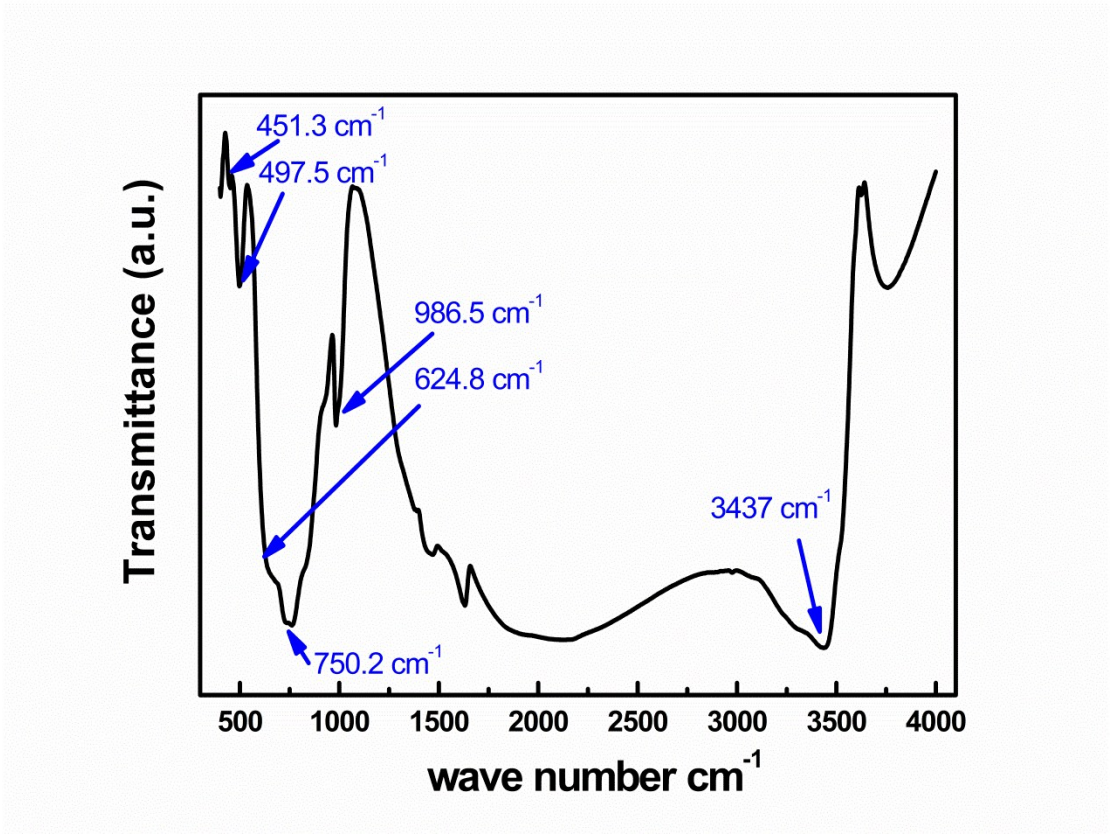

Fig. S2. Room temperature Fourier transform infrared spectroscopy (FT-IR) of Dy,Fe,Cr-3D-ICF.

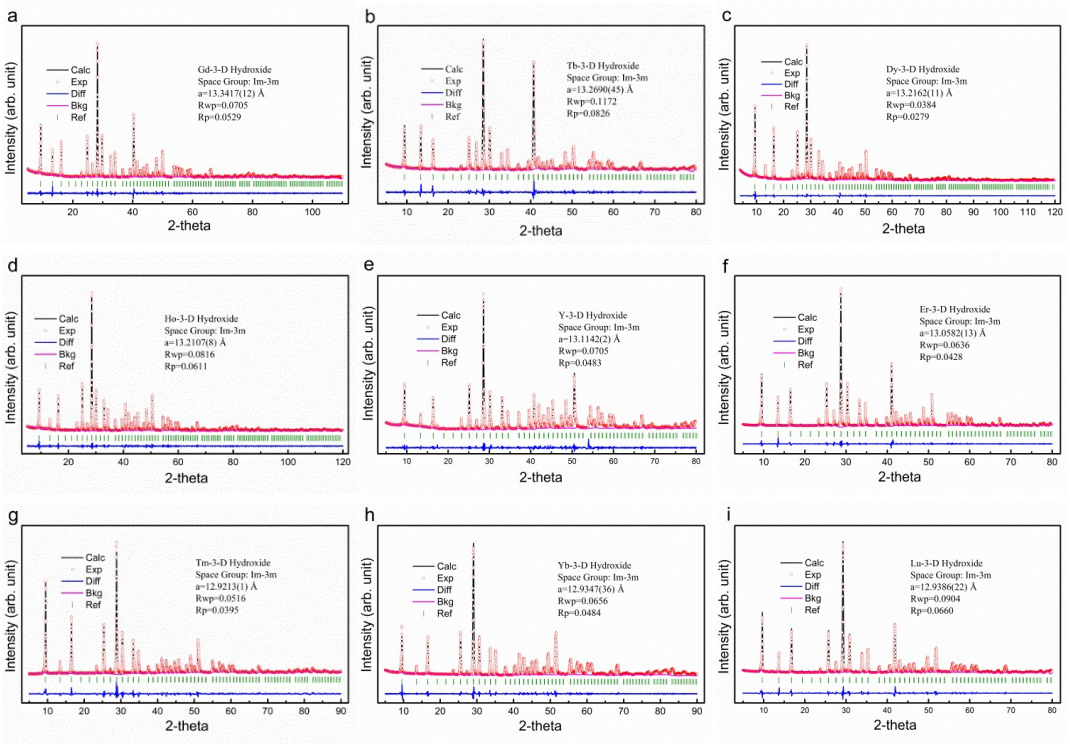

Fig. S3. PXRD results and Pawley refinement of lattice parameters of 3D-ICFs. a, Gd,Fe,Cr-3D-ICF; b, Tb,Fe,Cr-3D-ICF; c, Dy,Fe,Cr-3D-ICF; d, Ho,Fe,Cr-3D-ICF; e, Y,Fe,Cr-3D-ICF; f, Er,Fe,Cr-3D-ICF, g, Tm,Fe,Cr-3D-ICF; h, Yb,Fe,Cr-3D-ICF; i, Lu,Fe,Cr-3D-ICF.

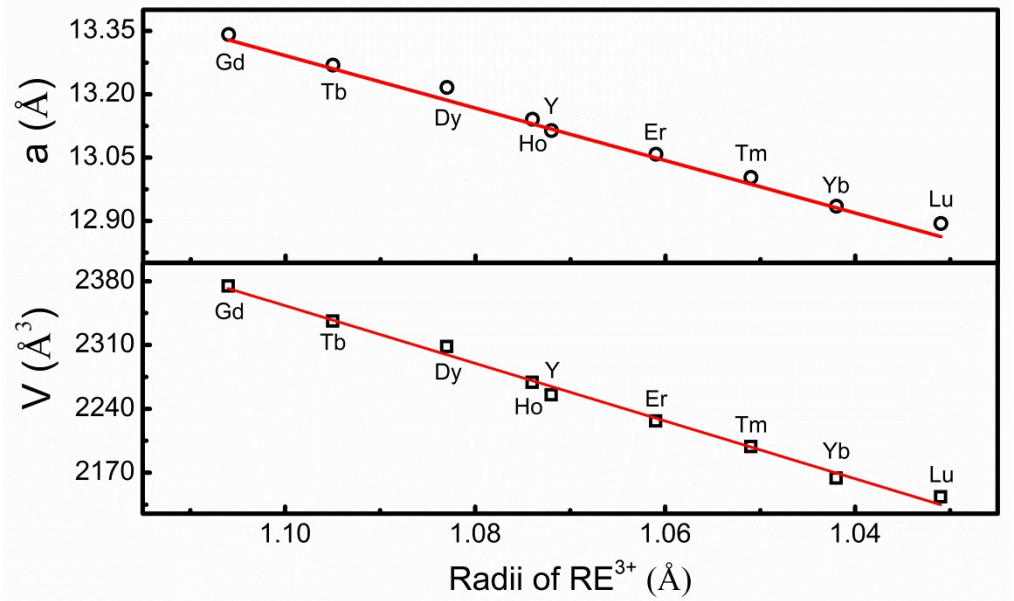

Fig. S4. Variation of lattice parameter (a) and cell volume (V) with effective ionic radii of RE,Fe,Cr-3D-ICFs. Red lines are linear fit to the data.

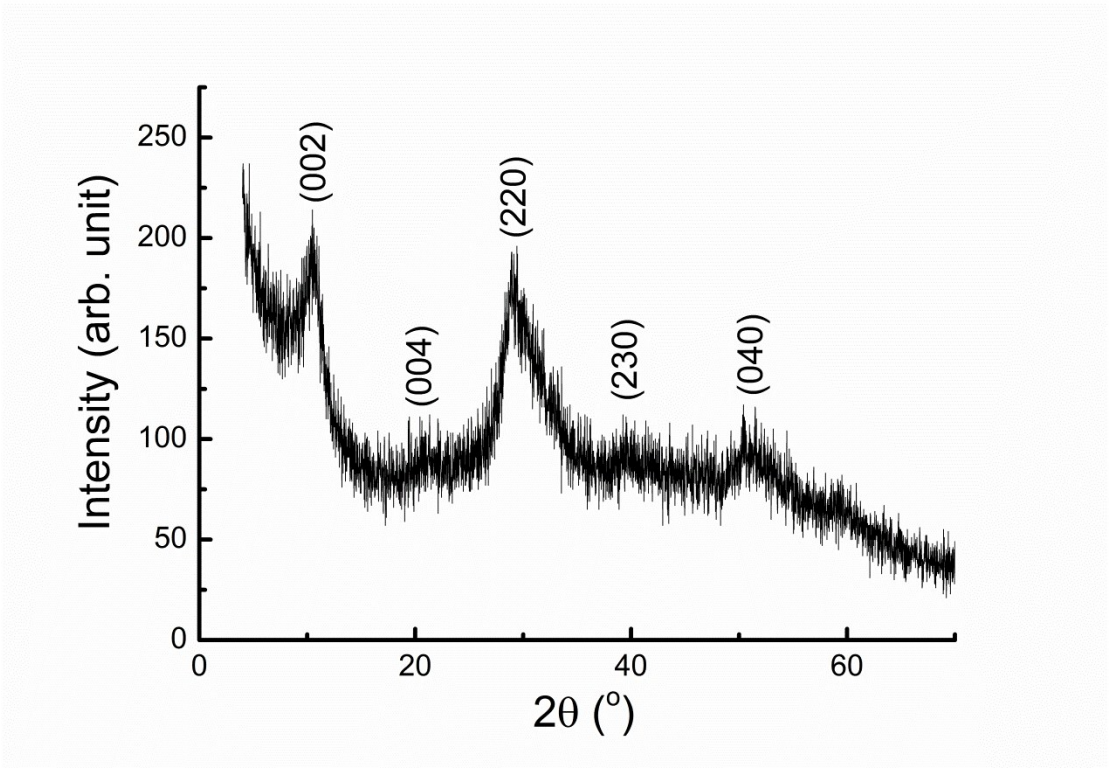

Fig. S5. PXRD of Cr-modified LDyH precursor.

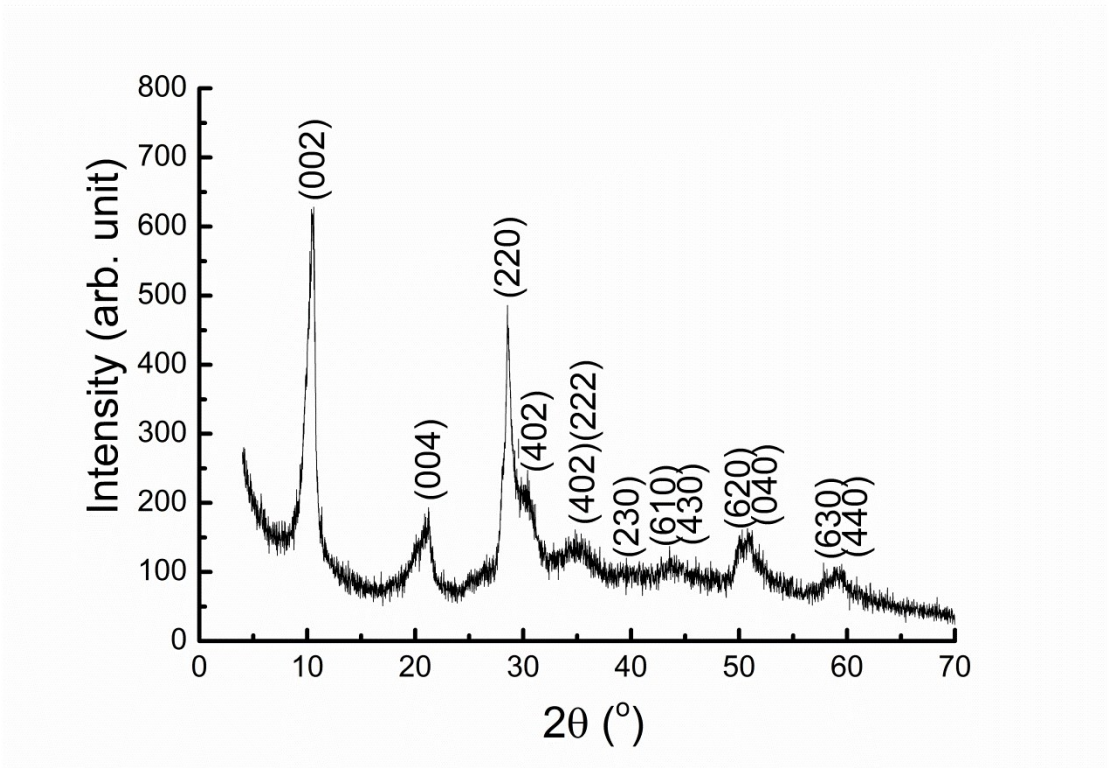

Fig. S6. PXRD of Fe-modified LDyH precursor.

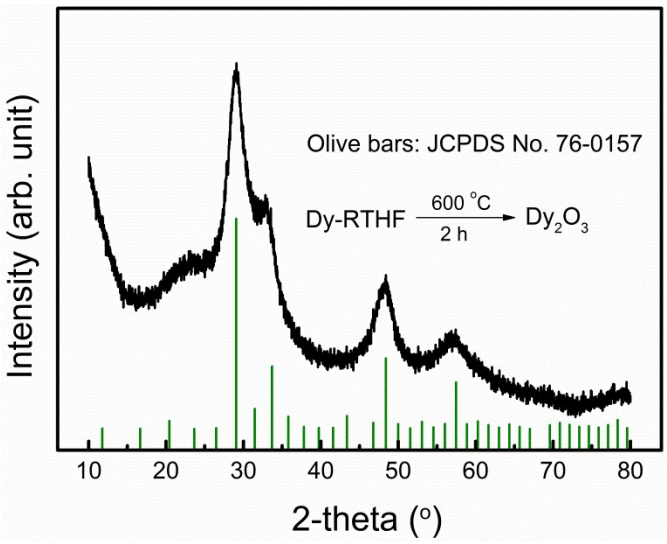

Fig. S7. PXRD of thermal decomposition product of Dy,Fe,Cr-3D-ICF. Vertical olive bars are peak position and intensity of the resulted Dy_2O_3 phase.

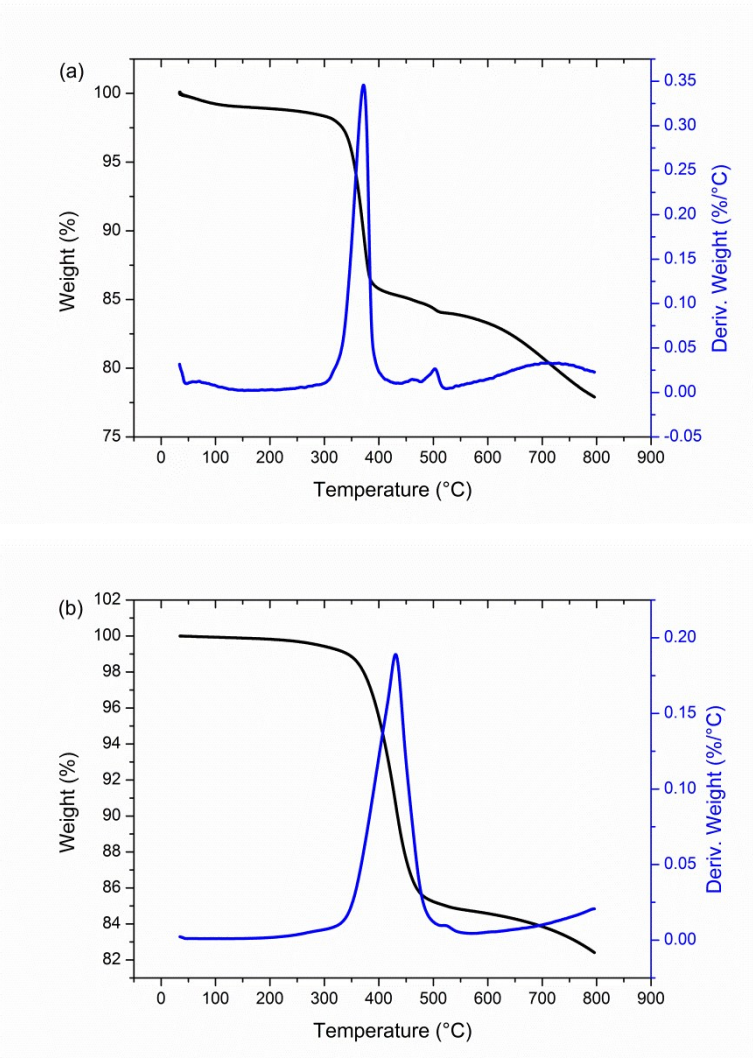

Fig. S8. TG-DTA results of (a) Tb,Fe,Cr-3D-ICF and (b) Y,Fe,Cr-3D-ICF.

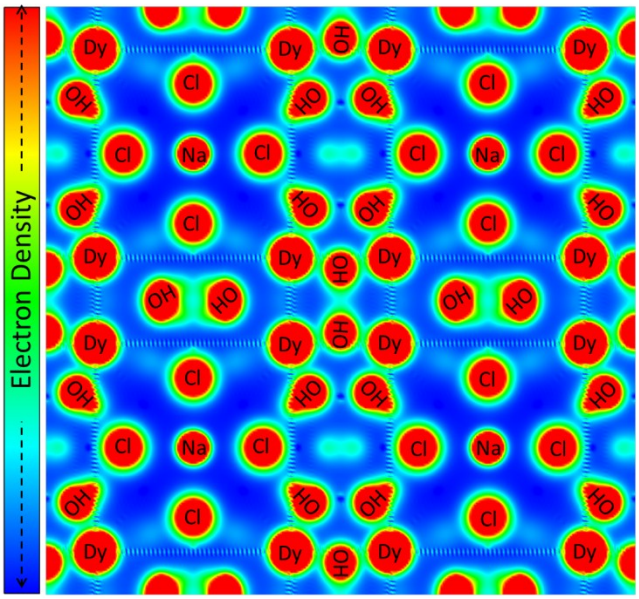

Fig. S9. Electron density map of {001} plane of Dy,Fe,Cr-3D-ICF visualized with VESTA 3 program.

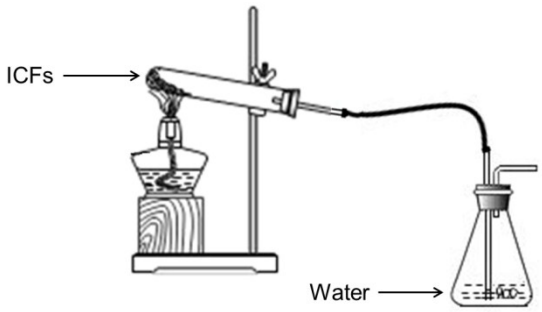

Fig. S10. HCl collecting device for thermal decomposition of 3D-ICFs.

Table S3. Amounts of HCl (gas molecule) storage in RE,Fe,Cr-3D-ICFs.

Sample Name	HCl production (experimental)/mL·g^{-1}	HCl production (calculation)/mL·g^{-1}
Gd,Fe,Cr-3D-ICF	40.65	40.80
Tb,Fe,Cr-3D-ICF	40.39	40.50
Dy,Fe,Cr-3D-ICF	39.50	39.89
Ho,Fe,Cr-3D-ICF	39.27	39.48
Er,Fe,Cr-3D-ICF	38.94	39.09
Tm,Fe,Cr-3D-ICF	38.80	38.82
Yb,Fe,Cr-3D-ICF	37.92	38.17
Lu,Fe,Cr-3D-ICF	37.69	37.88
Y,Fe,Cr-3D-ICF	57.99	58.06

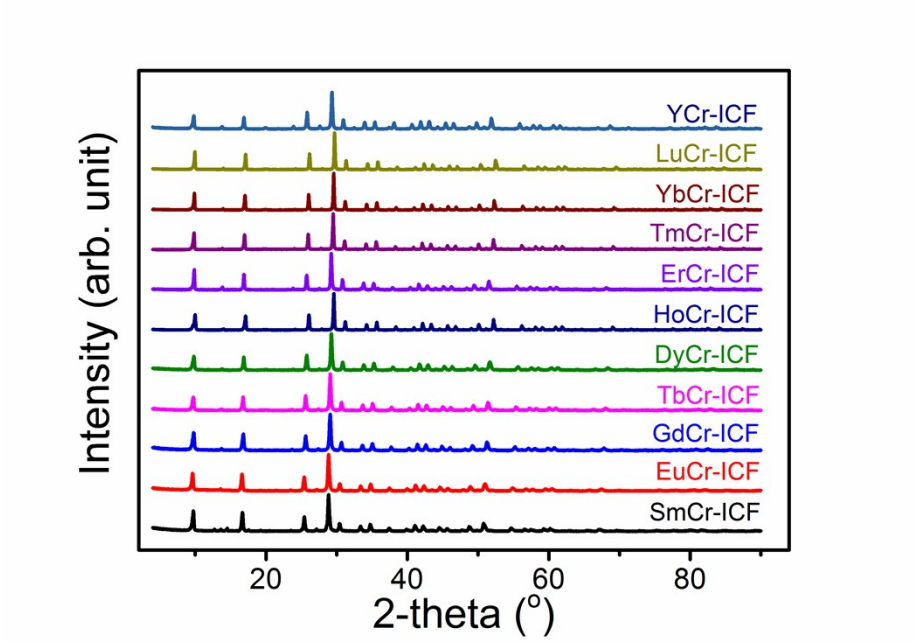

Fig. S11. Powder x-ray diffraction results of RE,Cr-3D-ICFs.

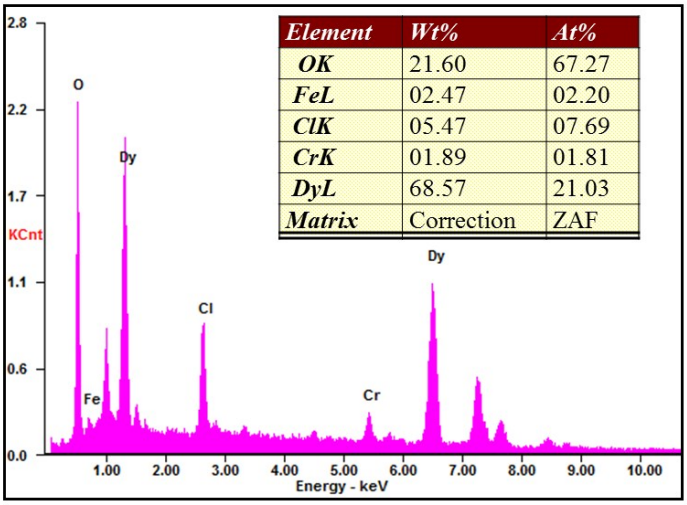

Fig. S12. Typical EDS result of Dy,Fe,Cr-3D-ICF single crystal.