

Supporting Information

Entropy Stabilized Cubic $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ with Reduced Lithium Diffusion Activation Energy

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Experimental Procedures

1. Materials

Lithium nitride (LiNO_3), lanthanum(III) nitrate hexahydrate ($\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$), zirconium(IV) chloride (ZrCl_4 , anhydrous), niobium(V) chloride (NbCl_5 , anhydrous), tantalum(V) chloride (TaCl_5 , anhydrous), tungsten(VI) chloride (WCl_6 , anhydrous), tin(IV) chloride (SnCl_4 , anhydrous), hafnium(IV) chloride (HfCl_4 , anhydrous), citric acid, anhydrous ethanol were purchased from commercial sources (Fisher Scientific, Sigma-Aldrich) and were used without further purification.

2. Synthesis of Single-Metal $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) and High-entropy LLZO (HE-LLZOs)

2.1 The synthesis of single metal $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$:

5.42 g citric acid was dissolved in 50 mL of ethanol under 70 °C. Then 9.1 mmol LiNO_3 , 3 mmol $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 2 mmol ZrCl_4 were added to the above non-aqueous solution to form a transparent solution, which was then heated at 70 °C to evaporate all the solvents and to form a dry gel. After calcining at 250 °C for 5 hours, the dry gel was ground into a powder, which was then calcinated at 700 °C for 12 hours in a MgO crucible to afford the single-metal LLZO.

2.2 The synthesis of high-entropy $\text{Li}_{5.4}\text{La}_3(\text{Zr}_{0.4}\text{Sn}_{0.4}\text{Nb}_{0.4}\text{Ta}_{0.4}\text{W}_{0.4})\text{O}_{12}$:

5.42 g citric acid was dissolved in 50 mL of ethanol under 70 °C. Then 7.02 mmol LiNO_3 , 3 mmol $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 0.4 mmol ZrCl_4 , 0.4 mmol SnCl_4 , 0.4 mmol NbCl_5 , 0.4 mmol TaCl_5 , 0.4 mmol WCl_6 , were added to the above non-aqueous solution to form a transparent solution, which was then heated at 70 °C to evaporate all the solvents and to form a dry gel. After calcining at 250 °C for 5 hours, the dry gel was ground into a powder, which was then calcinated at 700 °C for 12 hours in a MgO crucible to afford the high-entropy $\text{Li}_{5.4}\text{La}_3(\text{Zr}_{0.4}\text{Sn}_{0.4}\text{Nb}_{0.4}\text{Ta}_{0.4}\text{W}_{0.4})\text{O}_{12}$.

2.3 The synthesis of high-entropy $\text{Li}_{5.4}\text{La}_3(\text{Zr}_{0.4}\text{Hf}_{0.4}\text{Nb}_{0.4}\text{Ta}_{0.4}\text{W}_{0.4})\text{O}_{12}$:

5.42 g citric acid was dissolved in 50 mL of ethanol under 70 °C. Then 7.02 mmol LiNO_3 , 3 mmol $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 0.4 mmol ZrCl_4 , 0.4 mmol HfCl_4 , 0.4 mmol NbCl_5 , 0.4 mmol TaCl_5 , 0.4 mmol WCl_6 , were added to the above non-aqueous solution to form a transparent solution, which was then heated at 70 °C to evaporate all the solvents and to form a dry gel. After calcining at 250 °C for 5 hours, the dry gel was ground into powder, which was then calcinated

at 700 °C for 12 hours in a MgO crucible to afford the high-entropy $\text{Li}_{5.4}\text{La}_3(\text{Zr}_{0.4}\text{Hf}_{0.4}\text{Nb}_{0.4}\text{Ta}_{0.4}\text{W}_{0.4})\text{O}_{12}$.

3. Characterization

Powder X-ray diffraction (XRD) patterns were tested by a PANalytical Empyrean diffractometer at 45 kV and 40 mA with Cu $K\alpha$ radiation. Field emission scanning electron microscopy (SEM) observations and elemental maps were performed on a Hitachi S-4800 microscope operated at an accelerating voltage of 20.0 kV. NMR experiments were performed on a Solid-State NMR Varian INOVA 400 MHz, equipped with a 5 mm Chemagnetic CPMAS probe. ^7Li static spectra were acquired with a single pulse experiment at a Larmor frequency of 155.38 MHz, with a 90° pulse of $5\mu\text{s}$ and a recycle delay of 3.0 s. Due to the relative smaller quadrupole moment of ^6Li compared to that of ^7Li , ^6Li NMR has better spectral resolution. ^6Li spectra were acquired with a single pulse MAS experiment, at a Larmor frequency of 58.89 MHz. MAS rate was 10 kHz, recycle delay 40.0 s, and 90° pulse length $6.0\mu\text{s}$. Both ^6Li and ^7Li chemical shifts were referenced to the Li signal of a LiCl solution. All spectra were simulated with DMFIT software utilizing the G/L mode.

Scanning transmission electron microscopy (STEM) data was collected using Nion® UltraSTEM 200 microscope operated at 200 kV and equipped with cold field emission gun. The images in Fig. 3 are representative of a larger dataset and at 2048×2048 pixels and 32×32 nm provide an optimal combination of real and reciprocal space information. Dwell time per pixel used was $4\mu\text{s}$.

4. The calculations of the configurational entropy

$$\text{Calculation of configurational entropy } S_{\text{config}}: S_{\text{config}} = -R \left[\sum_{m=1}^n X_m \ln(X_m) \right]$$

where X_m is the mole fraction of the metal ions present at the M site and R is the gas constant $8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$. For the high entropy HE-LLZOs (M = 5 different metal ions), the mole fractions of the metal ions are from the EDX spectra (Figure S5 and Figure S7). To be specific, the S_{config} of the afforded $\text{Li}_{5.4}\text{La}_3(\text{Zr}_{0.4}\text{Sn}_{0.4}\text{Nb}_{0.4}\text{Ta}_{0.4}\text{W}_{0.4})\text{O}_{12}$ and $\text{Li}_{5.4}\text{La}_3(\text{Zr}_{0.4}\text{Hf}_{0.4}\text{Nb}_{0.4}\text{Ta}_{0.4}\text{W}_{0.4})\text{O}_{12}$ are 1.59 R, and 1.60 R, respectively, which are much higher than that of the obtained single metal LLZO (0 R).

5. Machine learning for the exploration of probable relationships or trends between

various metal ions and the ionic conductivity of LLZO

Raw key dataset came from the literature^[1] and is available at a GitHub repository: <https://github.com/abd-adhyatma/llzo-improvement>.

The R code is shown at the end of this document.

Specifically, the OLS regression was firstly used because it is a simple but powerful prediction methods and according to the results of OLS regression, W, Ta, Sb, and Nb among the 13 diverse elements have the greatest influence on ionic conductivity. However, OLS regression makes huge assumptions about structure and may be possibly influenced by over-fitting problem when the model is "too complex". Unlike OLS regression, the KNN method makes very mild structural assumptions and often gives accurate predictions. To avoid over-fitting, ridge regression limits the regression coefficients by imposing a penalty on the number of explanatory variables. PCR and PLS boost the reliability of the OLS by removing correlated variables that do not contribute to any decision making and hence aid in overcoming over-fitting concerns by reducing the number of predictors. The RF method is used to investigate potential nonlinear relationships that may be overlooked by linear models. As shown in Figure S1, the radar charts illustrate the relative contribution or importance of each metal element to the prediction of ionic conductivity. Nb, Ta, W are the most important three predictors based on PCR, RF, and KNN methods; Nb, W, and Bi are the most significant in PLS and Ridge regression; and W, Nb, and Ta rank the top 3 important in OLS regression. As a result, we concluded that Nb, W, and Ta play crucial roles in determining lithium diffusion properties.

Supplementary figures and tables

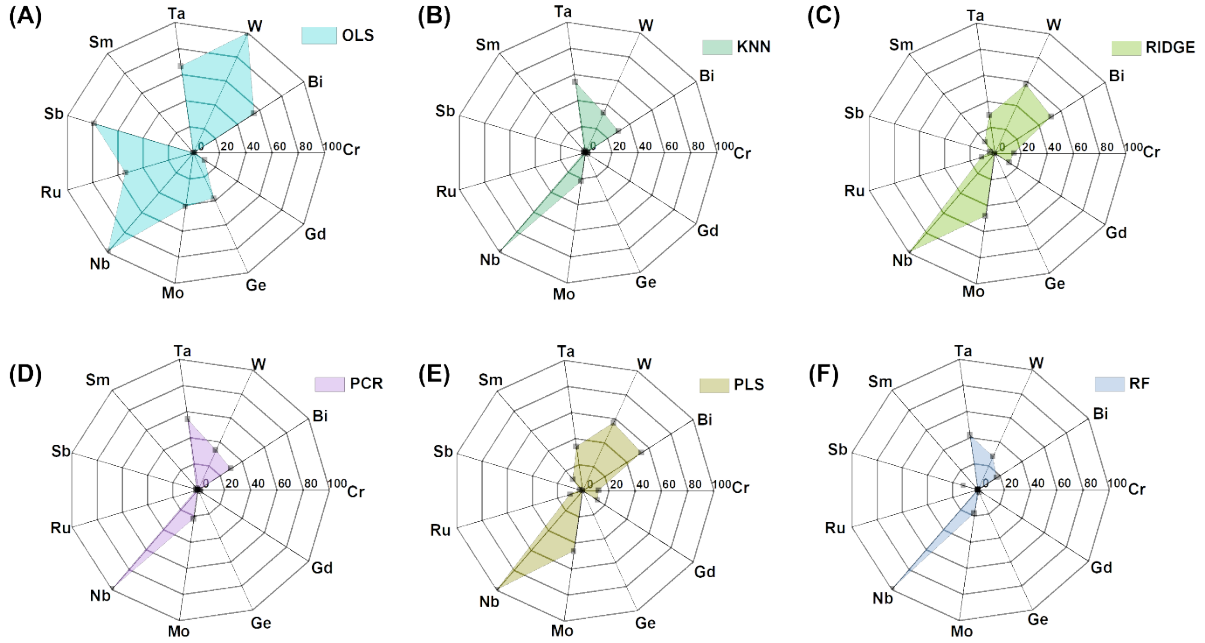


Figure S1. The radar charts of variable importance of various metal elements at Zr^{4+} site of LLZO by machine learning via different methods.

Table S1. Unit-Cell Parameters ($a=b=c$), Cell Volume (V), Weighted Profile Residual (R_{wp}) of various cubic garnet electrolytes

	Cell parameter a (Å)	volume(Å ³)	R_p (%)	R_{wp} (%)
Zr	13.01949	2206.8962	3.66	4.82
ZrSnNbTa W	12.84544	2119.5661	4.21	5.43
ZrHfNbTaW	12.85418	2123.8954	3.82	5.31

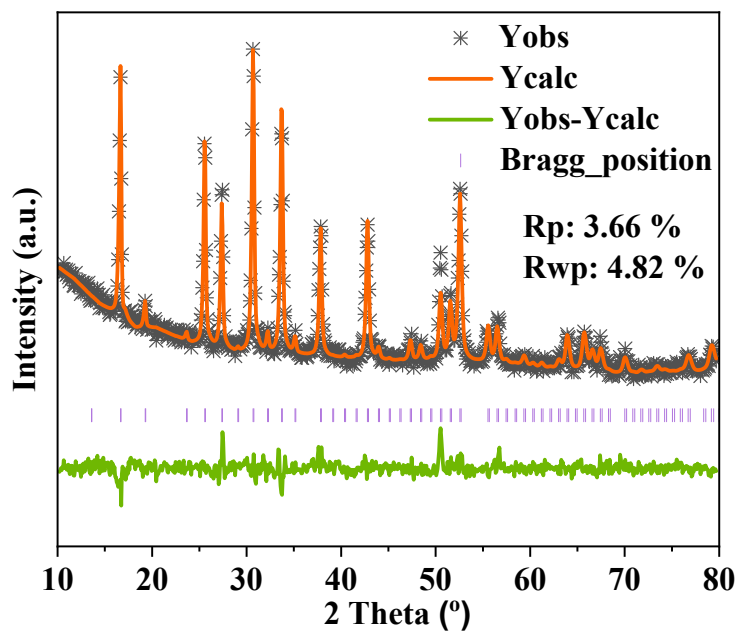


Figure S2 Rietveld refinement analysis of single-metal cubic $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ stored at 200 °C.

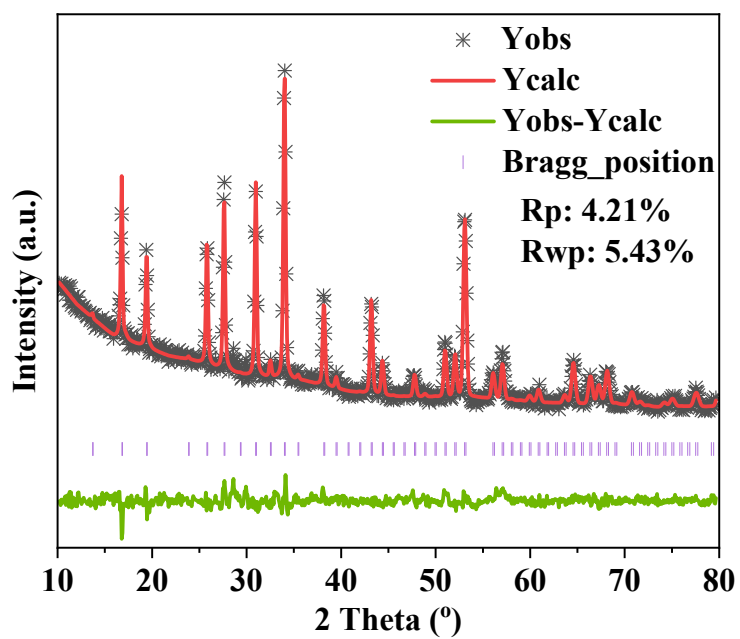


Figure S3 Rietveld refinement analysis of $\text{Li}_{5.4}\text{La}_3(\text{Zr}_{0.4}\text{Sn}_{0.4}\text{Nb}_{0.4}\text{Ta}_{0.4}\text{W}_{0.4})\text{O}_{12}$.

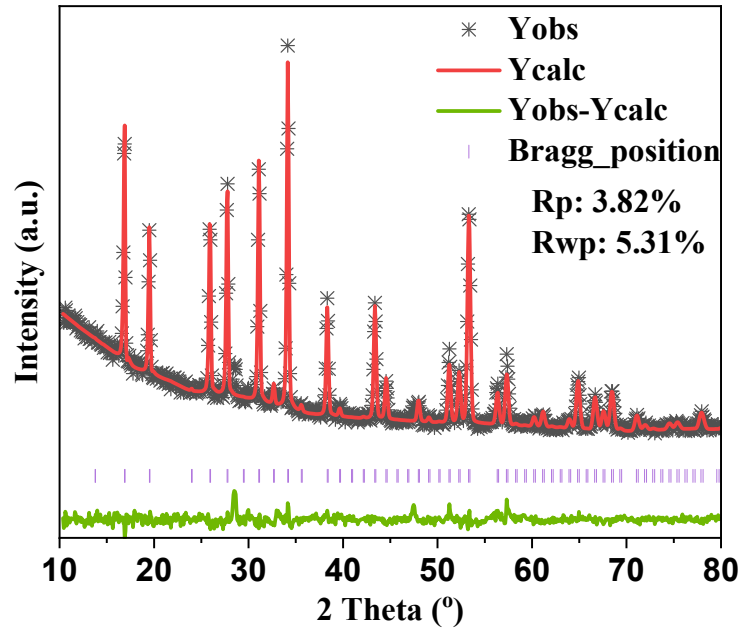


Figure S4 Rietveld refinement analysis of $\text{Li}_{5.4}\text{La}_3(\text{Zr}_{0.4}\text{Hf}_{0.4}\text{Nb}_{0.4}\text{Ta}_{0.4}\text{W}_{0.4})\text{O}_{12}$.

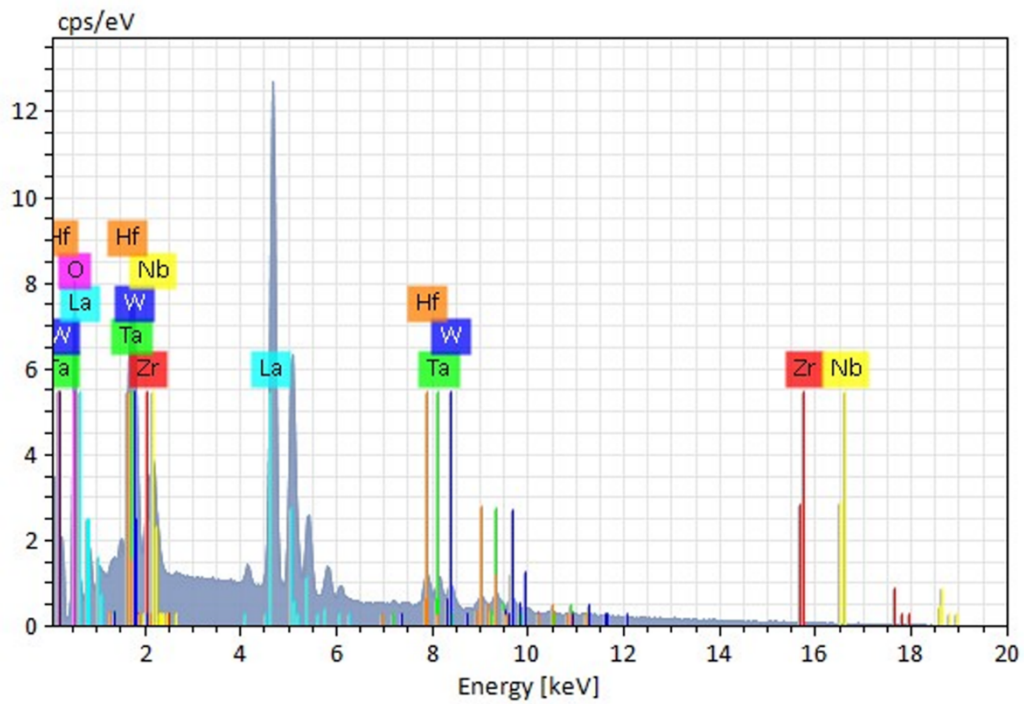


Figure S5 EDX spectrum of the high entropy $\text{Li}_{5.4}\text{La}_3(\text{Zr}_{0.4}\text{Hf}_{0.4}\text{Nb}_{0.4}\text{Ta}_{0.4}\text{W}_{0.4})\text{O}_{12}$.

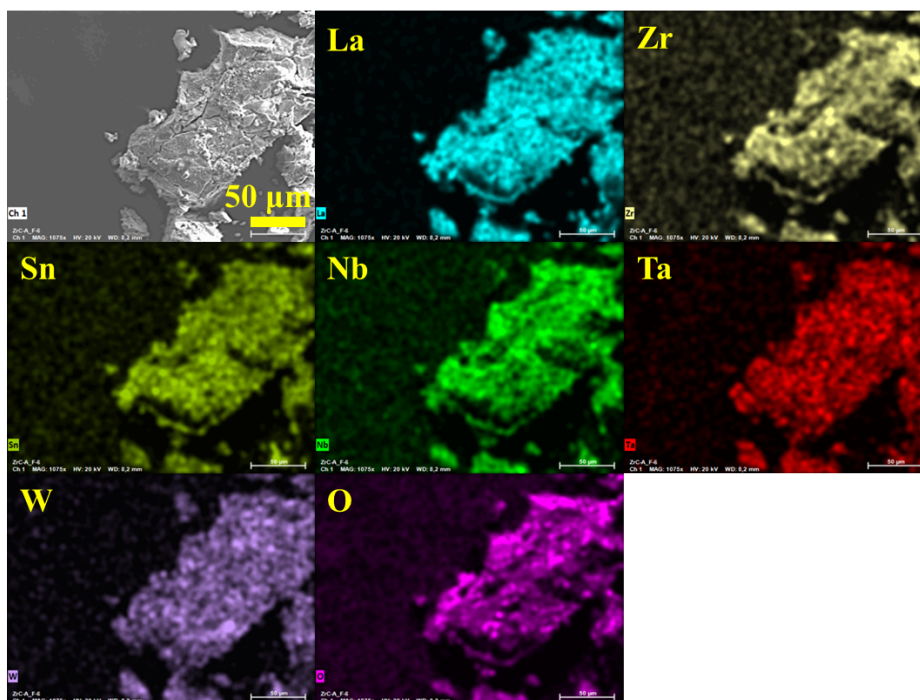


Figure S6 EDX mapping of the high entropy $\text{Li}_{5.4}\text{La}_3(\text{Zr}_{0.4}\text{Sn}_{0.4}\text{Nb}_{0.4}\text{Ta}_{0.4}\text{W}_{0.4})\text{O}_{12}$.

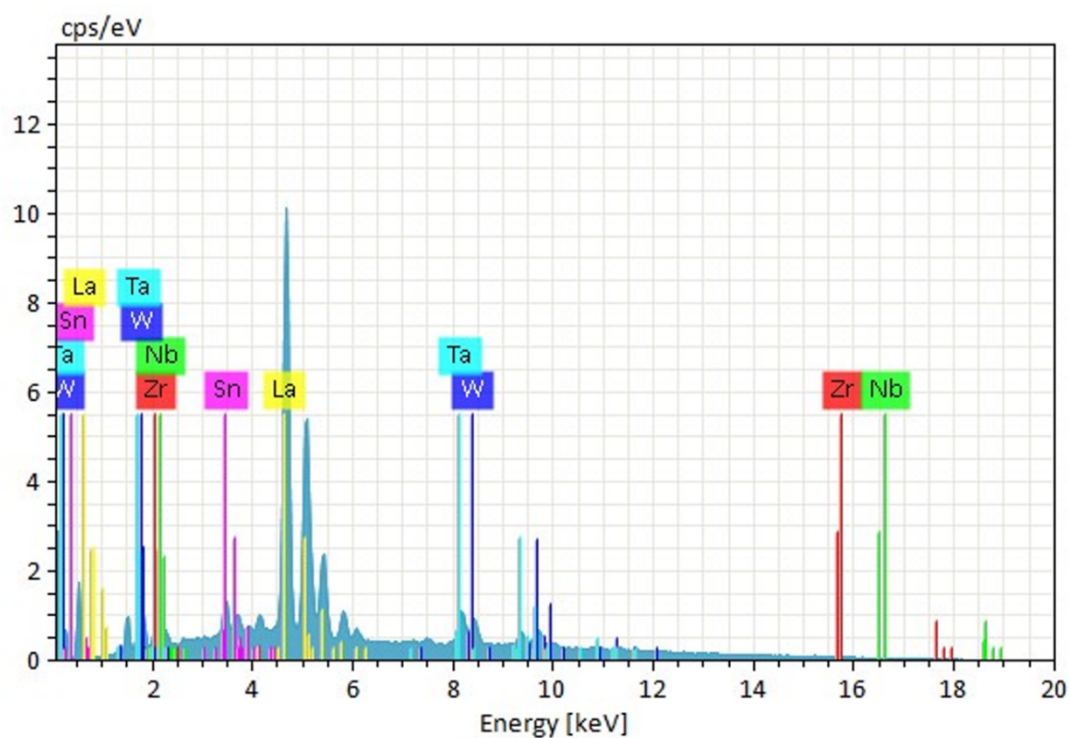


Figure S7 EDX spectrum of the high entropy $\text{Li}_{5.4}\text{La}_3(\text{Zr}_{0.4}\text{Sn}_{0.4}\text{Nb}_{0.4}\text{Ta}_{0.4}\text{W}_{0.4})\text{O}_{12}$.

The EDX spectrum (Figure S7) showed that the atomic ratio of Zr:Sn:Nb:Ta:W is 0.168:0.145:0.228:0.250:0.209, indicating near equiatomic ratio of different metal ions at the Zr site.

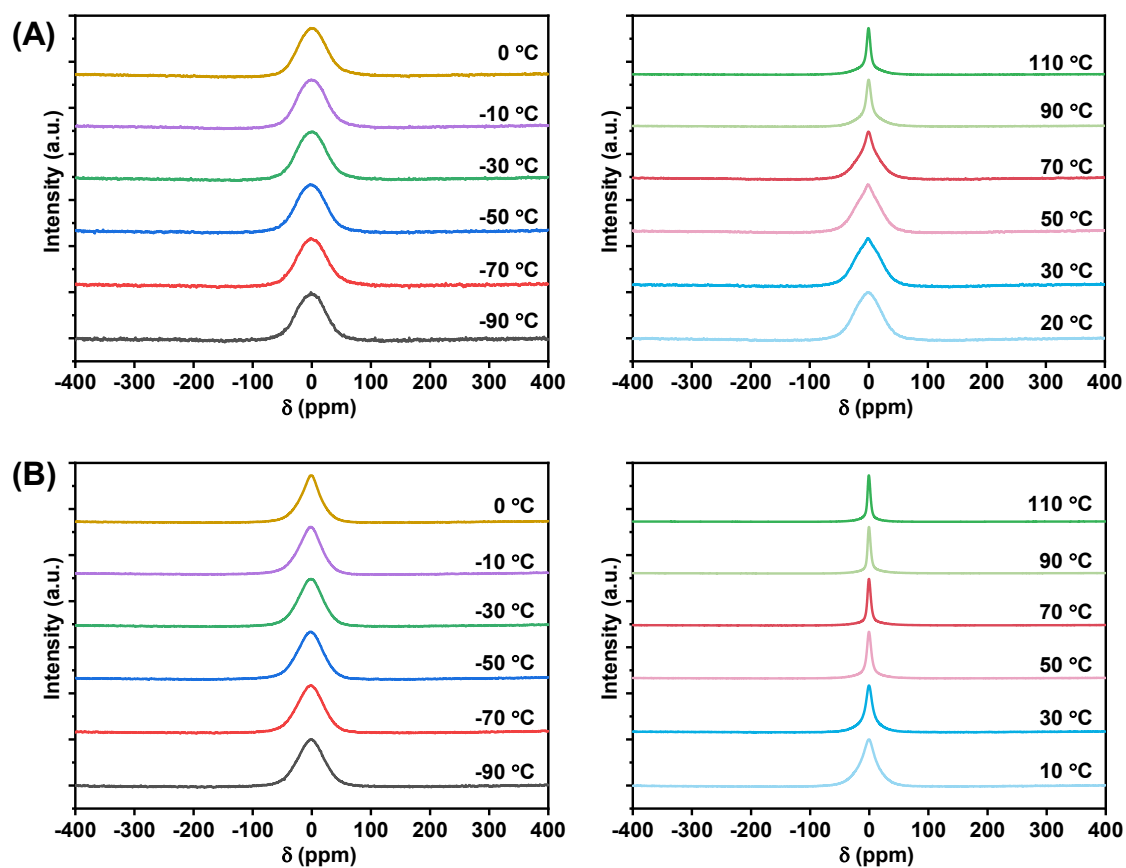


Figure S8 Static ${}^7\text{Li}$ NMR at different temperatures from $-90\text{ }^\circ\text{C}$ to $110\text{ }^\circ\text{C}$ of the (A) single metal $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$. (B) high entropy $\text{Li}_{5.4}\text{La}_3(\text{Zr}_{0.4}\text{Sn}_{0.4}\text{Nb}_{0.4}\text{Ta}_{0.4}\text{W}_{0.4})\text{O}_{12}$ (The peaks were re-scaled to show similar intensities.).

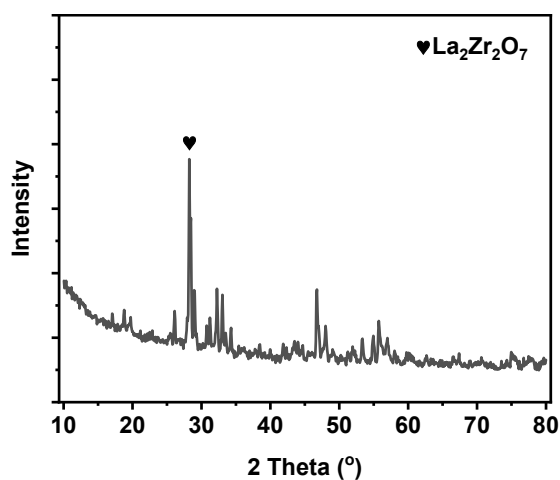


Figure S9 XRD patterns of as-synthesized particles sintering at $900\text{ }^\circ\text{C}$ for 12 h.

R code is as follows:

```
# code version R 4.1.3
```

```
library(keras)
```

```

library(nnet)
library(caret)
library(pls)
library(fmsb)

data <- read.csv('llzo_dataset_edat1.csv',header = T)[1:73,c(8,2,3,5,6,7)]
labels <- class.ind(data$zr_dopant)
data<-cbind(data,labels)
for (i in 7:ncol(data)){
  data[,i]<-data[,i]*data[,3]
}
data[,3:4]<-NULL
data[,1]<-data[,1]*100000
data<-data[,1:15]
seed <- 1209
set.seed(seed); train.rows <- sample(1:nrow(data), 0.8*nrow(data))
TRAIN <- data[train.rows,]; HOLDOUT <- data[-train.rows,]
fitControl <- trainControl(method="cv",number=4)
# Multiple Linear Regression
set.seed(seed);
LM <- train(Ionic.conductivity~., data = TRAIN,method = 'glm',
           trControl = fitControl, preProc = c("center", "scale") )
# Ridge Regression
glmnetGrid <- expand.grid(alpha = 0, lambda = 10^seq(-4,2,by = .5))
set.seed(seed);
Ridge <- train(Ionic.conductivity~., data = TRAIN, method = 'glmnet',
              trControl = fitControl, tuneGrid = glmnetGrid,
              preProc = c("center", "scale") )
# Principal Components Regression
pccrGrid <- expand.grid(ncomp = c(1:13))

```

```

set.seed(seed);
PCR <- train(Ionic.conductivity~., data = TRAIN, method = 'pcr',
            trControl = fitControl, tuneGrid = pcrGrid,
            preProc = c("center", "scale"))
# Partial Least Squares Regression
plsGrid <- expand.grid(ncomp = c(1:13))
set.seed(seed);
PLS <- train(Ionic.conductivity~., data = TRAIN, method = 'pls',
            trControl = fitControl, tuneGrid = plsGrid,
            preProc = c("center", "scale") )
# K-Nearest Neighbors
knnGrid <- expand.grid(k = c(1:13))
set.seed(seed);
KNN <- train(Ionic.conductivity~., data = TRAIN, method = 'knn',
            trControl = fitControl, tuneGrid = knnGrid,
            preProc = c("center", "scale"))
# Random Forest
rfGrid <- expand.grid(mtry = 1:sqrt(ncol(TRAIN)))
set.seed(seed);
rf <- train(Ionic.conductivity~.,data = TRAIN, method = "rf",
            trControl = fitControl, tuneGrid = rfGrid,
            preProc = c("center","scale"))

data_radar<-cbind(varImp(LM)$importance, varImp(PCR)$importance[1:14,],
                varImp(PLS)$importance[1:14,], varImp(KNN)$importance[1:14,],
                varImp(rf)$importance[1:14,], varImp(Ridge)$importance[1:14,])
row.names(data_radar)[1:3]<-c("Zr.sto","Zr.rad.,"Zr.ele.")
colnames(data_radar)<-c("OLS","PCR","PLS","KNN","RF","RIDGE")
data_radar <- t(as.matrix(data_radar))
data_radar <- rbind(rep(100,14) , rep(0,14), data_radar)

```

```

data_radar <- as.data.frame(data_radar)
colors_border <- c(rgb(0.2,0.5,0.5,0.9), rgb(0.8,0.2,0.5,0.9), rgb(0.7,0.5,0.1,0.9),
                    rgb(0.2,0.5,0.5,0.4), rgb(0.8,0.2,0.5,0.4), rgb(0.7,0.5,0.1,0.4),
                    rgb(0.2,0.5,0.9,0.4))

data_radar<-data_radar[,c(5:14,4)]
colnames(data_radar)<-c("Cr", "Gd", "Ge", "Mo", "Nb", "Ru", "Sb", "Sm", "Ta", "W", "Bi")
data_radar<-data_radar[c(1:3,5:8,4),]
#normalize variable importance
data_max <- apply(data_radar, 1, max, na.rm=TRUE)
for (i in 3:nrow(data_radar)){
  data_radar[i,]<-data_radar[i,]*100/data_max[i]
}
# plot radar chart:
radarchart(data_radar, axistype=1, pcol=10:17,plwd=4, plty=1,
            cglty=3, cglcol="navy", axislabcol="Blue",
            caxislabels = seq(0,100,25), cglwd=1, vlce=2)
legend(x=1, y=1.3, legend = rownames(data_radar[-c(1,2),]),
       bty = "n", pch=10, col=10:17, text.col = "black", cex=1, pt.cex=2)

```

[1] A. Adhyatma, Y. Xu, N. H. Hawari, P. Satria Palar, A. Sumboja, *Mater. Lett.* **2022**, 308, 131159.