Supplementary for Structure Determination Feasibility of Three-Dimensional Electron Diffraction in Case of Limited Data

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Bond Valence Calculations

In order to estimate the quality of the structure via the global optimization method, we have used the Bond valence technique, which compares the calculated oxidation state for each atom with the known oxidation state of the atom. Bond valence calculations are carried out in VESTA software [91]. The published structure acted as a reference and was compared with the best solution for each data set obtained from Endeavour (atomic coordinates of the structure presented in Tables 1, 2, 3, 4). Results from the bond calculated are listed in S1, S2, and S3. No further bond valence calculations were performed when all the light atoms' positions were not found. For bond valence calculations, parameters are taken from the published paper of I. D. Brown [92, 93]. For bond valence calculations and fair comparison with the reference structure, it is essential to have all the expected atom positions in the structure. For $PrBa_2Cu_3O_7$, it has been reported [60] that both Cu^{2+} and Cu^{3+} are present in this material. In the, we only considered the Cu^{2+}state. For $BaCuO_2$. In the following not all atom positions were determined. Therefore no further bond valence calculations were performed. For $LiAl_{0.8}Fe_{0.2}(SiO_3)_2$, bond valence calculations, it was assumed that there are no Fe atoms and the Al atoms have full occupancy.

The intensity extraction process uses the max-integrated intensity and fitted integrated intensity, except for $(LiAl(SiO_3)_2$ sample, which only used the maximum integrated intensity. Not all atom positions were located by ab initio structure solution. Therefore bond valence calculations were not performed for any of the structures obtained via ab initio structure solution.

To better understand the structure's quality, all the RMSD values in Table 1, Table 3, and Table 4 are presented in a Pie chart (Figure S1). The bar chart shows the best quality structure solution obtained from the 3D ED dataset of $LiAl(SiO_3)_2$ compound.

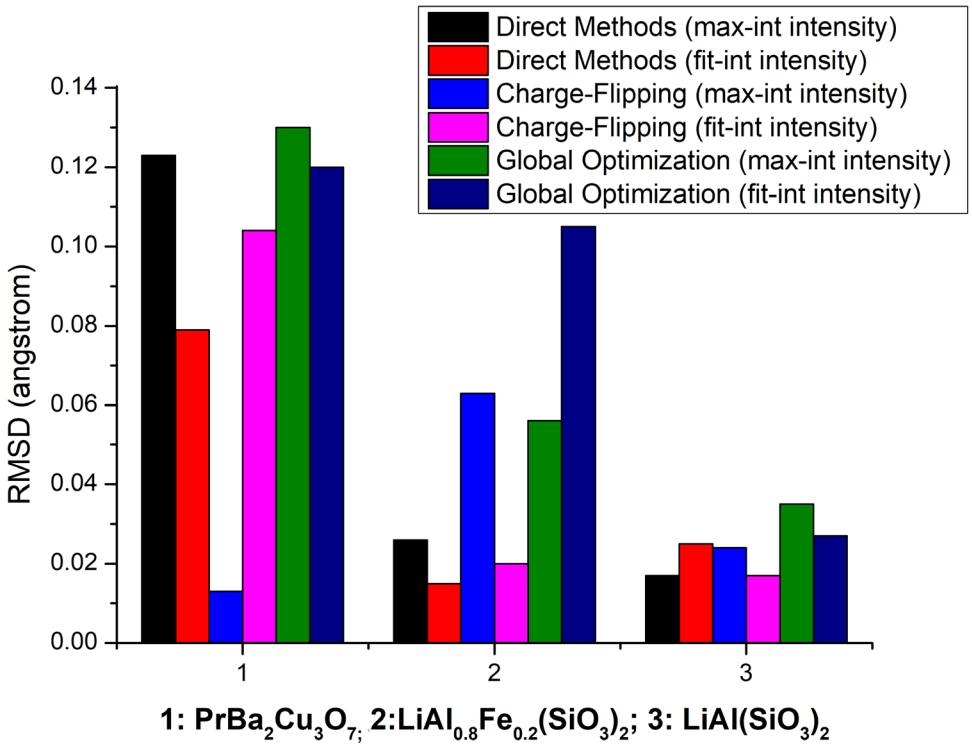

Figure S1: RMSD plot for the values presented in Table 1, Table 3, Table 4

Table S1: Bond valence calculations for Pr, Ba, Cu atoms using the reference structure PrBa2Cu3O7 (COD-1520852.cif) and structure obtained using global optimization method in Endeavour

$PrBa_2Cu_3O_7$	*Oxidation State*	*Reference X-Ray Structure (COD-1520852.cif)*	*eADT*	*PETS2*
Pr	*3*	*3.53903*	*4.79357*	*4.70764*
Ba	*2*	*2.16000*	*1.95602*	*1.96412*
Cu1	*2*	*1.81330*	*1.49469*	*1.56503*
Cu2	*2*	*2.07097*	*2.05817*	*2.03377*

Table S2: Bond valence calculations for Li, Al, Si atoms using the reference structure LiAl0.8Fe0.2(SiO3)2and structure obtained using global optimization method in Endeavour

$LiAl_{0.8}Fe_{0.2}(SiO_3)_2$	*Oxidation State*	*Reference X-Ray Structure [65]*	*eADT*	*PETS2*
Li	*1*	*0.81857*	*0.80299*	*0.83677*
Al	*3*	*2.94670*	*2.54653*	*2.37208*
Si	*4*	*4.04814*	*4.0054*	*4.93187*

Table S3: Bond valence calculations for Li, Al, Si atoms using the reference structure and structure obtained using global optimization method in Endeavour

$LiAl(SiO_3)_2$	*Oxidation State*	*Reference X-Ray Structure [65]*	*eADT*	*PETS2*
Li	*1*	*0.81857*	*0.83647*	*0.84425*
Al	*3*	*2.94670*	*2.88374*	*2.92854*
Si	*4*	*4.04814*	*4.40925*	*4.34244*

In conclusion, bond valence calculations demonstrate that the models obtained from global optimization are robust and comparable to the known structure models derived from X-ray crystallography for all three specimens studied.

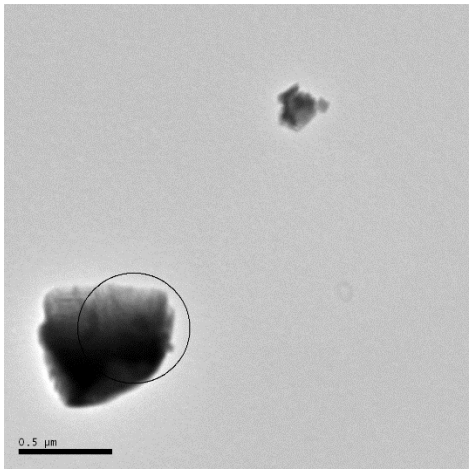

Figure S2: TEM image of the PrBa2Cu3O7 crystal, black circle shows the area from where 3D ED data was collected.

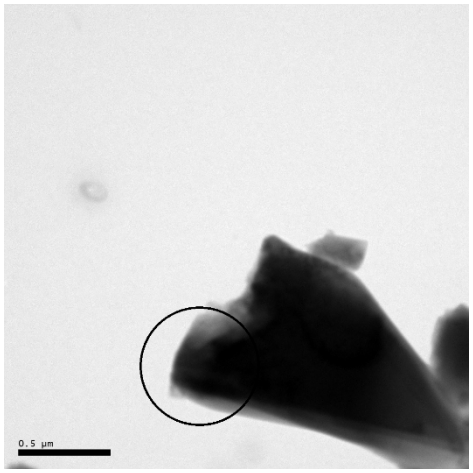

Figure S3: TEM image of the LiAl0.8Fe0.2(SiO3)2 crystal, black circle shows the area from where 3D ED data was collected.