Electronic Supplementary Material (ESI) for CrystEngComm.

Large-sized Crystal Growth and Piezoelectric properties of the single crystals $LiNa_5Mo_9O_{30}$

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1. Table S1. Local dipole moment calculation of five different MoO_6 octahedrons

MoO_6 (1)			Cart. Coord.			Distance	Unit vector				Dipole moment for each		
Z	**Atom**	**Charges**	**X**	**Y**	**Z**	**Å**	**x**	**y**	**z**	**Unitized**	**C_{grav}**	**C_{charge}**	**u_{debye}**
42	Mo01	6.09370	1.54036	12.98748	9.52190								
8	O1	-1.676	0.62334	12.99900	11.00760	1.746	0.52523	-0.00660	-0.85094	1	0.16	0.21227	19.96711
8	O00A	-0.537	3.40704	13.07330	8.44556	2.156	-0.86562	-0.03979	0.49912	1	0.16	0.19209	14.76170
8	O00E	-1.642	0.37270	13.05472	8.27679	1.708	0.68352	-0.03936	0.72887	1	0.16	0.21169	19.30556
8	O00G	-1.186	2.14448	11.25366	9.41867	1.839	-0.32851	0.94283	0.05614	1	0.16	0.20371	17.39772
8	O00M	-0.849	2.16398	14.85875	9.48330	1.973	-0.31611	-0.94852	0.01957	1	0.16	0.19772	15.98684
8	O1N	-0.204	3.19108	12.99899	11.45824	2.544	-0.64874	-0.00453	-0.76099	1	0.16	0.18599	14.00178
				Cell Volume		4817.61			Dipole Moment			Magnitude	
				Z		4			x	y	z		
				Total Dipole Moment =			0.00848 esu*cm/A^3		-8.9474	-0.3032	-4.9175	**10.2142**	debye
MoO_6 (2)			**Cart. Coord.**			**Distance**	**Unit vector**				**Dipole moment for each**		
Z	**Atom**	**Charges**	**X**	**Y**	**Z**	**Å**	**x**	**y**	**z**	**Unitized**	**C_{grav}**	**C_{charge}**	**u_{debye}**
42	Mo02	6.11518	1.55039	16.78576	9.69713								
8	O00B	-1.680	0.50055	16.70291	11.08839	1.745	0.60167	0.04748	-0.79733	1	0.16	0.21244	20.01318
8	O00C	-0.434	3.42221	16.68545	8.46711	2.242	-0.83487	0.04474	0.54862	1	0.16	0.19030	14.45213
8	O00F	-1.560	0.48971	16.70625	8.33425	1.729	0.61353	0.04599	0.78833	1	0.16	0.21037	18.99571
8	O00H	-1.314	2.12787	18.48614	9.61437	1.798	-0.32123	-0.94588	0.04604	1	0.16	0.20607	17.96913
8	O00K	-0.397	3.05601	16.58031	11.39361	2.278	-0.66108	0.09020	-0.74488	1	0.16	0.18963	14.34329
8	O00M	-0.730	2.16398	14.85875	9.48330	2.034	-0.30172	0.94758	0.10514	1	0.16	0.19567	15.53336
				Cell Volume		4817.611			Dipole Moment			Magnitude	
				Z		4			x	y	z		
				Total Dipole Moment =			0.00709 esu*cm/A^3		-8.3110	1.4866	-1.2768	**8.5389**	debye
MoO_6 (3)			**Cart. Coord.**			**Distance**	**Unit vector**				**Dipole moment for each**		
Z	**Atom**	**Charges**	**X**	**Y**	**Z**	**Å**	**x**	**y**	**z**	**Unitized**	**C_{grav}**	**C_{charge}**	**u_{debye}**
42	Mo03	6.10514	3.61145	18.5753	7.99258								
8	O00B	-0.988	3.42221	16.68545	8.46710	1.958	0.09667	0.96535	-0.24239	1	0.16	0.20026	16.97853
8	O00B	-0.882	3.80069	20.46515	8.46710	1.958	-0.09667	-0.96535	-0.24239	1	0.16	0.19836	16.13845
8	O00H	-0.482	2.12787	18.37469	9.61437	2.207	0.67218	0.09089	-0.73479	1	0.16	0.19114	14.63868
8	O00H	-0.482	5.09503	18.66446	9.61437	2.200	-0.67441	-0.04053	-0.73724	1	0.16	0.19114	14.59008
8	O00J	-1.636	2.31133	18.72762	6.89254	1.710	0.76037	-0.08908	0.64335	1	0.16	0.21163	19.29326
8	O00J	-1.636	4.91157	18.42298	6.89254	1.710	-0.76037	0.08908	0.64335	1	0.16	0.21163	19.29326
				Cell Volume		4817.611			Dipole Moment			Magnitude	
				Z		4			x	y	z		
				Total Dipole Moment =			0.00412 esu*cm/A^3		0.0812	1.5502	-4.7153	**4.9642**	debye
MoO_6 (4)			**Cart. Coord.**			**Distance**	**Unit vector**				**Dipole moment for each**		
Z	**Atom**	**Charges**	**X**	**Y**	**Z**	**Å**	**x**	**y**	**z**	**Unitized**	**C_{grav}**	**C_{charge}**	**u_{debye}**
42	Mo04	6.09559	3.95172	10.99658	8.40588								
8	O00A	-0.616	3.40704	13.07330	8.44556	2.147	0.25365	-0.96712	-0.01848	1	0.16	0.19353	15.38436
8	O00C	-0.259	2.30627	11.16004	6.59989	2.449	0.67198	-0.06676	0.73755	1	0.16	0.18701	14.02222
8	O00D	-1.560	3.55728	9.313655	8.36836	1.729	0.228142	0.97339	0.02170	1	0.16	0.21027	18.96821

8	O00F	-0.638	1.94729	11.25366	9.41867	2.260	0.88674	-0.11373	-0.44805	1	0.16	0.19392	16.39411
8	O00I	-1.644	5.07987	11.16376	9.67721	1.708	-0.66055	-0.09788	-0.74438	1	0.16	0.21173	19.31496
8	O00J	-1.379	4.86173	11.28264	6.90511	1.778	-0.51174	-0.16086	0.84395	1	0.16	0.20712	18.21319
				Cell Volume		4817.611			Dipole Moment			Magnitude	
				Z		4			x	y	z		
				Total Dipole Moment =			0.00966 esu*cm/A^3		10.1111	-4.0362	4.1175	**11.6395**	debye
MoO_6 (5)			**Cart. Coord.**			**Distance**	**Unit vector**				**Dipole moment for each**		
Z	**Atom**	**Charges**	**X**	**Y**	**Z**	**Å**	**x**	**y**	**z**	**Unitized**	**C_{grav}**	**C_{charge}**	**u_{debye}**
42	Mo05	6.12640	4.02323	14.83832	8.405345								
8	O1	-0.276	2.42906	14.86396	6.51910	2.470	0.64546	-0.01038	0.76372	1	0.16	0.18744	14.36452
8	O2	-1.097	3.40704	13.07330	8.44556	1.870	0.32952	0.94390	-0.02151	1	0.16	0.20230	17.07262
8	O00B	-0.914	3.42221	16.68545	8.46711	1.943	0.30926	-0.95045	-0.03178	1	0.16	0.19902	16.30349
8	O00C	-1.756	5.14559	14.84538	9.65746	1.682	-0.66747	-0.00420	-0.74463	1	0.16	0.21380	19.81494
8	O00E	-0.547	2.16398	14.85875	9.48330	2.149	0.86507	-0.00951	-0.50155	1	0.16	0.19241	14.85158
8	O00L	-1.537	4.99680	14.86396	6.96974	1.735	-0.56121	-0.01478	0.82754	1	0.16	0.21002	18.91400
				Cell Volume		4817.611			Dipole Moment			Magnitude	
				Z		4			x	y	z		
				Total Dipole Moment =			0.00799 esu*cm/A^3		8.9467	-0.0337	3.5337	**9.6193**	debye

2. Determination method of the spatial distribution of the piezoelectric coefficients

The orientation of the piezoelectric wafer corresponding to the maximum piezoelectric coefficient was obtained by the piezoelectric matrix changed with the coordination after two rotations. For different cut specimens, the piezoelectric matrix is transformed according to the Bond matrix (including M matrix and N matrix), which the Bond matrix is two 6×6 matrices related to the angle between each coordinate axis of the two coordinate systems. Considering that the cutting specimens are secondary rotation, the corresponding matrix $d_{ij}^{"}$ was obtained through following process and formula: first the matrix d_{ij} was rotated θ around Y-axis and then rotated φ around Z-axis, where the coordinate transformation matrices rotating around Y-axis and Z-axis are [Ay] and [Az], respectively, and the corresponding Bond matrices are [My], [Mz], [Ny] and [Nz].

$$\left[d_{ij}^{"}\right]=[Az][Ay][d][Ny][Nz]$$

In which:

$$[Ay]=\begin{bmatrix}\cos\theta & 0 & \sin\theta\\ 0 & 1 & 0\\ -\sin\theta & 0 & \cos\theta\end{bmatrix},\quad [Az]=\begin{bmatrix}\cos\varphi & -\sin\varphi & 0\\ \sin\varphi & \cos\varphi & 0\\ 0 & 0 & 1\end{bmatrix}$$

$$[Ny]=\begin{bmatrix}\cos^2\theta & 0 & \sin^2\theta & 0 & \sin 2\theta & 0\\ 0 & 1 & 0 & 0 & 0 & 0\\ \sin^2\theta & 0 & \cos^2\theta & 0 & -\sin 2\theta & 0\\ 0 & 0 & 0 & \cos\theta & 0 & -\sin\theta\\ -\sin\theta\cos\theta & 0 & \sin\theta\cos\theta & 0 & \cos^2\theta-\sin^2\theta & 0\\ 0 & 0 & 0 & \sin\theta & 0 & \cos\theta\end{bmatrix},$$

$$[Nz]=\begin{bmatrix}\cos^2\varphi & \sin^2\varphi & 0 & 0 & 0 & -\sin 2\varphi\\ \sin^2\varphi & \cos^2\varphi & 0 & 0 & 0 & \sin 2\varphi\\ 0 & 0 & 1 & 0 & 0 & 0\\ 0 & 0 & 0 & \cos\varphi & \sin\varphi & 0\\ 0 & 0 & 0 & -\sin\varphi & \cos\varphi & 0\\ \sin\varphi\cos\varphi & -\sin\varphi\cos\varphi & 0 & 0 & 0 & \cos^2\varphi-\sin^2\varphi\end{bmatrix}.$$