Interstitial Oxide Ion Distribution and Transport Mechanism in Aluminum-doped Neodymium Silicate Apatite Electrolytes

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RAMAN ACTIVE MODES

For $Nd_{9.33}Si_6O_{26}$, the total number of expected Raman active modes is 63 (21 A + 21 E_1 + 21 E2) in $P6_3$ and 33 (12 A_g + 8 E_{1g} + 13 E_{2g}) in $P6_3/m$ space groups, respectively, while each split oxygen site leads to extra 9 (3A + 3 E_1 + 3 E_2) modes in $P6_3$ and 9 (3 A_g + 3 E_{1g} + 3 E_{2g}) modes in $P6_3/m$. Therefore, the total expected Raman active modes is 90 (30 A + 30 E_1 +30 E_2) in $P6_3$ and 51 (18 A_g + 14 E_{1g} + 19 E_{2g}) in $P6_3/m$ space groups, respectively, in accordance with the split of oxygen sites O(1)', O(3)' and O(4)' in $P6_3$ (Table 1) and O(1)' and O(3)' in $P6_3/m$ (Table 2) as determined by the neutron diffraction performed at 2K. For internal modes of unperturbed SiO_4, 27 modes are expected for $P6_3$ and 15 are expected for $P6_3/m$.

Table S1. Raman activity in $P6_3$ space group.

Atom	Site symmetry	Raman activity	Number of modes
Nd(1)	2*b*	A + E_1 + E_2	3
Nd(2)	2*b*	A + E_1 + E_2	3
Nd(3)	6*c*	3 A + 3 E_1 + 3 E_2	9
Si	6*c*	3 A + 3 E_1 + 3 E_2	9
O(1)	6*c*	3 A + 3 E_1 + 3 E_2	9
O(2)	6*c*	3 A + 3 E_1 + 3 E_2	9
O(3)	6*c*	3 A + 3 E_1 + 3 E_2	9
O(4)	6*c*	3 A + 3 E_1 + 3 E_2	9
O(5)	2*a*	A + E_1 + E_2	3
		Total (without split sites):	63
Split site	Site symmetry	Raman activity	Number of modes
O(1)'	6*c*	3 A + 3 E_1 + 3 E_2	9
O(3)'	6*c*	3 A + 3 E_1 + 3 E_2	9
O(4)'	6*c*	3 A + 3 E_1 + 3 E_2	9
		Total (with split sites):	90

Table S2. Raman activity in $P6_3/m$ space group.

Atom	Site symmetry	Raman activity	Number of modes
Nd(1)	4*f*	$A_g + E_{1g} + E_{2g}$	3
Nd(2)	6*h*	$2\,A_g + E_{1g} + 2\,E_{2g}$	5
Si	6*h*	$2\,A_g + E_{1g} + 2\,E_{2g}$	5
O(1)	6*h*	$2\,A_g + E_{1g} + 2\,E_{2g}$	5
O(2)	6*h*	$2\,A_g + E_{1g} + 2\,E_{2g}$	5
O(3)	12*i*	$3\,A_g + 3\,E_{1g} + 3\,E_{2g}$	9
O(4)	2*a*	E_{2g}	1
		Total (without split sites):	33
Split site	Site symmetry	Raman activity	Number of modes
O(1)'	6*h*	$3\,A_g + 3\,E_{1g} + 3\,E_{2g}$	9
O(3)'	12*i*	$3\,A_g + 3\,E_{1g} + 3\,E_{2g}$	9
		Total (with split sites):	51

Table S3. Internal modes of SiO_4 in $P6_3$ space group. The site group (C_1) is correlated to the factor group (C_6) as: A → $A + B + E_1 + E_2$.

Internal modes	Molecular group (T_d)	Site group (C_1)	Factor group (C_6)	Raman activity	Number of modes
ν_1	A_1	A	$A + B + E_1 + E_2$	$A + E_1 + E_2$	3
ν_2	E	2A	$2\,A + 2\,B + 2\,E_1 + 2\,E_2$	$2\,A + 2\,E_1 + 2\,E_2$	6
ν_3	T_2	3A	$3\,A + 3\,B + 3\,E_1 + 3\,E_2$	$3\,A + 3\,E_1 + 3\,E_2$	9
ν_4	T_2	3A	$3\,A + 3\,B + 3\,E_1 + 3\,E_2$	$3\,A + 3\,E_1 + 3\,E_2$	9
				Total:	27

Table S4. Internal modes of SiO_4 in $P6_3/m$ space group. The site group (C_s) is correlated to the factor group (C_{6h}) as: A' → $A_g + E_{2g} + B_u + E_{1u}$ and A" → $B_g + E_{1g} + A_u + E_{2u}$.

Internal modes	Molecular group (T_d)	Site group (C_s)	Factor group (C_{6h})	Raman activity	Number of modes
ν_1	A_1	A'	$A_g + E_{2g} + B_u + E_{1u}$	$A_g + E_{2g}$	2
ν_2	E	A' + A"	$A_g + E_{2g} + B_u + E_{1u} + B_g + E_{1g} + A_u + E_{2u}$	$A_g + E_{1g} + E_{2g}$	3
ν_3	T_2	2A' + A"	$2\,A_g + 2\,E_{2g} + 2\,B_u + 2\,E_{1u} + B_g + E_{1g} + A_u + E_{2u}$	$2\,A_g + E_{1g} + 2\,E_{2g}$	5
ν_4	T_2	2A' + A"	$2\,A_g + 2\,E_{2g} + 2\,B_u + 2\,E_{1u} + B_g + E_{1g} + A_u + E_{2u}$	$2\,A_g + E_{1g} + 2\,E_{2g}$	5
				Total:	15

Table S5. Raman activity of possible oxygen interstitials in $P6_3/m$ space group.

O_{int} site symmetry	Coordinates	Raman activity	Number of modes
4*e*	(0 0 *z*)	$A_g + E_{1g} + E_{2g}$	3
2*b*	(0 0 0)	*None*	0
6*h*	(*x y* ¼)	$2\,A_g + E_{1g} + 2\,E_{2g}$	5

Table S6. Internal modes of perturbed SiO_4 in $P6_3/m$ space group. The site group symmetry is lowered from C_s to C_1, which is correlated to the factor group (C_{6h}) as: $A \rightarrow A_g + A_u + B_g + B_u + E_{1g} + E_{1u} + E_{2g} + E_{2u}$.

Internal modes	Molecular group (T_d)	Site group (C_1)	Factor group (C_{6h})	Raman activity	Number of modes
ν_1	A_1	A	$A_g + A_u + B_g + B_u + E_{1g} + E_{1u} + E_{2g} + E_{2u}$	$A_g + E_{1g} + E_{2g}$	3
ν_2	E	2A	$A_g + A_u + B_g + B_u + E_{1g} + E_{1u} + E_{2g} + E_{2u}$	$2\,A_g + 2\,E_{1g} + 2\,E_{2g}$	6
ν_3	T_2	3A	$A_g + A_u + B_g + B_u + E_{1g} + E_{1u} + E_{2g} + E_{2u}$	$3\,A_g + 3\,E_{1g} + 3\,E_{2g}$	9
ν_4	T_2	3A	$A_g + A_u + B_g + B_u + E_{1g} + E_{1u} + E_{2g} + E_{2u}$	$3\,A_g + 3\,E_{1g} + 3\,E_{2g}$	9
				Total:	27