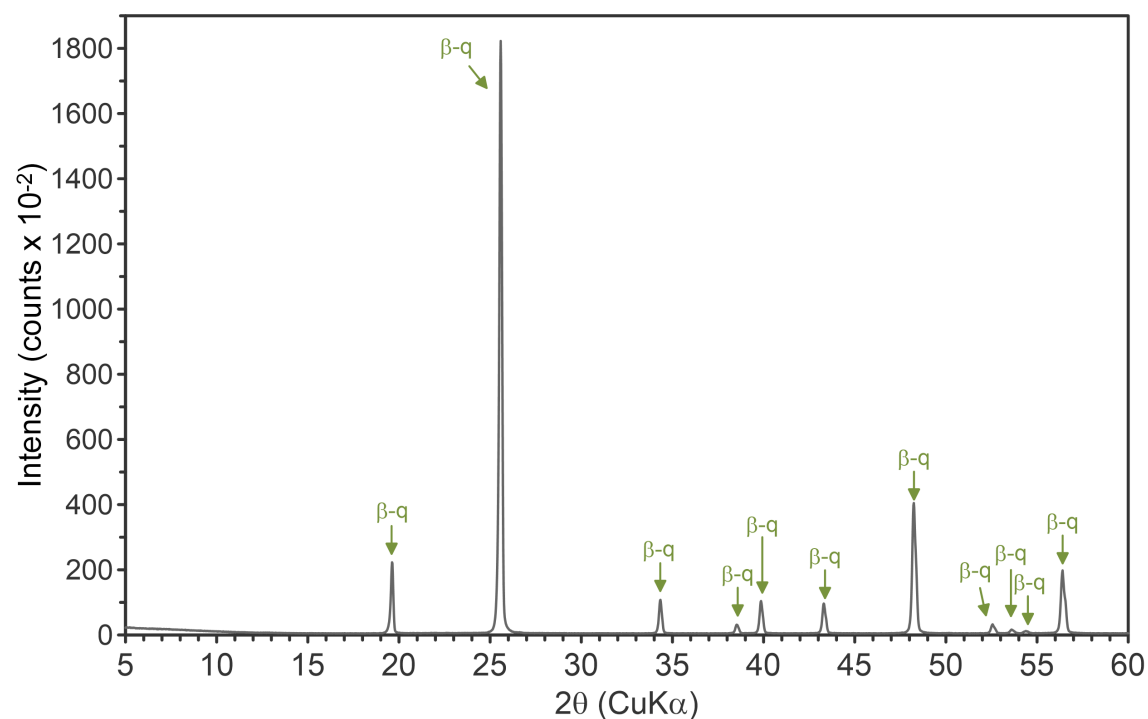


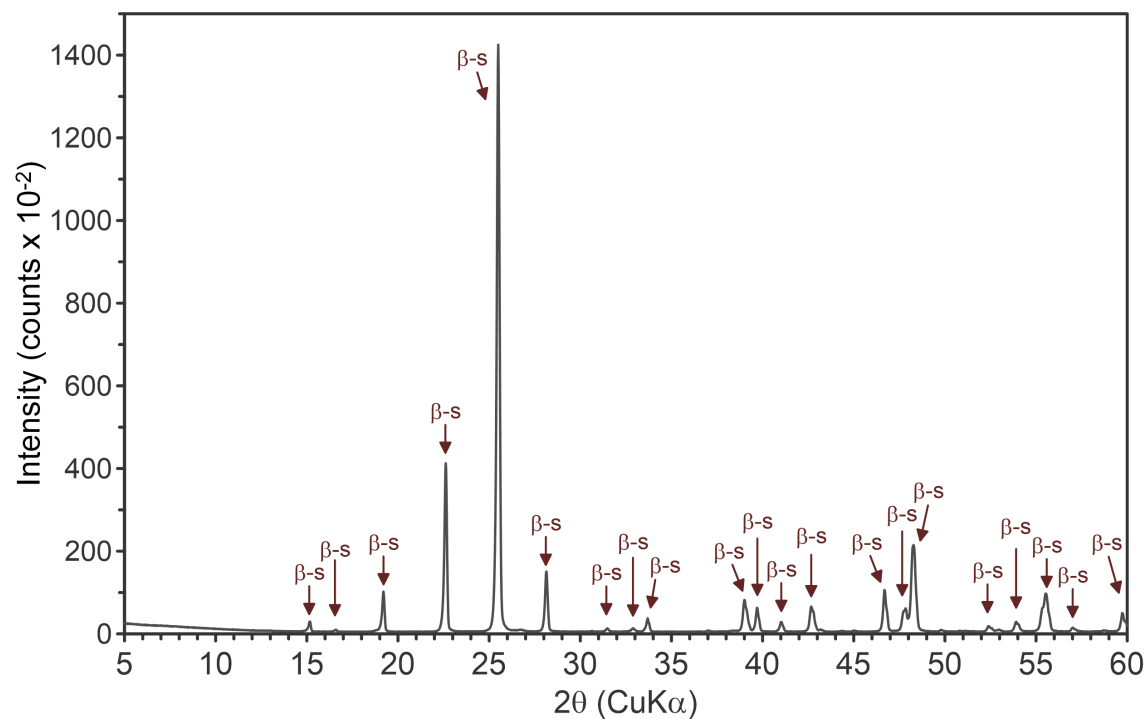
# Investigating exchange efficiencies of sodium and magnesium to access lithium from $\beta$ -spodumene and Li-stuffed $\beta$ -quartz ( $\gamma$ -spodumene)

## Supplementary information

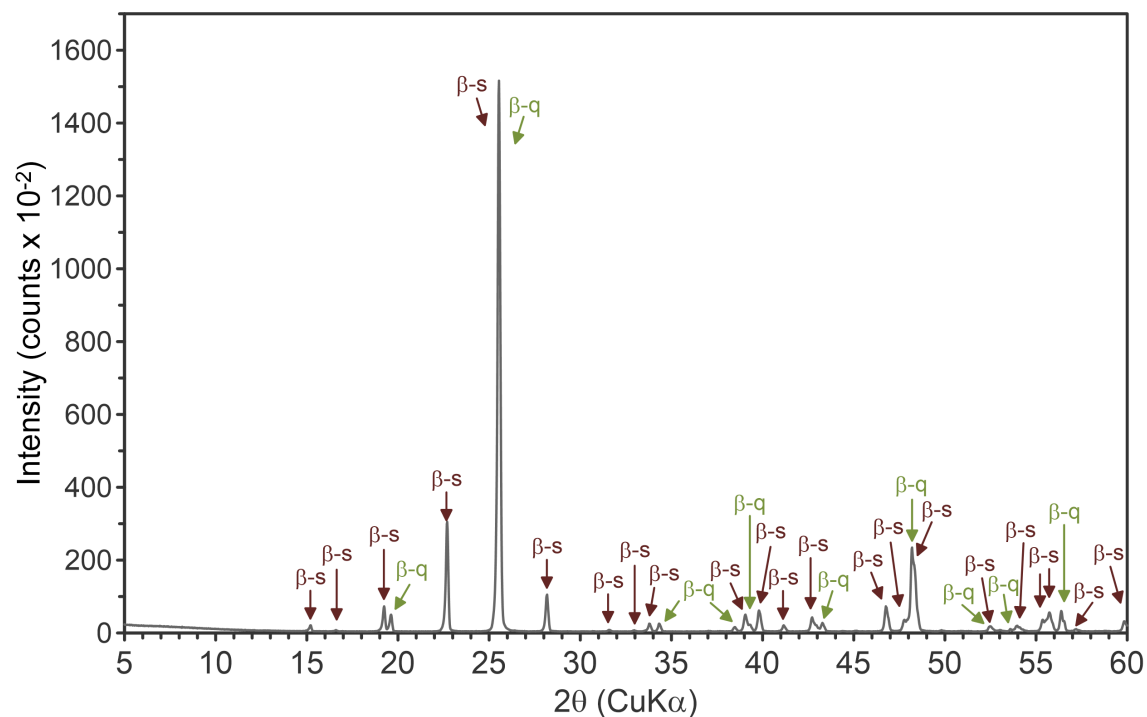
### 1. Powder XRD patterns displayed with the full range in $2\theta$ from $5^\circ$ to $60^\circ$



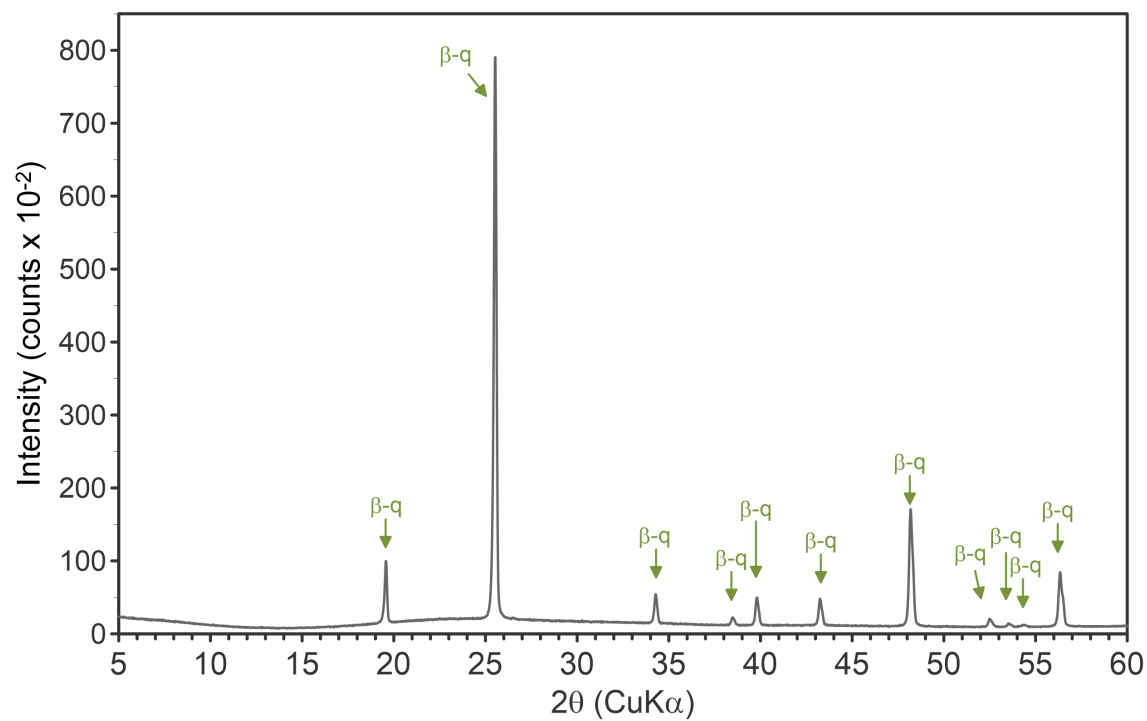
**Figure S1.** Extended range powder-XRD pattern corresponding to Figure 3a.  $\beta$ -s:  $\beta$ -spodumene;  $\beta$ -q:  $\beta$ -quartz.



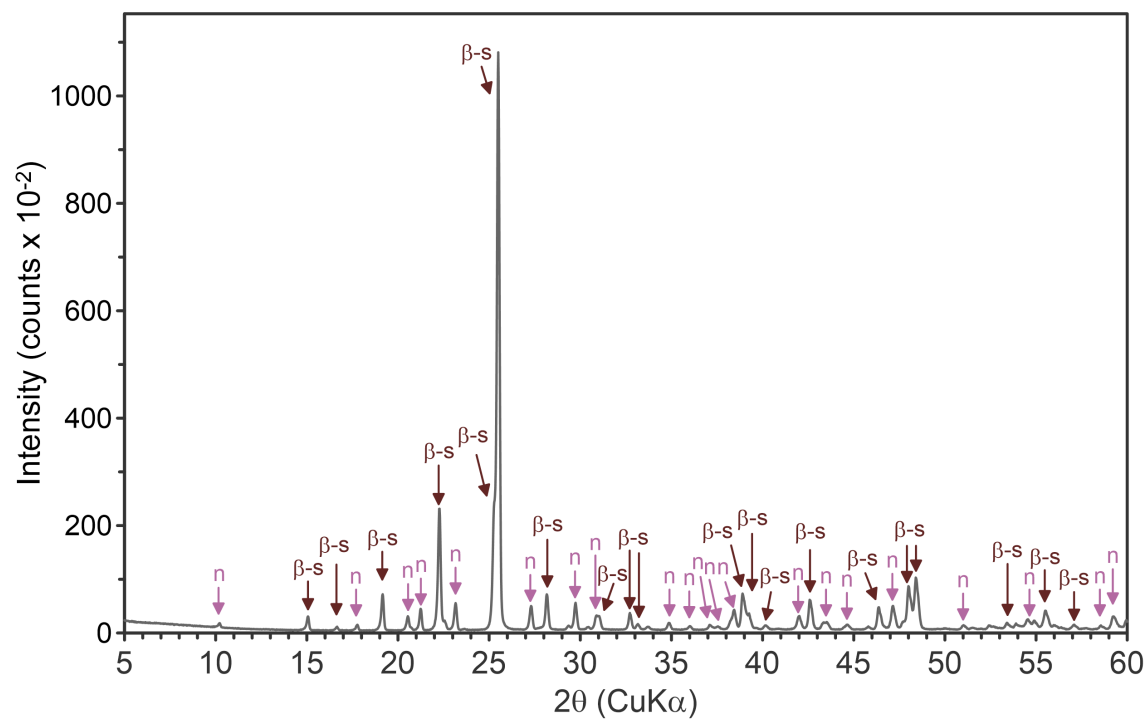
**Figure S2.** Extended range powder-XRD pattern corresponding to Figure 3c.  $\beta$ -s:  $\beta$ -spodumene;  $\beta$ -q:  $\beta$ -quartz.



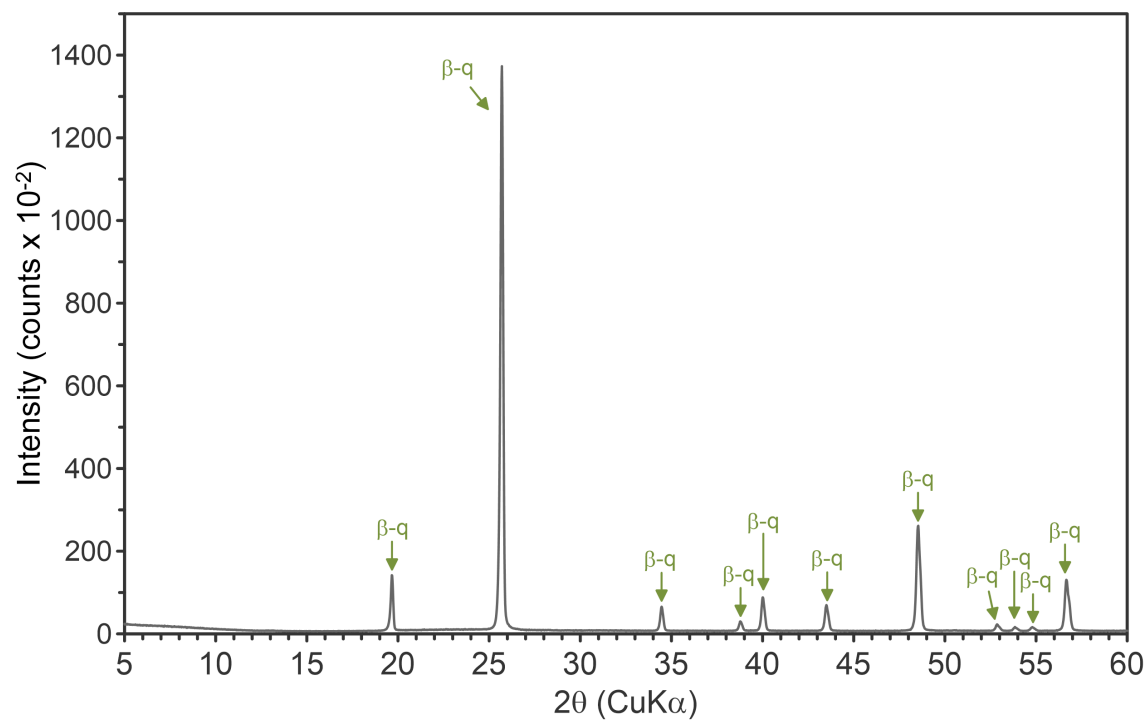
**Figure S3.** Extended range powder-XRD pattern corresponding to Figure 5a.  $\beta$ -s:  $\beta$ -spodumene;  $\beta$ -q:  $\beta$ -quartz.



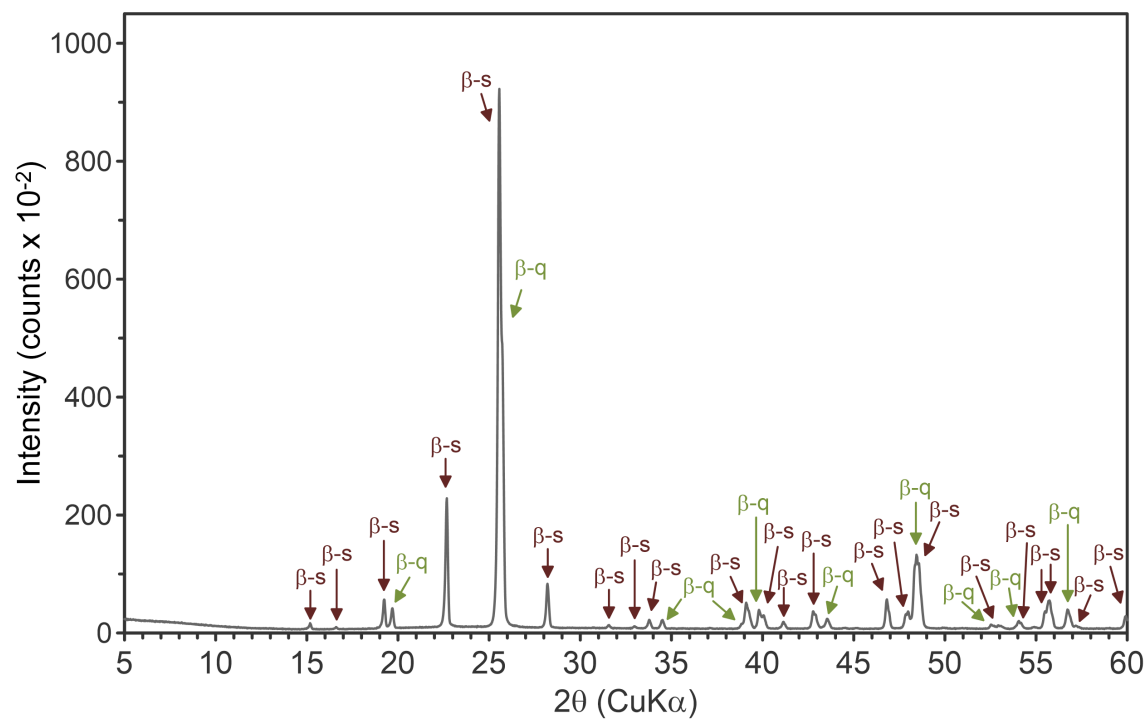
**Figure S4.** Extended range powder-XRD pattern corresponding to Figure 6a.  $\beta$ -s:  $\beta$ -spodumene;  $\beta$ -q:  $\beta$ -quartz.



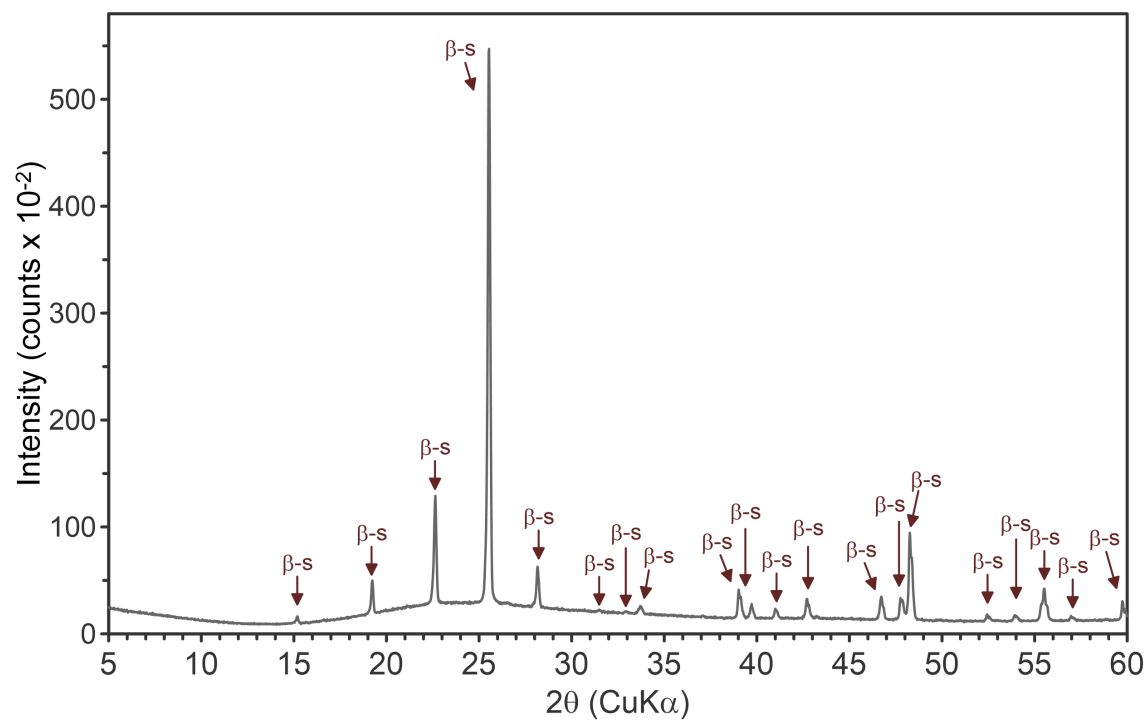
**Figure S5.** Extended range powder-XRD pattern corresponding to Figure 8a.  $\beta$ -s:  $\beta$ -spodumene;  $\beta$ -q:  $\beta$ -quartz; n: nepheline.



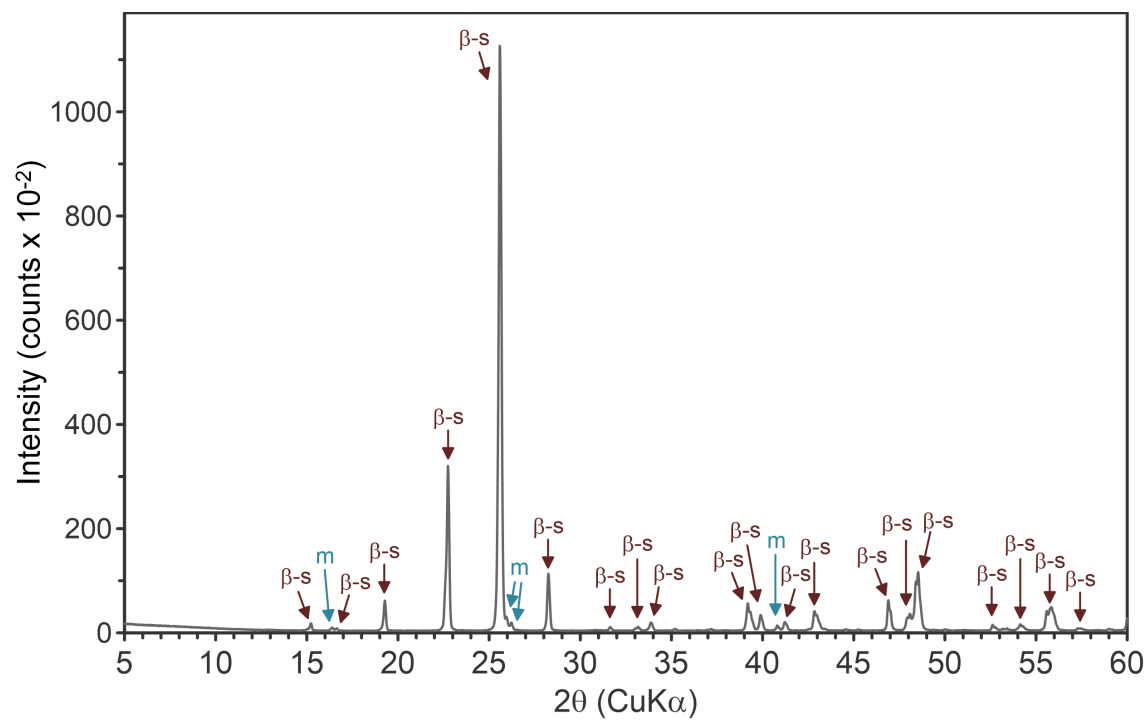
**Figure S6.** Extended range powder-XRD pattern corresponding to Figure 9a.  $\beta$ -s:  $\beta$ -spodumene;  $\beta$ -q:  $\beta$ -quartz.



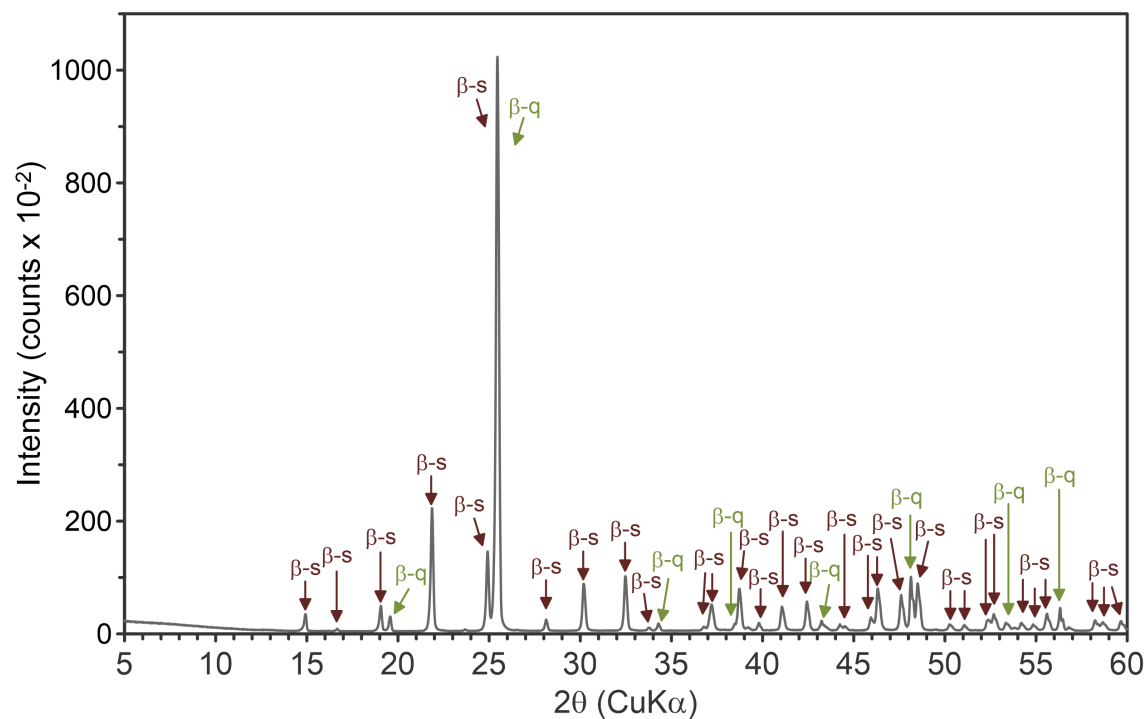
**Figure S7.** Extended range powder-XRD pattern corresponding to Figure 10a.  $\beta$ -s:  $\beta$ -spodumene;  $\beta$ -q:  $\beta$ -quartz.



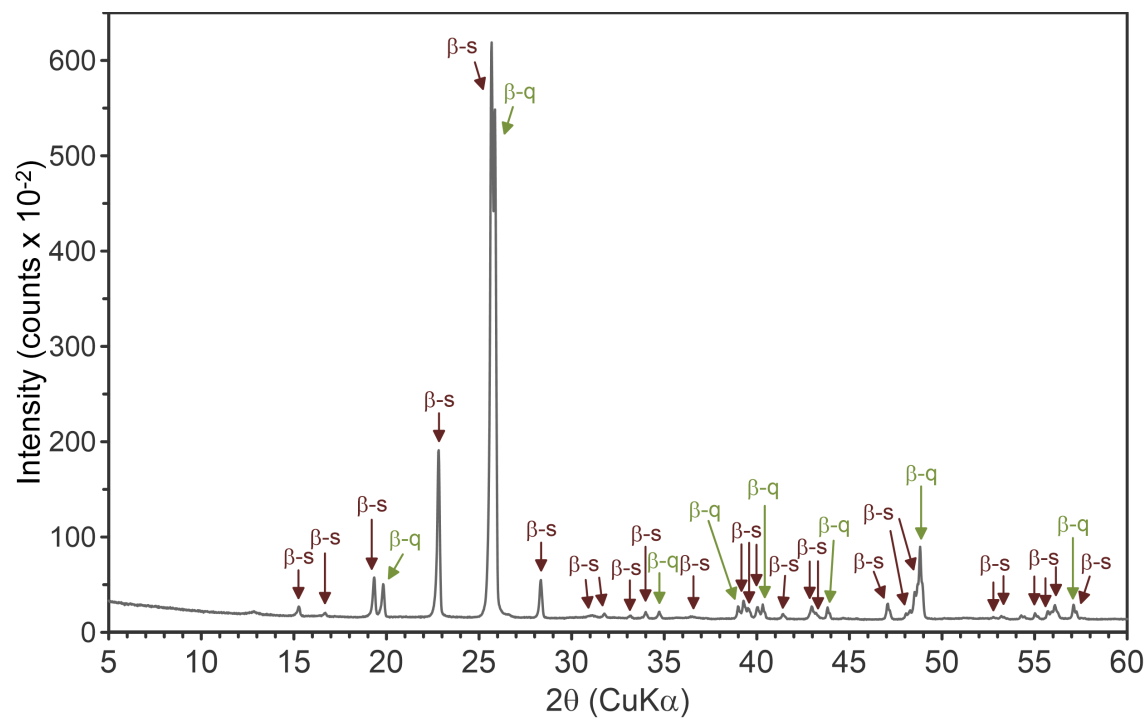
**Figure S8.** Extended range powder-XRD pattern corresponding to Figure 11a.  $\beta$ -s:  $\beta$ -spodumene;  $\beta$ -q:  $\beta$ -quartz.



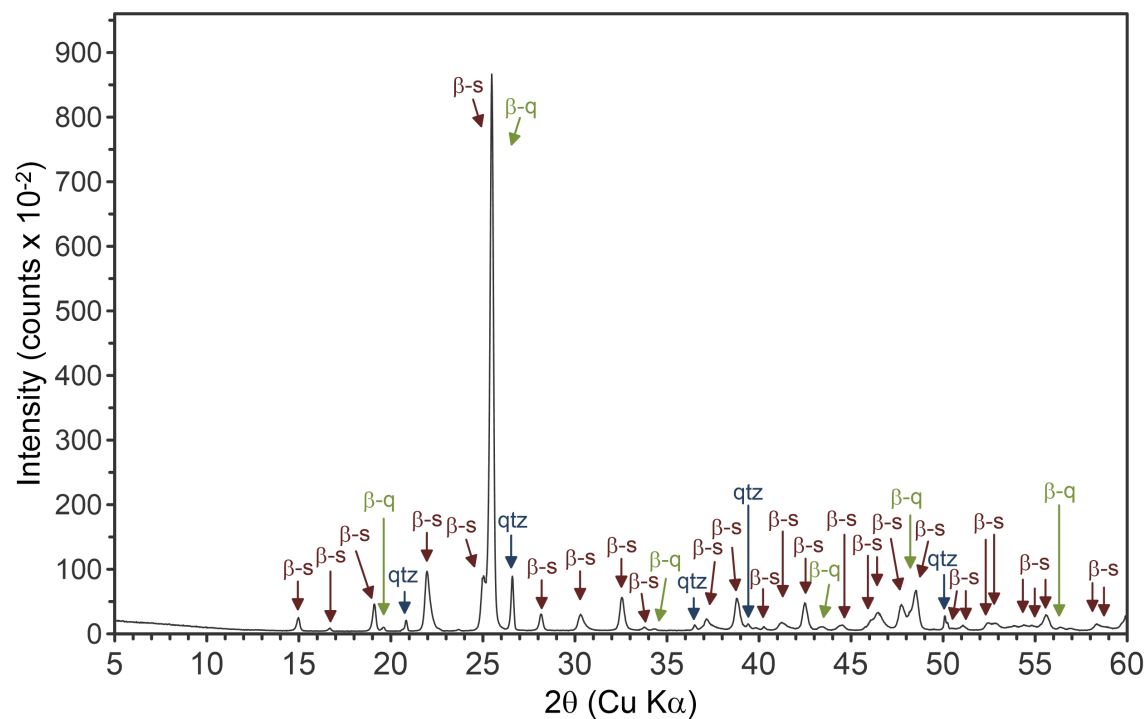
**Figure S9.** Extended range powder-XRD pattern corresponding to Figure 12a.  $\beta$ -s:  $\beta$ -spodumene;  $\beta$ -q:  $\beta$ -quartz; m: mullite.



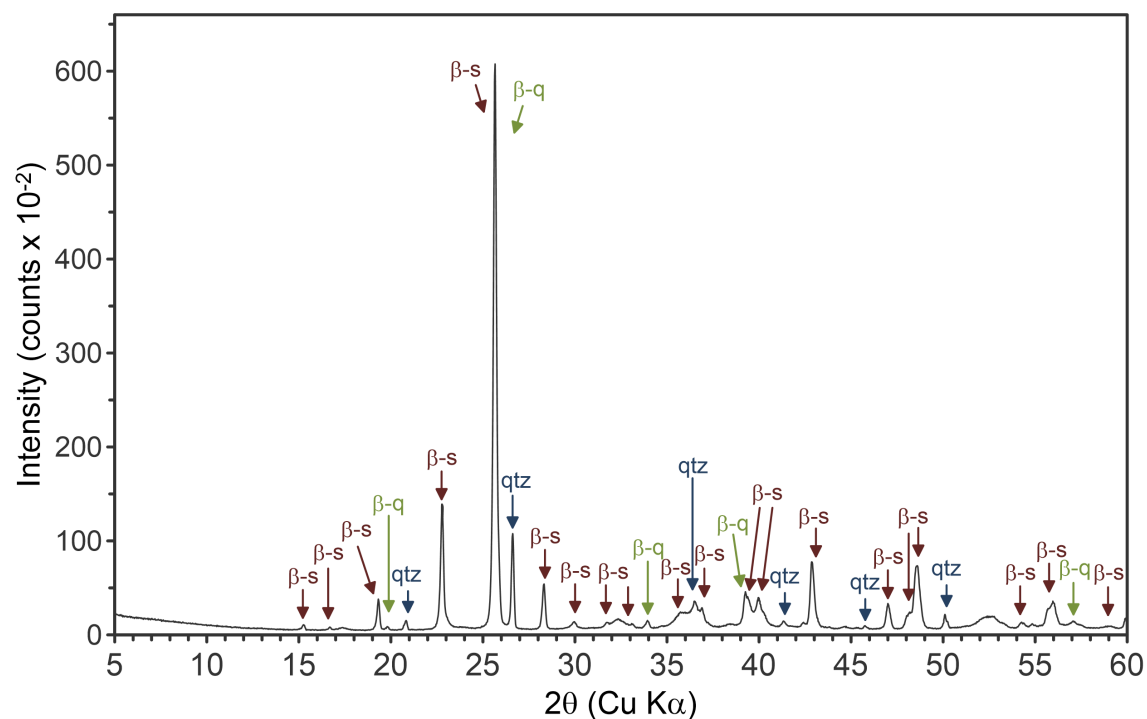
**Figure S10.** Extended range powder-XRD pattern corresponding to Figure 13a. β-s: β-spodumene; β-q: β-quartz.



**Figure S11.** Extended range powder-XRD pattern corresponding to Figure 14a. β-s: β-spodumene; β-q: β-quartz.



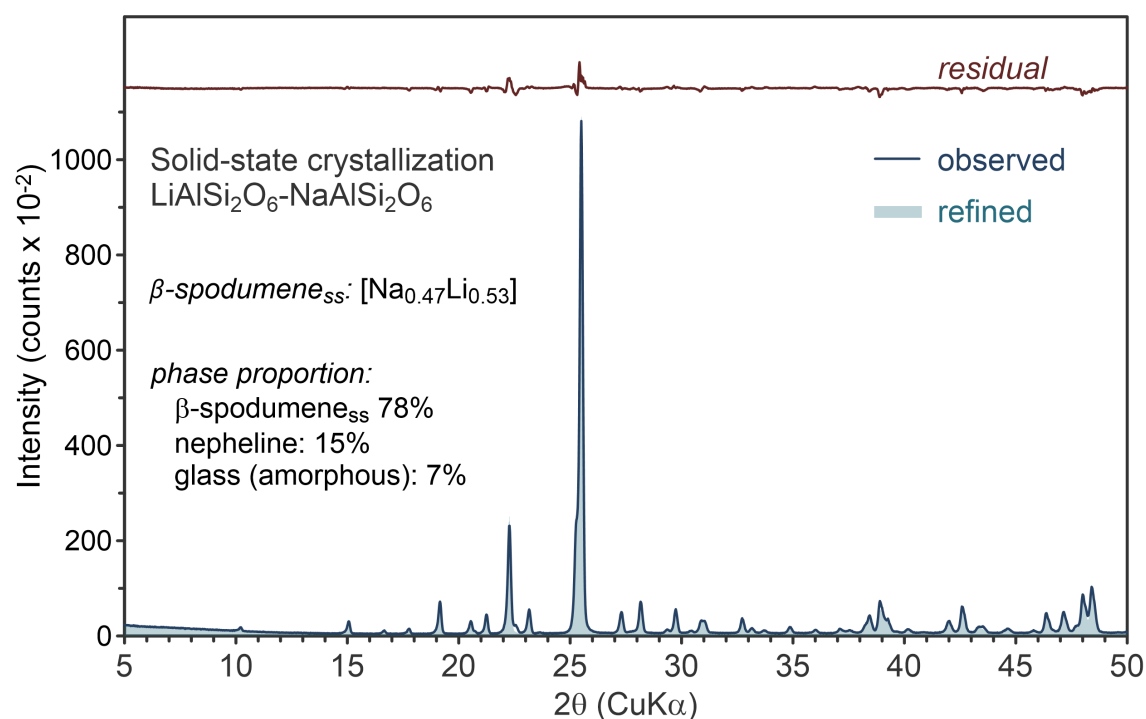
**Figure S12.** Extended range powder-XRD pattern collected on the decrepitated spodumene concentrate after exchange in molten  $\text{NaNO}_3$  corresponding to Figure 15a.  $\beta$ -s:  $\beta$ -spodumene;  $\beta$ -q:  $\beta$ -quartz, qtz: quartz.



**Figure S13.** Extended range powder-XRD pattern collected on the decrepitated spodumene concentrate after exchange in molten  $0.6 \text{ MgCl}_2 / 0.4 \text{ KCl}$  corresponding to Figure 15b.  $\beta$ -s:  $\beta$ -spodumene;  $\beta$ -q:  $\beta$ -quartz, qtz: quartz.

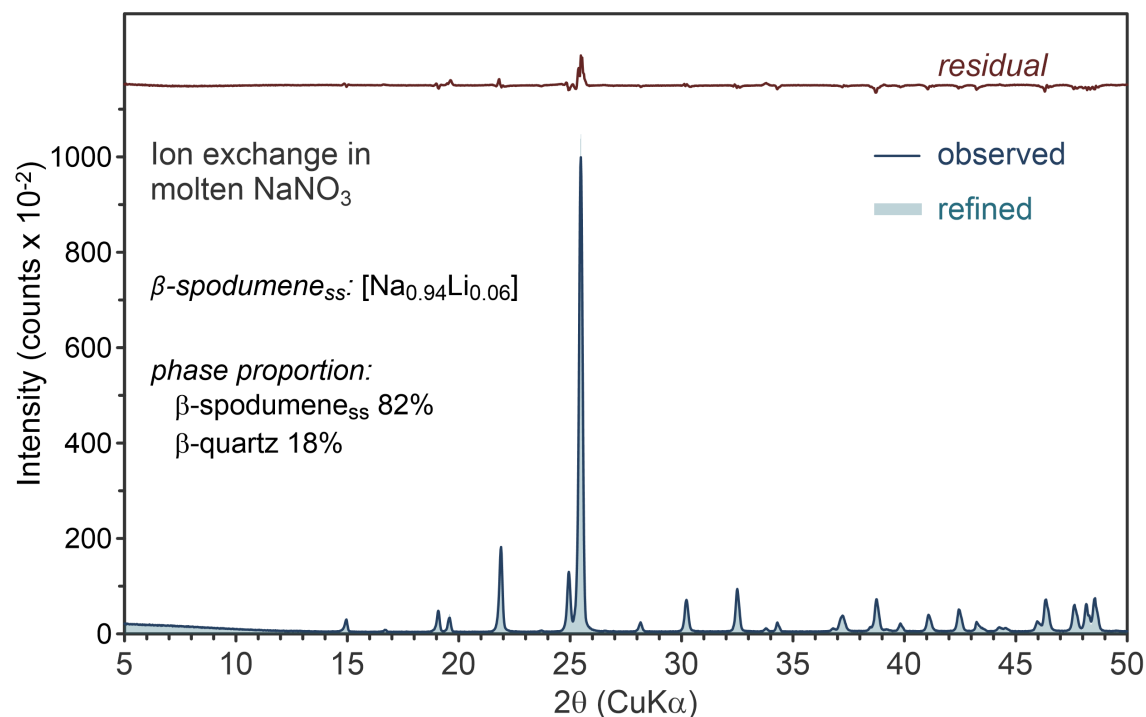
## Rietveld analysis

Rietveld analysis of the XRD patterns obtained from the product of the solid state crystallization experiment performed using the  $\text{NaAlSi}_2\text{O}_6$  glass and  $\beta$ -spodumene<sub>ss</sub> endmembers (Section 3.1.1, Figure 8a, S5) and of the  $\text{NaNO}_3$  molten salt exchange experiment performed on synthetic fragments with coexisting crystals of  $\beta$ -spodumene<sub>ss</sub> and  $\beta$ -quartz<sub>ss</sub> (Section 3.3, Figure 13a, S10). The refinement was conducted using JADE version 9 with initial structural parameters of  $\beta$ -spodumene<sub>ss</sub> (tetragonal  $\text{P4}_32_12$  [1]),  $\beta$ -quartz<sub>ss</sub> (hexagonal  $\text{P6}_222$  [2]), Na-keatite (tetragonal  $\text{P4}_32_12$  [3]), and nepheline (hexagonal  $\text{P6}_3$  [4]). As the main objective was to evaluate the impact of sodium for lithium substitution in  $\beta$ -spodumene on the unit cell dimensions, the Na/Li ratio was refined by fixing the total alkali site occupancy factor to 0.5 (e.g. Li and Peacor [1]) and linking the sodium content to that of lithium ( $0.5 - \text{Li}$ ). The atomic coordinates of all sites were left unconstrained, however, the  $[\text{Si}:\text{Al}]_{\text{atomic}}$  ratio in the appropriate sites was kept constant according to the  $(\text{Li},\text{Na})\text{AlSi}_2\text{O}_6$  stoichiometry ( $\text{Si}_{0.667}\text{Al}_{0.333}$ ). The contribution of glass (amorphous component) in the XRD pattern obtained from the product of the solid state crystallization experiment was accounted for using a pseudo-Voigt profile.

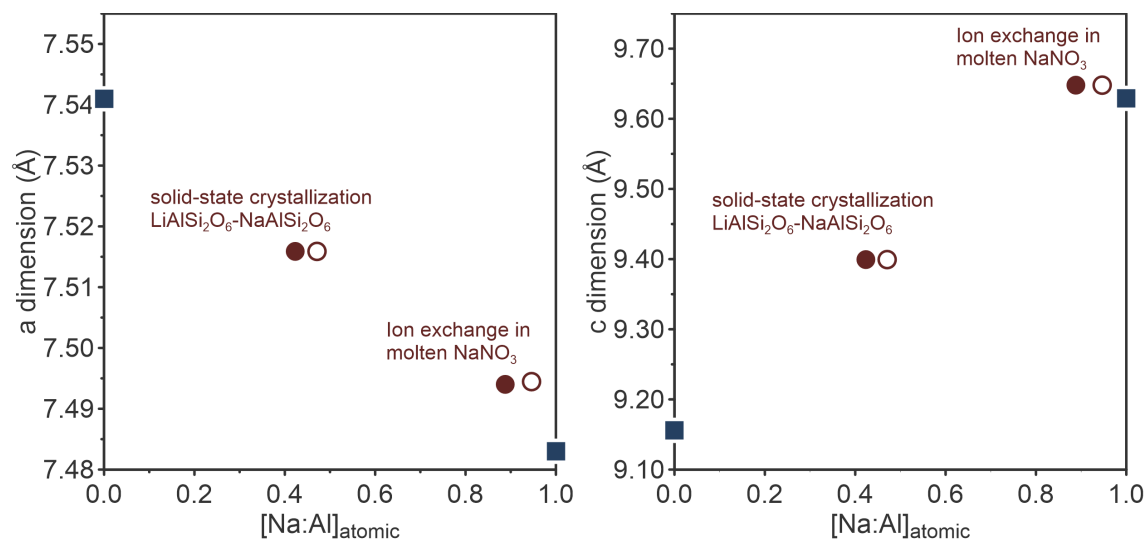


**Figure S14.** Observed and calculated XRD patterns from the product of the solid state crystallization experiment performed using the  $\text{NaAlSi}_2\text{O}_6$  glass and  $\beta$ -spodumene<sub>ss</sub> endmembers. The residual pattern is plotted at the same intensity scale but offset for clarity. Also shown are the calculated relative proportion of Na and Li in  $\beta$ -spodumene<sub>ss</sub> as well as the phase proportion derived from the Rietveld refinement.

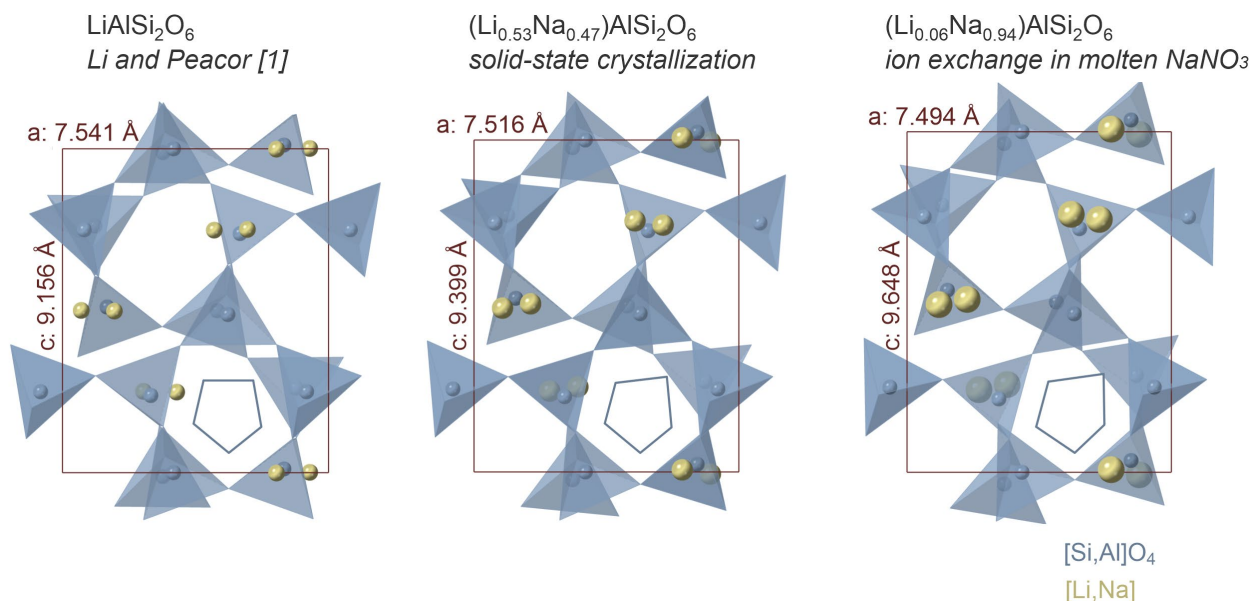




**Figure S15.** Observed and calculated XRD patterns from the product of the  $\text{NaNO}_3$  molten salt exchange experiment performed on synthetic fragments with coexisting crystals of  $\beta\text{-spodumene}_{\text{ss}}$  and  $\beta\text{-quartz}_{\text{ss}}$ . The residual pattern is plotted at the same intensity scale but offset for clarity. Also shown are the calculated relative proportion of Na and Li in  $\beta\text{-spodumene}_{\text{ss}}$  as well as the phase proportion derived from the Rietveld refinement.



**Figure S16.** Variation of the a and c unit cell dimensions of  $\beta\text{-spodumene}_{\text{ss}}$  as a function of the  $[\text{Na:Al}]_{\text{atomic}}$  ratio as measured by EPMA (filled circles) and calculated by Rietveld refinement (empty circles). The blue squares correspond to the cell dimensions values for the  $\text{LiAlSi}_2\text{O}_6$  and  $\text{NaAlSi}_2\text{O}_6$  endmembers from Li and Peacor [1] and Baumgartner and Müller [3], respectively.



**Figure S17.**  $\beta$ -spodumene<sub>ss</sub> model structures (constructed with CrystalMaker X) projected along the [100] direction for the LiAlSi<sub>2</sub>O<sub>6</sub> endmember (crystal data from Li and Peacor [1]) and those resulting from the Rietveld refinement of the XRD patterns shown in Figure S14 and S15. The small drawn pentagons emphasize the progressive deformation of the tetrahedral framework ([Si,Al]O<sub>4</sub>), resulting in an expansion along the c axis and a slight contraction along the a direction. As Li and Na are considered disordered, the alkali cation (yellow) is displayed with an effective size corresponding to the average of the ionic radii of Li and Na in fourfold coordination [5] weighted by their calculated relative concentrations in the alkali site.

## References

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- [4] Kumar, A.; Dhoble, S.J.; Peshwe, D.R.; Bhatt, J. Structural and photoluminescence properties of nepheline-structure NaAlSiO<sub>4</sub>:Dy<sup>3+</sup> nanophosphors. *J. Alloys Compd.* **2014**, *609*, 100–106. <https://doi.org/10.1016/j.jallcom.2014.04.153>
- [5] Shannon, R.D. Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallogr.* **1976**, *A32*, 751–767. <https://doi.org/10.1107/S0567739476001551>