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Quest for Sustainable all-solid-state Battery Components

Glass-to-Crystal Transition in the NASICON Glass-Ceramic System $Na_{1+x}Al_xM_{2-x}(PO_4)_3$ (M = Ge, Ti)

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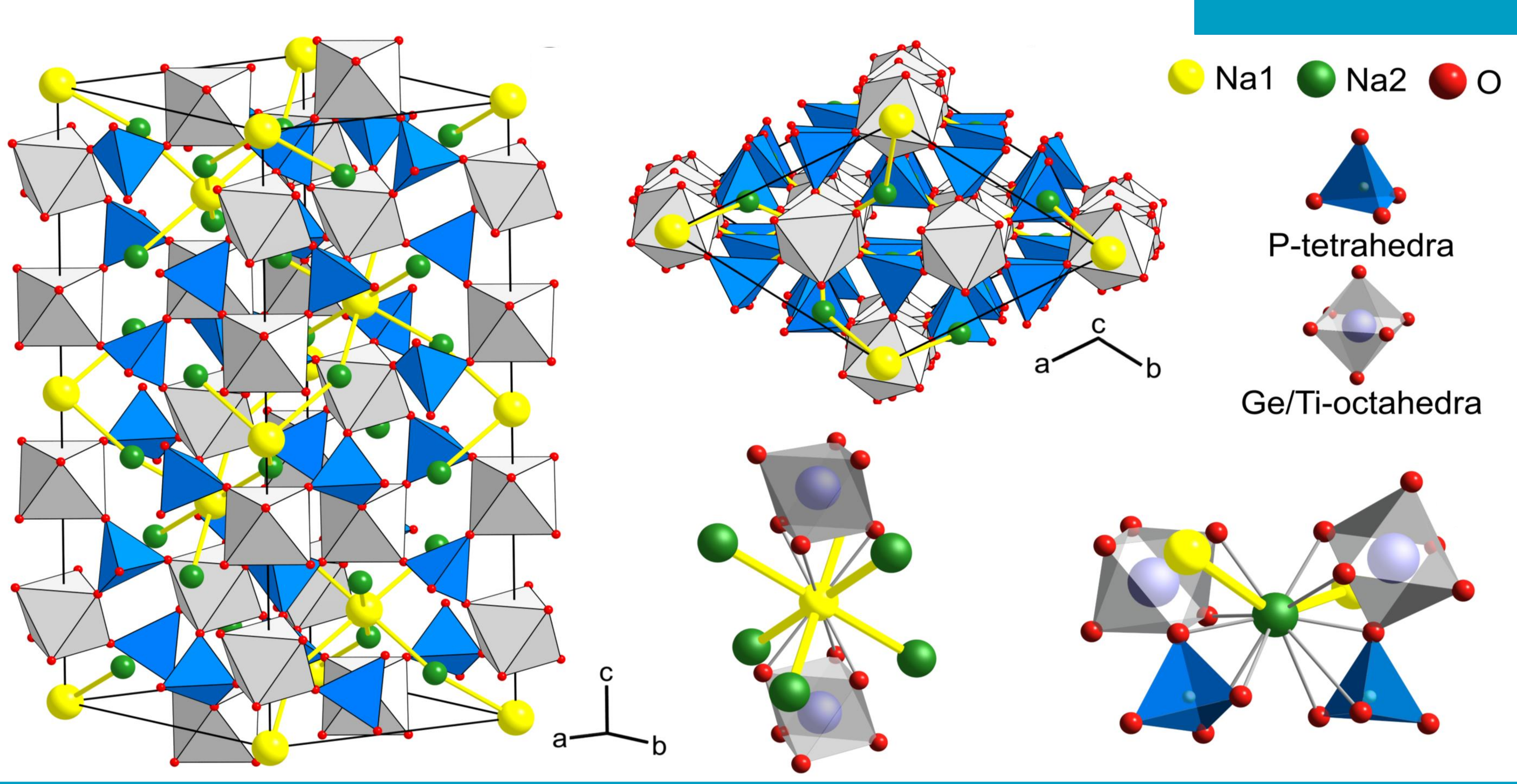
Objectives

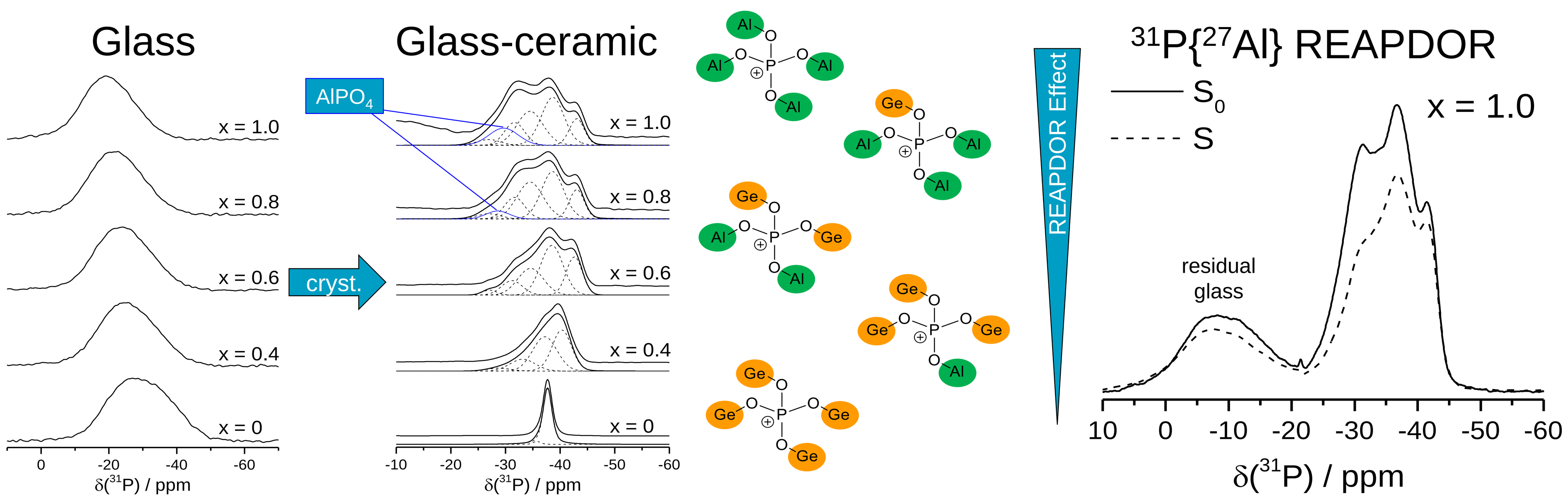


Recently, much effort has been devoted to the development of high-energy storage devices and all-solid-state batteries with improved cycling stability and operating safety compared to liquid electrolyte lithium-ion batteries.[1,2] Crystalline compounds possessing the Na-superionic conductor (NASICON) structure are important solid electrolyte and separator materials in such systems.[2] While Li-containing NASICON materials are have already been commercialized for this application, the present study explores analogous sodium-bearing materials. This work is motivated by the (compared to lithium) 500-fold atomic abundance of the element sodium, guaranteeing that large-scale efforts will be sustainable and attractive to national energy economies. While materials have been traditionally prepared via solid-state reactions ("sintering route"), preparations involving the crystallization of precursor glasses ("glass-ceramic route") have resulted in more homogeneous materials with controllable microstructures and morphologies. Therefore, in the present contribution we have analyzed glasses and glass-ceramics of composition $Na_{1+x}Al_xGe_{2-x}(PO_4)_3$ (NAGP) and $Na_{1+x}Al_xTi_{2-x}(PO_4)_3$ (NATP) ($0.4 \le x \le 1.0$) together with the aluminum free compositions ($x = 0$). In particular, we made extensive use of solid-state nuclear magnetic resonance (NMR) spectroscopy, which has been widely applied for the study of lithium-containing NASICON materials[3-6] and a few related sodium-containing NASICON crystalline powders, to characterize the glass-to-crystal transition in the NAGP and NATP systems.

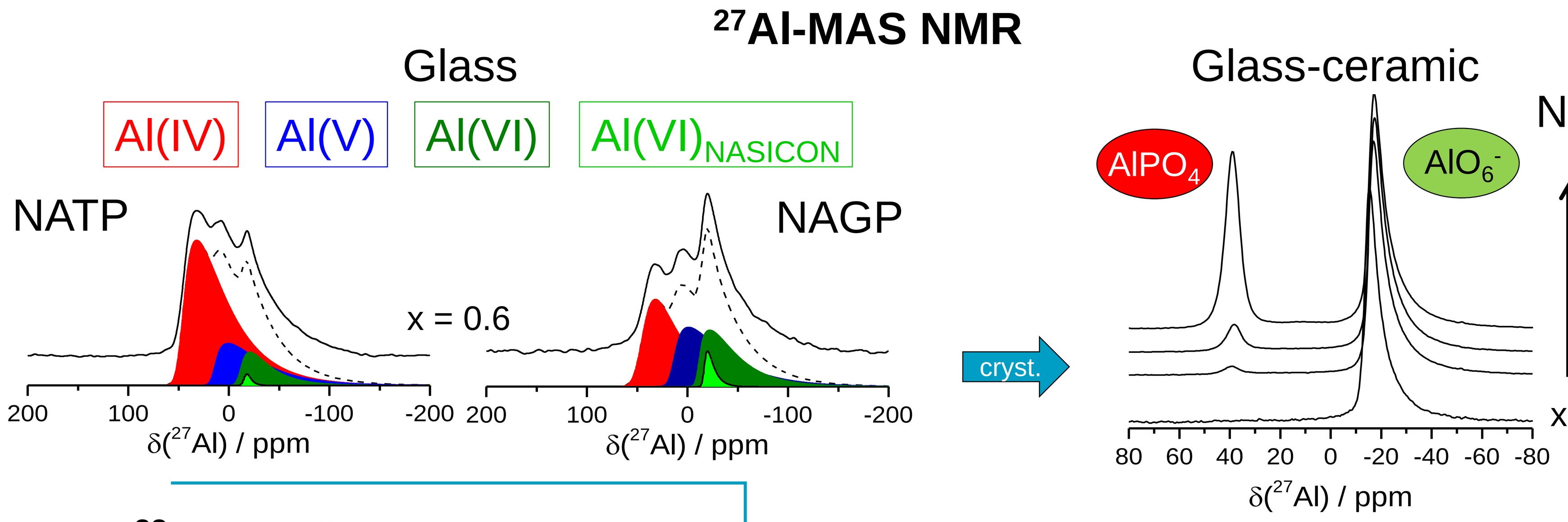
Glass-to-Crystal Transition

^{31}P-MAS NMR

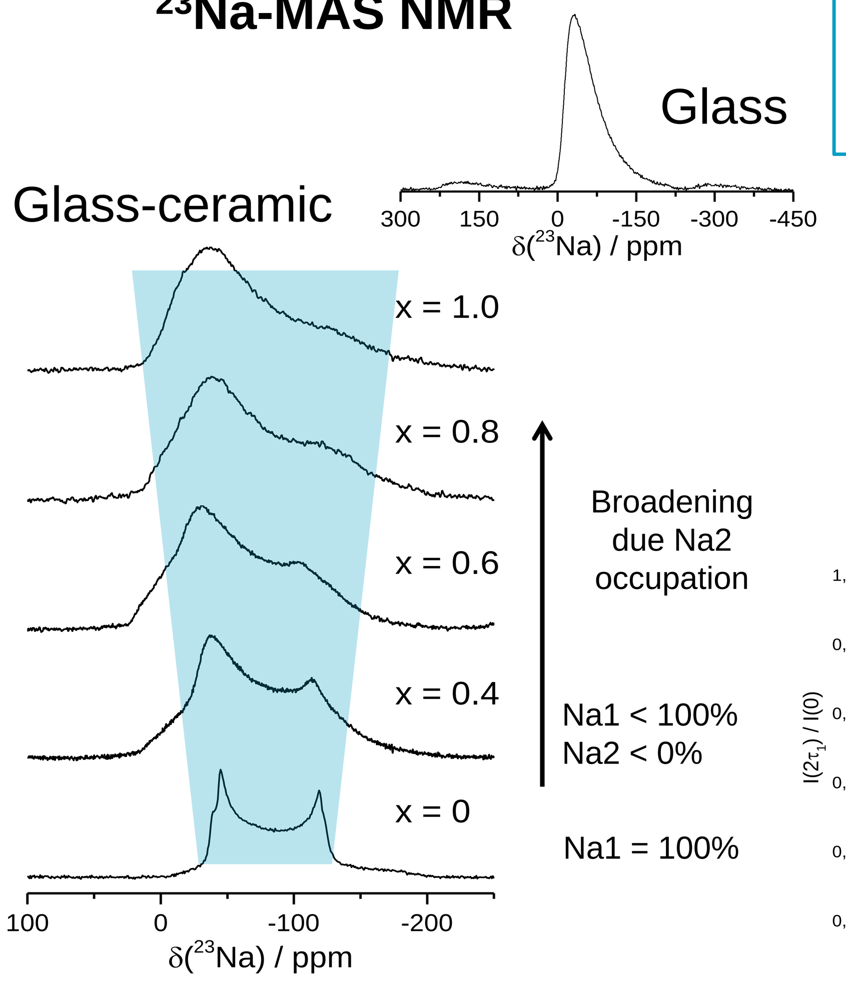
^{31}P MAS NMR experiments show that P^3 species, connected to Ge and Al in varying coordination states, dominate the glassy samples. Crystallization leads to an ordering of the local environments in a manner that the crystalline state P^4 species with varying numbers of Ge and Al ligands subjected to a binomial distribution.



^{27}Al-MAS NMR



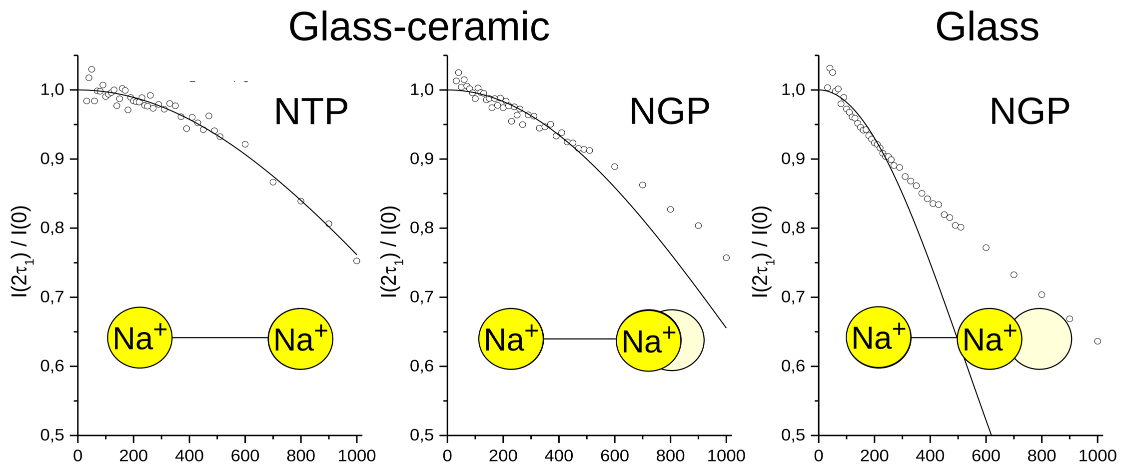
^{23}Na-MAS NMR



Both glass systems differ significantly with respect to the coordination distribution of the tetravalent ions, which also affects the average coordination number of aluminum.

^{23}Na spin-echo decay

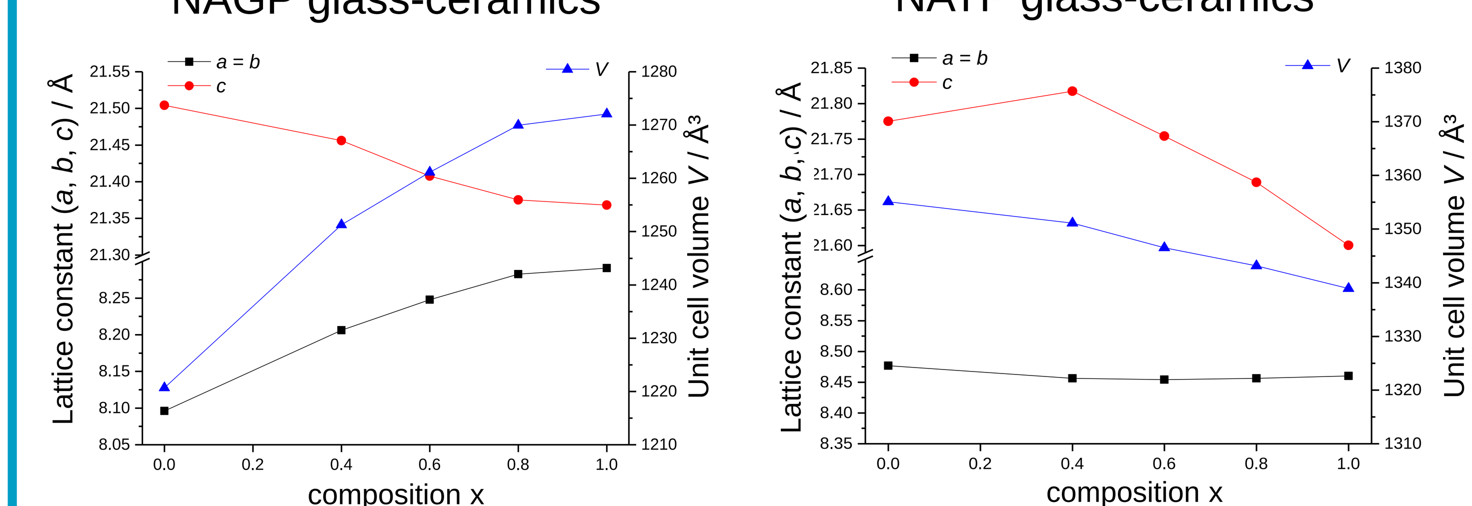
^{23}Na spin-echo decay measurements of the aluminium free components show slight differences between the NASICON unit cell of germanium and titanium system. Shorter average ^{23}Na-^{23}Na distances in NGP glass, indicate fundamental structural changes upon crystallization.



Structure Elucidation

XRD Analysis

X-ray powder diffraction (XRD) reveals a significant lattice expansion in the NAGP system upon aliovalent substitution of Ge by Al compared to the NATP system.



DSC Analysis

NAGP

x	T_g / K	T_x / K
0,0	884	939
0,4	843	918
0,6	833	917
0,8	813	919
1,0	794	919

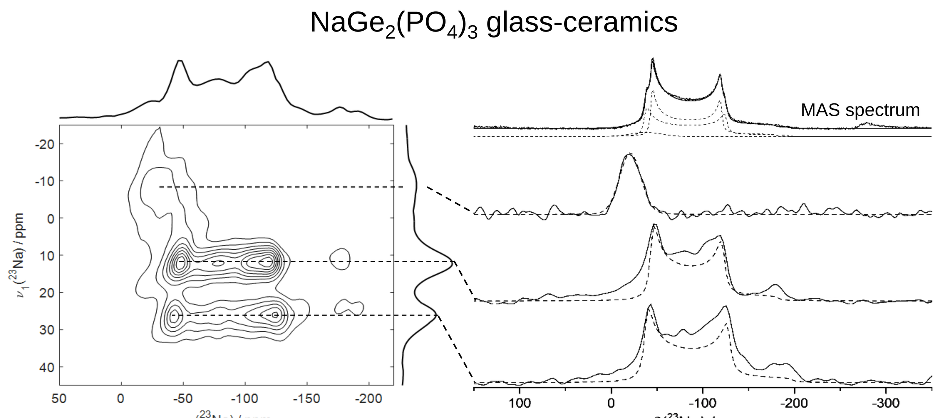
NATP

x	T_g / K	T_x / K
0,4	950	992
0,6	918	970
0,8	876	949
1,0	845	940

^{23}Na TQMAS

^{23}Na TQMAS measurements demonstrate the presence of two slightly different Na sites in NGP, indicating minor structural differences in the crystal structure as opposed to the titanium system.

$NaGe_2(PO_4)_3$ glass-ceramics



Conclusion

Even though NASICON glasses satisfy the $T_g/T_f < 0.6$ criterion for homogeneous crystallization, the profound structural diferences between the glasses and their isochemical crystals, regarding the local environments of both network former and network modifier species, suggest a heterogeneous nucleation mechanism.

Acknowledgements

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