

Comparative Analysis of Reactivity of Al and Ga Doped Garnet Solid State Electrolyte at the Interface with Li Metal

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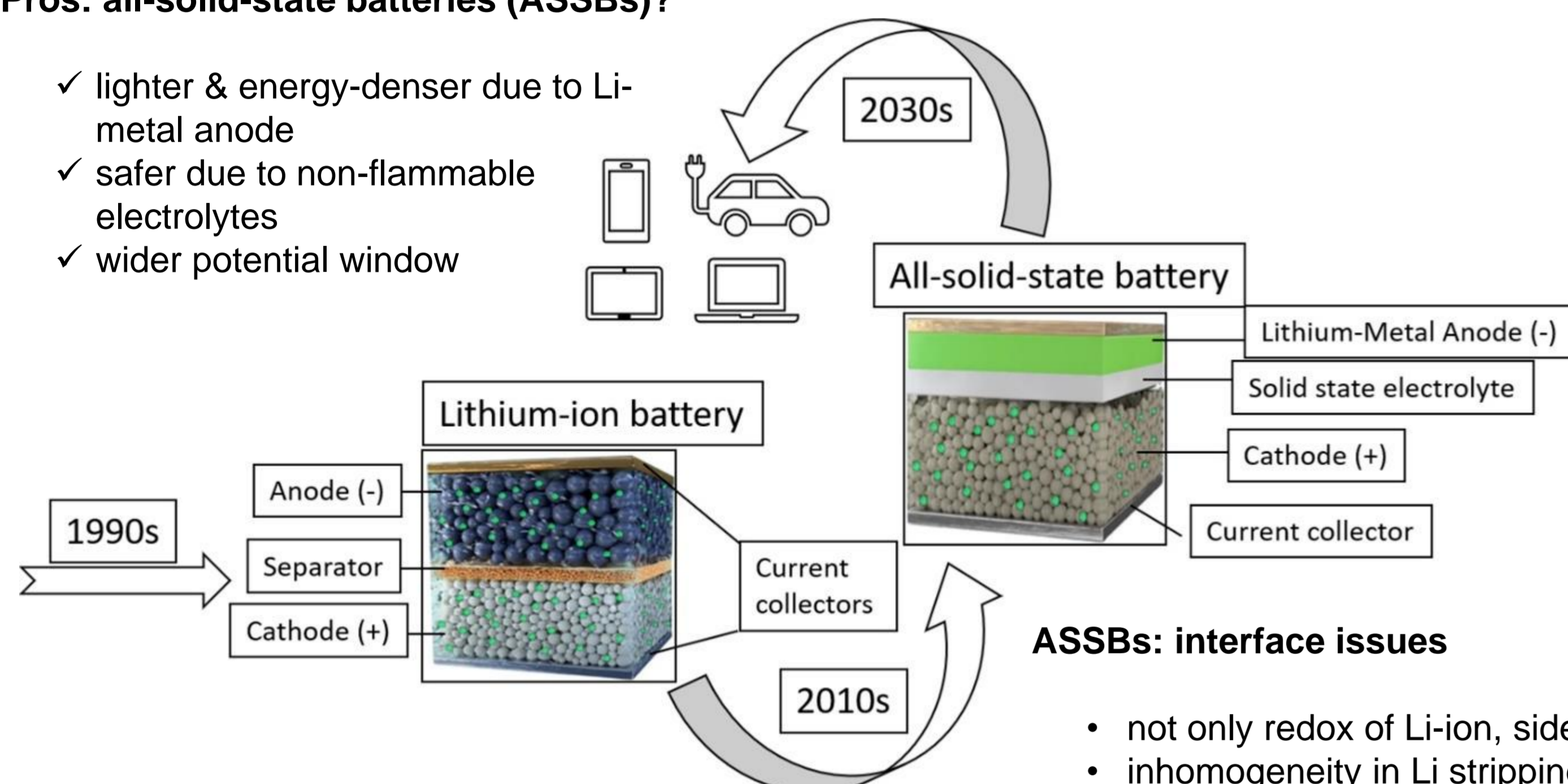
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All-solid-state batteries and LLZO, a garnet-type solid electrolyte

Pros: all-solid-state batteries (ASSBs)?

- ✓ lighter & energy-denser due to Li-metal anode
- ✓ safer due to non-flammable electrolytes
- ✓ wider potential window



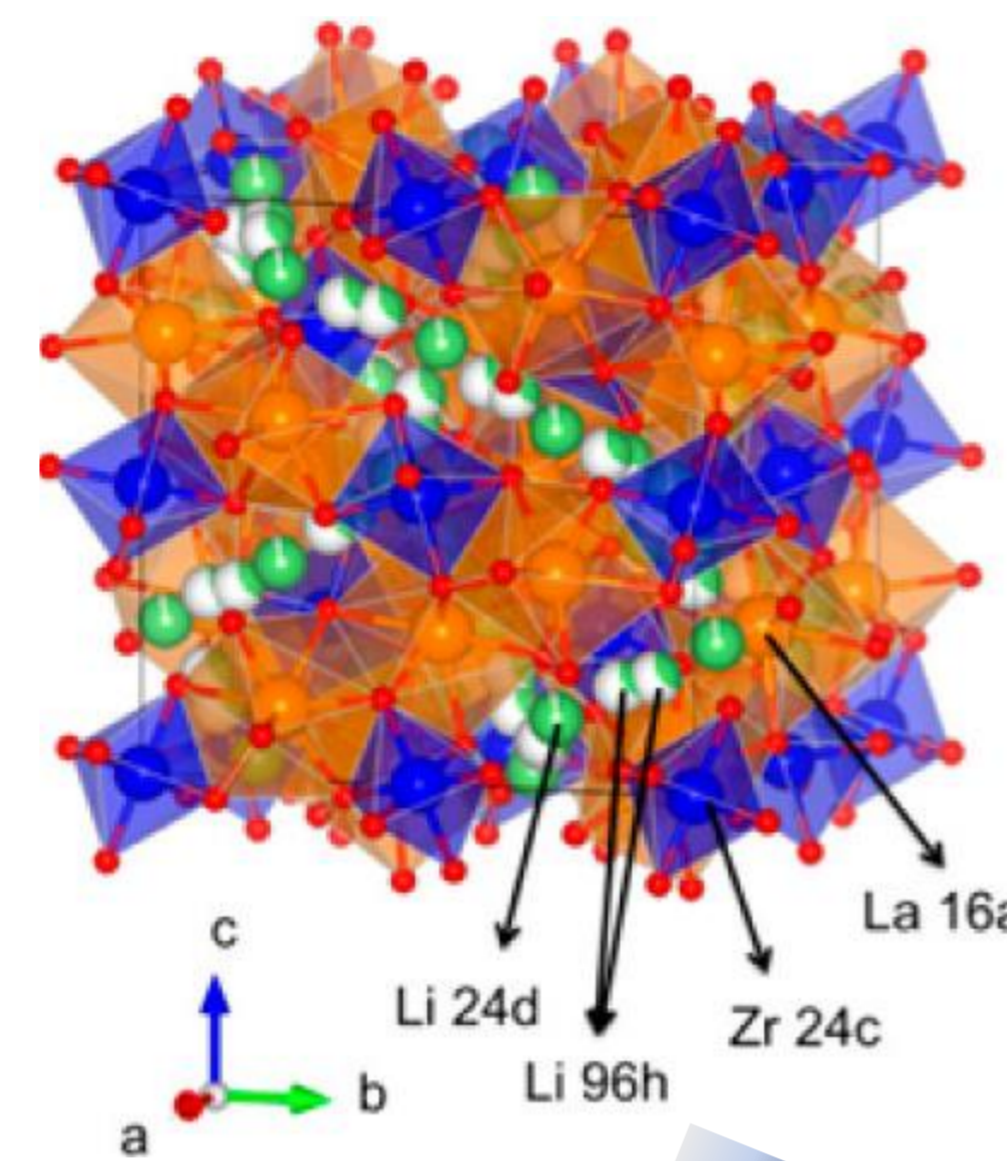
ASSBs: interface issues

- not only redox of Li-ion, side reactions
- inhomogeneity in Li stripping/plating
- poor physical contact
- high interfacial impedance / low ionic conductivity

C. Bubulinca et. al., Batteries 2023, 9(3), 157

R. Jalem et. al. Chem. Mater. 2013, 25, 3, 425

Solid electrolytes are typically thermodynamically unstable w.r.t Li metal anode, resulting in a kinetically stable mixed-conductive interface



Advantages of LLZO

- high ionic conductivity at RT (0.1 to 1 mS/cm)
- high toughness
- wide potential stability window

Challenges with LLZO (Li₇La₃Zr₂O₁₂)

- stability in contact with Li anode during cycling is debatable
- kinetics of the reactivity of Li metal with LLZO, role of dopant needs further investigation

cubic-type LLZO show high Li ionic conductivity

Li atoms occupy face shared tetrahedral sites (24d) and octahedral sites (96h) forming a 3D structure leading to fast Li conduction

tetragonal-type LLZO show lower conductivity

why Ga-doped LLZO is fundamentally limited by its reaction with Li metal ?

- dope Li tetrahedral sites by either Al or Ga - allow interaction with Li metal
- compare using DFT, XPS, EID, ND

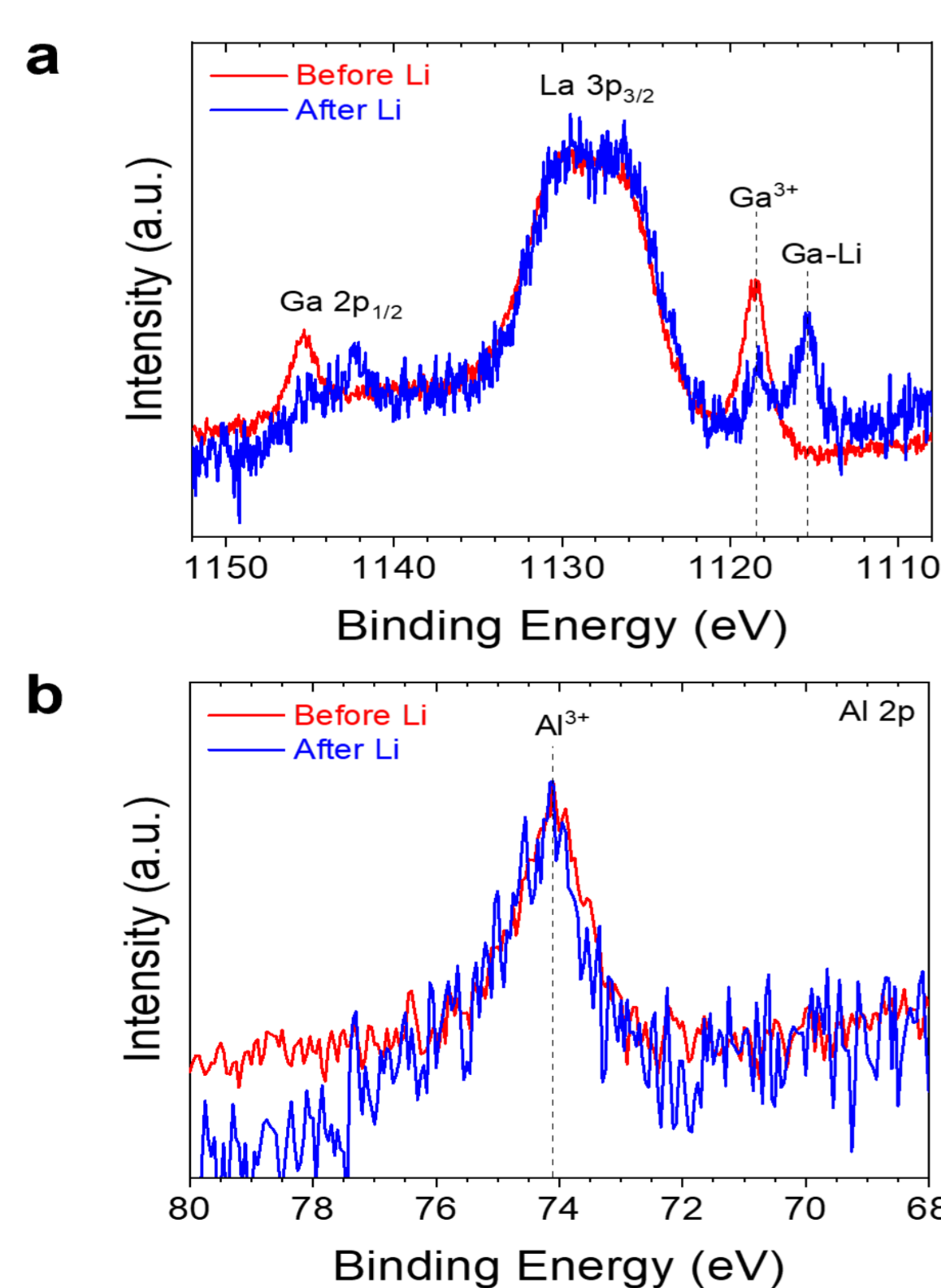
Reactivity of Al-doped LLZO and Ga-doped LLZO with Li metal

Density functional theory calculations

DFT calculations revealed:

- while Al³⁺ and Ga³⁺ nominally occupy the same sites in the cubic LLZO lattice, **Ga-O bonding is weaker than Al-O**, lowering the barrier to Ga migration.
- **Ga is energetically favored to reside at the LLZO surface and alloy with Li** as compared with Al, making it easily reduced at the Li electrode interface, and likely at grain boundaries as well

X-ray photoelectron spectroscopy



XPS spectra of (a) Ga-doped LLZO and (b) Al-doped LLZO samples before and after Li deposition

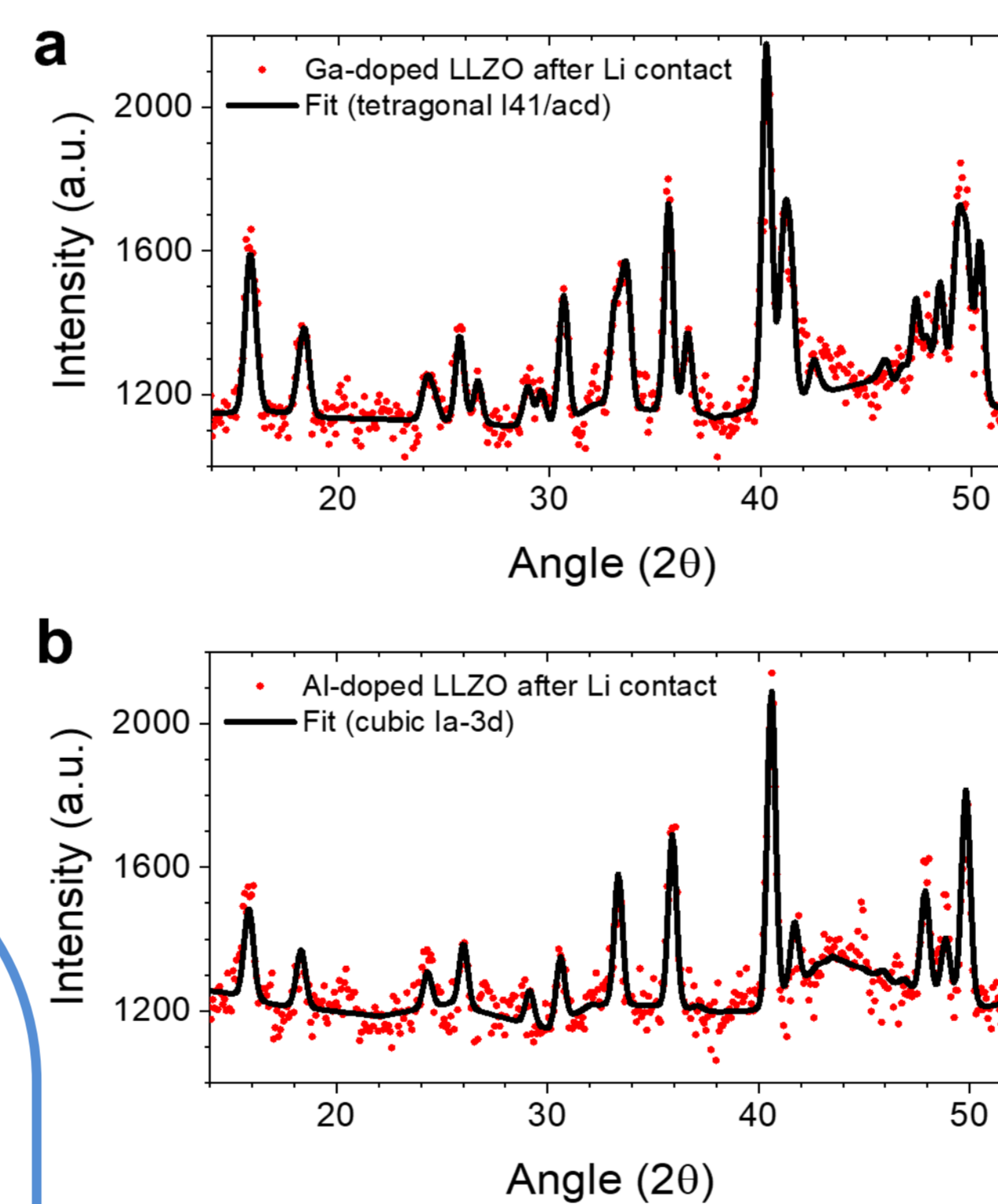
Before Li metal deposition,

- single peaks associated with the Ga 3p_{3/2} and Al 2p core levels
- each dopant exhibiting the expected +3 valence in the LLZO lattice

After Li metal deposition,

- **additional peak** in the Ga 2p_{3/2} core level is observed (1115.5 eV), indicating significant **reduction of Ga** dopants by Li metal.
- position of the reduced Ga peak is below the binding energy of metallic Ga, which strongly suggests **alloying of Ga** dopants with the Li layer
- no changes to Al 2p core level

Neutron Diffraction



Neutron powder diffraction data of (a) Ga-doped LLZO sample after contact to Li metal and (b) Al-doped LLZO sample after contact to Li metal

Neutron diffractograms of Ga-doped LLZO and Al-doped LLZO powders were taken before and after their contact with Li

- **Al-doped LLZO** remains in the highly conducting **cubic** structural phase (Ia-3d) even after contact with Li metal
- pristine Ga-doped LLZO is highly conducting cubic phase (I-43d)
- **Ga-doped LLZO** sample that was in contact with Li metal could only be refined with a **tetragonal** phase (I41/acd)

Electrochemical Impedance Spectroscopy

EIS spectra collected from Li|Ga-LLZO|Li symmetric cells reveal significant evolution of the interfacial resistance as a function of time confirming ND and XPS results

- rapid decrease in R_{SEI}, suspected to be caused by **Ga-Li alloy** formation
- increase in R_{CT}, caused by **Ga depletion in LLZO**
- Li ions from Li metal diffuse into LLZO particles, causing increase in local lithium concentration there
- LLZO forced to revert to its tetragonal polymorph, an overall less conductive phase

- Li interaction with Ga-doped LLZO causes reduction of Ga dopants, formation of Ga-Li alloy, Ga to move from LLZO, it changes to low conductivity tetragonal polymorph
- Al-doped LLZO is robust at the interface and in the bulk against Li metal, showing no dopant reduction or phase transformation

Neutron measurements were carried out at the CANAM infrastructure of the NPI CAS Rez with support of Charles Hervoche