

## Real structures of complex alkali- alkaline earth intermetallics

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A number of binary and ternary compounds between alkali and alkaline earth elements have been reported most of them exhibiting the characteristics of structural complexity [1-6], like large unit cells and a low symmetry. In several instances the structure analyses indicate disorder phenomena which could stem from domains with sizes smaller than the coherence length of X-rays. The combination of complexity and nanoscale domains makes these compounds ideal subjects for TEM examinations; however, experimental difficulties complicate the electron microscopy characterization of the real structures.

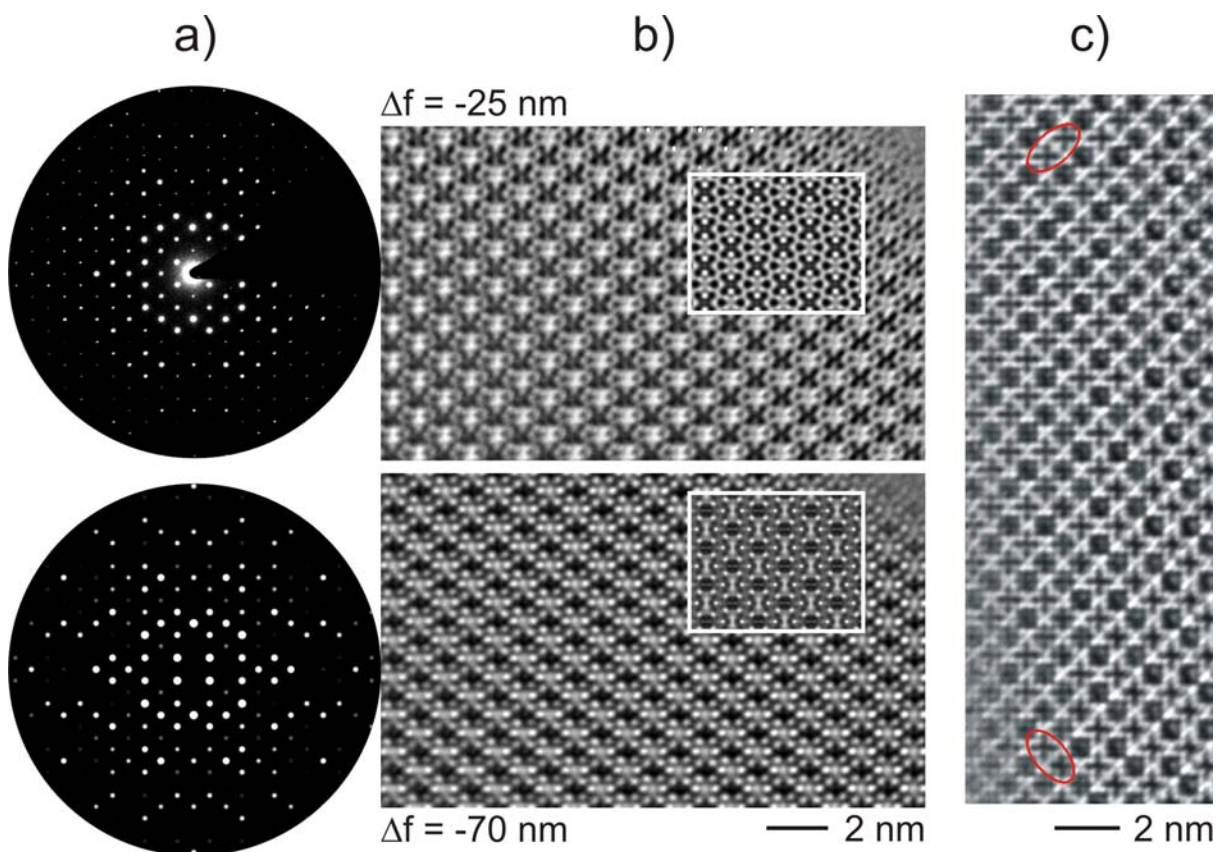
All compounds are extremely moisture sensitive, which requires that all manipulations for the TEM preparation and the transfer of the samples to the microscope must be carried out with a self-constructed device [7] under dry argon atmosphere. Further complication comes from the inhomogeneity of the samples and the remarkably low melting points of the crystals. Despite the application of low-dose techniques, the phases rapidly transform or melt under the influence of the electron beam. Therefore rapid techniques for the phase identification, like the precession electron diffraction (PED, [8]) are necessary. In this contribution we report about the real structures and in situ transformations occurring in ternary crystals Li-Ba-Ca, Li-Ba-Na and the new binary phase  $\text{Sr}_{19}\text{Li}_{44}$ .

TEM examinations in the system Li-Ba-Ca allowed to verify the structure of  $\text{Ba}_{19}\text{Li}_{44}$ , however, isostructural compounds with variable content of Ca were also found (Ba:Ca = 5.8-12.1). In these phases Ca can substitute Ba as in a recently characterized compound of the same ternary system with an approximate composition of  $\text{Li}_{33}\text{Ba}_{13}\text{Ca}_3$ .

For the system Li-Ba-Na the main component  $\text{Li}_{19}\text{Ba}_5\text{Na}_8$  rapidly decomposes by electron beam impact into a highly crystalline product. The crystals are multiple twins, and the single domains can be assigned to the cubic NaBa-type structure, cf. Fig. 1a and b. Despite this transformation the raw structure model of  $\text{Li}_{19}\text{Ba}_5\text{Na}_8$  which was initially determined on twinned crystals via XRD was refined by PED and HRTEM performed on single domains. The new structure model exhibits no averaging phenomena, and all anomalies of the raw structure were eliminated.

For the new compound  $\text{Sr}_{19}\text{Li}_{44}$  the X-ray investigations were complicated by twinning which was observed on many crystals selected for XRD. Initially the unit cell was found to be either tetragonal with lattice parameters  $a=31.8458$ ,  $c=15.9242$  Å, or cubic ( $a \sim 31.85$ Å). TEM showed that the cubic metrics originate from superposition of tetragonal domains in terms of a twinning by reticular pseudomerohedry, cf. Fig. 1c. The HRTEM micrograph was recorded close to Scherzer focus, thus, the twinning is evident by the systematic arrangement of the dark spots (see marks) correlating with the Sr atoms. The electron microscopy observations verify the isostructural nature of  $\text{Sr}_{19}\text{Li}_{44}$  and the corresponding Ba compound.

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**Figure 1.** a) Experimental (top) and calculated (bottom) PED pattern recorded on a single domain with NaBa-type structure, zone axis [110] b) HRTEM micrographs with inserted simulations (zone axis [110],  $t = 3.2 \text{ nm}$ , focus values specified). c) Twinned domains in  $\text{Sr}_{19}\text{Li}_{44}$ , common zone axis [100].