Figure 1. The 2D borophosphate anionic partial structure and infrared absorption spectrum of $CsAl_2BP_6O_{20}$.

Keywords: New topology of borophosphate, solid state reaction method

MS15-P3 Mixed alkali/alkaline earth trielides of the BaAl$_4$-type structure: A combined synthetic, crystallograhic and theoretical case study for the 'coloring' in polar intermetallics

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The 'coloring' [1], the distribution of different atoms M among the apical/basal site of the pyramids in the BaAl$_4$-type (d), has already been extensively investigated for hundreds of ternary TM/p-block compounds (cf. references in [2-4]). Concerning the electronic stability the optimized 'bond energy' of 14 ve/fu is sufficiently proven [5,6], even though the structure type occurs from 12 to almost 15 ve/fu. Using metallic M and ionic A^{n+} radii, the ratio r_M:r_A of the BaAl$_4$-type ranges from 0.89 to 1.04 [4].

The 'coloring' of the M anion by the triels, which differ both in size and electronegativity χ, have been systematically investigated for the Ba series (Al/Ga/In), SrGa$_4$ to SrAl$_4$ (+In, [7]) (14 ve/fu) as well as for the Ga-containing K/Rb tetraindides (13 ve/fu). Carefully performed powder/single crystal structure analysis of distinct compounds (black symbols) reveal the ThCr$_2$Si$_2$ ordering only ($I4/mmm$), no indications towards the CaBe$_2$Ge$_2$ or other 1:1:3 ordering variants are observed.

The calculated (FP-LAPW DFT) Bader volumes (V_{BB}) of the binary trielides indicate no significant size differences for M_a and M_b, but a substantial more negative charge (q) of M_a, due to the larger Coulomb interaction M_a—A. Accordingly, all Ga-phases show a strong preference for the electronegative Ga to occupy the M_a site (red curves in (a) and (b)). The preference is more restrictive for shorter A—M contacts, i.e. smaller r_A (e.g. difference Sr/Ba in (a)). The calculated 'coloring energy' ([5], ΔE_{tot} CaAl$^b_2$Ga$^a_2$⇔CaGa$^b_2$Al$^a_2$, 0.46 eV) is by far larger than the difference of the M_a-M_a bond energies for Al/Ga (0.14 eV).

For mixed Al/In compounds (c) the M distribution changes with r_A: For smaller Sr with higher 'site energy' A—M_a, In with larger χ occupies the M_a site. In contrast, for A=Ba the less electronegative element Al occupies this site. This change of the site preference could be verified by the calculations. It is a striking example for the important contribution of Coulomb interactions in the lattice energy of polar intermetallics.

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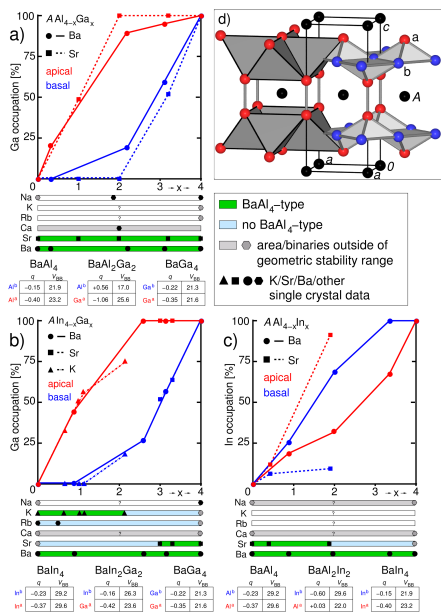[7] C. Meyer, K. Köhler, C. Röhr, *Z. Kristallogr. Suppl.* **35**, 86 (2015)

Figure 1. Triel-distribution in ternary compounds (investigated by means of single crystal data, black symbols) of the series $AAl_{4-x}Ga_x$ (a), $AIn_{4-x}Ga_x$ (b), $AAl_{4-x}In_x$ (c) forming the $BaAl_4$-type structure (d).

Keywords: Trielides, Gallides, Indides, Aluminides, Synthesis, Bandstructure Calculation

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Ternary rare earth fluorides are of interest for a wide range of optical applications like e.g. lasers, scintillators, luminescent materials or efficient up- and downconverters e.g. [1]. The understanding and interpretation of their optical properties relies on an unambiguous structure determination. However, structure determination is frequently difficult due to the occurrence of complex twinning. One of the underlying reasons for this is the close relationship of the materials to high symmetry structures like fluoride, pyrochlore or tveitite [2-4].

Surprisingly ternary fluorides with general composition $ALan_2F_7$ with A=K,Rb,Cs and Lan=rare earths and Y have been described in a large variety of different space groups, although the main structural motifs are very similar. It is also striking that for many of the described structures discussions about the correct space groups are ongoing.

We have investigated the compounds $CsLan_2F_7$ with Lan=Nd,Gd,Tb,Er,Yb,Lu and Y with single crystal x-ray diffraction using synchrotron radiation. All the compounds show a pseudo-hexagonal metrics with $a{\approx}b{\approx}15.5$-16.5 Å, $c{\approx}12.3$-12.7 Å and $\gamma \approx 120°$. A detailed analysis of the data shows that the structures are best described in the monoclinic space group $P112_1/b$ taking into account additional six-fold twinning. To better understand the underlying reasons for the frequent occurrence of twinning in the samples we performed a detailed analysis of the pseudosymmetry of the crystal structures, which showed that, in particular the cation array has a very high pseudosymmetry with respect to space group $P6_3/mmc$ with lattice parameter a_{hex}=1/2a, c_{hex}= c. Surprisingly, the resulting cation array in this high symmetry structure shows atomic positions which are equivalent to the ones observed in the hexagonal Laves phases Zn_2Mg. An analysis of the pseudosymmetry of the structures of the known $ALan_2F_7$ compounds shows the same highly symmetrical cation array.

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Keywords: ternary fluorides; twinning; pseudosymmetry; Laves phases