

**CRYSTAL-CHEMICAL PECULIARITIES OF RARE-EARTH
ALUMOSILICIDES AND ALUMOGERMANIDES**

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The chemical class grouping rare-earth aluminosilicates and aluminogermanides includes 145 ternary compounds, characterized by simple stoichiometries and a rare-earth metal content between 20 and 60 at.%. The majority of the compounds are located along the RX_2 - Al_2 , RX_2 - Al and RX - Al (R - rare-earth metal, X - Si or Ge) cross-sections of the ternary systems and 50 compounds contain 33 at.% R. The compounds crystallize with 23 different, but related, structure types, 10 of which (La_2AlGe_6 , $Ce_3Al_4Si_6$, $CeAlSi_2$, $Y_2Al_3Si_2$, $YAl_{1.4}Si_{0.6}$, $YAlGe$, Y_2AlGe_3 , $Yb_7Al_5Ge_8$, $Pr_4Al_3Ge_3$ and Tb_6Al_3Si) are defined on a rare-earth aluminosilicate or aluminogermanide. For 18 structure types rows of isotopic compounds containing from 3 to 28 representatives are known, whereas only four types have one single representative. The $CaAl_2Si_2$ (28 compounds), $YAlGe$ (15), α - $ThSi_2$ (13) and AlB_2 (11) structure types are common to rare-earth aluminosilicates and aluminogermanides. A differentiation with respect to the crystal structure is observed between compounds of light and heavy rare-earth metals for > 23% R atoms. In 18 structure types all or part of the X atoms centre trigonal prisms, formed either by R atoms, or by R and Al atoms in different ratios. The X and Al atoms are characterized by short interatomic distances and form pairs, chains, nets or three-dimensional frameworks. In some structures X and Al atoms are distributed statistically, however, phases with significant homogeneity ranges are not observed. Exceptions are the α - $ThSi_2$ type phases with up to 17 at.% broad homogeneity ranges.

Keywords: CRYSTAL CHEMISTRY ALUMOSILICIDES
ALUMOGERMANIDES

**RARE EARTH (R) TRANSITION METAL (T) ALUMINIDES $R_3T_4Al_{12}$
AND STRUCTURAL SYSTEMATICS OF RELATED INTER-
METALLICS**

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The new isotopic intermetallic compounds $R_3Ru_4Al_{12}$ (R=Y, Pr, Nd, Sm, Tb-Tm) and $R_3Os_4Al_{12}$ (R=Y, Ce-Nd, Sm, Gd-Tm) were prepared by reaction of the elemental components in an arc-melting furnace. Their $Gd_3Ru_4Al_{12}$ type structure [1] was determined from four-circle X-ray diffractometer data of $Y_3Ru_4Al_{12}$: $a = 877.7(1)$ pm, $c = 952.3(1)$ pm, $Z = 2$, $R = 0.028$ for 361 structure factors and 28 variable parameters. It was also refined for $Nd_3Os_4Al_{12}$ ($a = 889.2(1)$ pm, $c = 960.3(1)$ pm, $R = 0.025$ for 425 F values and 21 variables) and $Gd_3Os_4Al_{12}$ ($a = 884.7(1)$ pm, $c = 955.3(2)$ pm, $R = 0.023$; 427 F values, 21 variables). The refinements of the occupancy parameters revealed a mixed T/Al occupancy for one of the seven atomic sites resulting in the compositions $Y_3Ru_4.060(3)Al_{11.940(3)}$, $Nd_3Os_4.304(1)Al_{11.696(1)}$, and $Gd_3Os_4.309(2)Al_{11.691(2)}$, respectively. The structure is related to those found for $Y_2Co_3Ga_9$, $Er_4Pt_9Al_{24}$, $CeOsGa_4$, $Ho_3Ru_4Ga_{15}$, $YbFe_2Al_{10}$, $TbRe_2Al_{10}$, and $LuRe_2Al_{10}$. Topologically all of these structures may be viewed as consisting of atomic layers, although chemical bonding within and between the layers is of similar character. Two kinds of layers can be distinguished in these structures. One kind contains all of the rare earth and in addition aluminum or gallium atoms. The other kind of layers consists of the transition metal atoms and again aluminum or gallium atoms. These latter layers are hexagonally close packed and slightly puckered. The three different structures of the disilicides $TiSi_2$, $CrSi_2$, and $MoSi_2$ also contain these layers; however, in the disilicides these layers are flat.

References

[1] R. E. Gladyshevskii, O. R. Strusievicz, K. Cenzual & E. Parthe, Acta Cryst. B49, 474-478.

Keywords: STRUCTURAL SYSTEMATICS INTERMETAL LICs
TERNARY ALUMINIDES

**NEW OXIDE MATERIALS BASED ON STRONTIUM LITHIUM
TITANIUM OXIDE PHASE $SrLi_2Ti_6O_{14}$**

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A new strontium lithium titanate $SrLi_2Ti_6O_{14}$ has been discovered in the ternary oxide system SrO - Li_2O - TiO_2 . Single crystals of this compound have been grown by the flux method from a solution containing $LiBO_2$, SrO and TiO_2 in a ratio of 65:10:25 [mol%]. The structure of $SrLi_2Ti_6O_{14}$ has been solved using X-ray data collected on a CAD4-Enraf Nonius four-circle automatic diffractometer (MoK α radiation). The unit cell is orthorhombic, space group $Cmca$, with $a = 16.570(5)$ Å, $b = 11.150(2)$ Å, $c = 11.458(2)$ Å, $V = 2116.9(8)$ Å³. The crystal structure is built by edge and corner sharing TiO_6 octahedra which form layers parallel to the (100) plane. Consecutive layers are linked by common corners in the [100] direction. Lithium atoms in tetrahedral coordination occupy vacancies of the titanium octahedra framework, while strontium atoms lie in 11-coordinated sites between two successive layers. Based on the structure of $SrLi_2Ti_6O_{14}$, a whole group of new oxide materials with various properties can be obtained by substitutions in different crystallographic sites: - $BaLi_2Ti_6O_{14}$ and $PbLi_2Ti_6O_{14}$ single crystals grown by the flux method. Preliminary X-ray powder diffraction studies indicate that these compounds are isostructural with $SrLi_2Ti_6O_{14}$; - a new phase, $KLi_2Ti_5NbO_{14}$, resulting from replacement of Sr by K and one of the Ti atoms by Nb. Single crystals of this compound have been grown by the flux method. The X-ray diffraction pattern can be indexed in orthorhombic lattice mode F, with cell parameters $a = 5.793$ Å, $b = 11.205$ Å, $c = 16.785$ Å, $V = 1089.5$ Å³.

Keywords: $SrLi_2Ti_6O_{14}$ $SrLi_2Ti_6O_{14}$ SUBSTITUTED COMPOUNDS
FLUX CRYSTALS GROWTH

**METAL -RICH RARE EARTH COMPOUNDS - DISORDER AND
DIFFUSE SCATTERING**

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Among a large number of metal-rich rare earth halides as well as boride carbides there are quite a few where parts of the structure exhibit short-range order only, leading to diffuse scattering. The structure of aluminium stabilised lanthanum moniodide is derived from the rocksalt type, however, the diffraction patterns show spheres of diffuse intensity around the weak uneven Bragg reflections. Upon annealing, a complex arrangement of weak, but sharp additional reflections occur. Terbium boride halide $Tb_{13}Br_{18}B_3$ (average structure: $Immm$, $a = 3.96$ Å, $b = 16.91$ Å, $c = 28.11$ Å) is characterised by trans-edge sharing Tb_6 octahedra which are connected via Br atoms to form a framework of layers with channel-like voids. These channels contain additional Tb octahedra which form a superstructure (C centred with 2a, 2b). Stacking disorder of the layers leads to diffuse scattering along rods hkl ($h, k = 2n+1$) instead of superstructure reflections. The intensity along these rods is modulated with a translation period corresponding to $c/7$. In tetragonal rare earth boride carbides a large variation of lattice parameters is caused by variation of interstitial boron carbon anions in the voids of a metal atom substructure. If different kinds of interstitials are present, they may be completely disordered, however, ordered variants and phase separation has also been observed. In some cases the tendency towards ordering or segregation is not strong enough to produce long-range order and then diffuse scattering occurs.

Keywords: DIFFUSE SCATTERING RARE EARTH HALIDES RARE
EARTH BORIDE CARBIDES