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Sr₈Ca₆Cu₂₄O₄₁ was synthesized by solid-state reaction at 920°C in air. It crystallizes with an incommensurate composite structure, which can be conveniently described by a commensurate superstructure. Structure refinements were carried out in the space group *Cccm* ($a = 11.377(1)$, $b = 12.983(1)$, $c = 27.395(2)$ Å) and the supergroup *P:F222:-1-11* ($a = 11.3745(7)$, $b = 12.9798(9)$, $c_1 = 2.7493(4)$, $c_2 = 3.9132(3)$ Å, $q = c_1/c_2 = 0.7026$) on powder X-ray diffraction data. It was found that Sr and/or Ca may be replaced by at least 5 wt.% Y, Pb or Bi. These three cations modify in different ways the Cu₂O₃ zigzag chains and CuO₂ straight chains of CuO₄ squares within the layers. In addition, in the case of substitution by yttrium, the translation period along the stacking direction of the layers (b -parameter) decreases. Syntheses with small amounts of PbO or Bi₂O₃ further decrease the decomposition temperature of the phase.

Keywords: cuprate, spin ladder compound, composite structure

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Influence of Al, Ga and In on the Crystal Structure of ErGe_{2+x}
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Samples of digermanides of rare-earth elements are frequently prepared by the flux method using indium, gallium or aluminum flux. We decided to undertake a systematic investigation of the influence of small quantities of Al, Ga and In on the crystal structure of "digermanides" in an extended sense (RGe_{2+x}).

The existence of the compounds ErGe_{2.83}, Er₂Ge₅, ErGe_{1.83}, ErGe_{1.5}, and Er₃Ge₄ was confirmed in the range 20-40 at.% Er of the binary system at 600°C.

The addition of small quantities of Al leads to the formation of substitutional solid solutions for Er₂Ge₅, ErGe_{1.83} and Er₃Ge₄ (up to 2, 3 and 5 at.% Al, respectively). On the contrary, the solid solution based on ErGe_{1.5} displays a progressive filling-up of the vacancies in the AlB₂-type binary structure (up to 5 at.% Al). ErGe_{2.83} does not dissolve any significant amount of Al. The crystal structure of the ternary compound ErGe_{1.85}Al_{0.15} (ZrSi₂-type structure, Pearson symbol *oS12*, *Cmcm*, $a = 4.0490(2)$, $b = 15.9791(7)$, $c = 3.9102(2)$ Å) was determined by X-ray powder diffraction.

The addition of Ga causes the formation of larger solid solutions, which can be explained by the similar values of the atomic radii of Ga and Ge. The existence of ErGe_{1.85}Ga_{0.15} with a ZrSi₂-type structure was confirmed. The formation of a ternary compound of composition Er(Ga,Ge)₃ was established. Its crystal structure can be derived from the defective ErGe_{2.83} structure. No significant solubility of indium in binary erbium germanides was observed.

Keywords: rare-earth germanide, solid solution, crystal structure

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Solid Solutions in the PrNi₂-PrAl₂-PrGe₂ System
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The isothermal cross-section of the phase diagram of the system Pr-Ni-Al-Ge at 33.3 at.% Pr in the PrGe₂-rich region at 600°C was constructed. The unit-cell parameters and homogeneity ranges of the solid solutions based on the binary compound PrGe_{2-x} with an α -ThSi₂-type structure and the ternary compounds PrAlGe (α -ThSi₂-type structure) and Pr(Ni,Ge)_{2-x} (AlB₂-type structure) were determined. For the solid solution with AlB₂-type structure it was found that the progressive substitution of Ge for Ni or Al deforms the trigonal prisms. This deformation can be interpreted as the result of increasing interactions between p -element atoms in the (0 0 1) plane with increasing Ge content. On the contrary, both unit-cell parameters

monotonically increase when Ni atoms are replaced by larger Al atoms. The structural investigation of a single crystal from an alloy of composition Pr_{33.3}Ni_{13.3}Al_{33.3}Ge_{20.0} indicates that the crystal structure is incommensurately modulated in the directions of [0 1 0] and [0 0 1] of the parent AlB₂-type structure ($a = 4.255(2)$, $c = 4.221(2)$ Å, $q_1 = 0.169b^*$, $q_2 = 0.154c^*$).

Keywords: intermetallic, solid solution, incommensurate structure

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Low Temperature Stability of Fluoride Pyrochlores Investigated by Neutron Powder Diffraction and Raman Spectroscopy
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Compounds that are isostructural to the mineral pyrochlore ((NaCa)₂(NbTa)₂O₆(F/OH)) form a populous family with more than 150 members. All of these compounds have a regular or distorted pyrochlore structure, which has the form A₂B₂X₆X' (where X and X' = O, F, S, OH), a face centered cubic lattice belonging to the *Fd-3m* space group and eight formulas per unit cell. Two families of fluoride compounds are known to crystallize in the pyrochlore structure: A(M²⁺_{1/2}M³⁺_{1/2})₂F₆ (the A₂X' sublattice is replaced by larger monovalent cations, such as Cs⁺ and Rb⁺) and (A¹⁺_{1/2}A²⁺_{1/2})₂B²⁺₂F₇ or, in a more compact form, AM²⁺M³⁺F₆ and A¹⁺A²⁺B²⁺F₇, respectively. Recent measurements of polarized Raman scattering and infrared reflectance spectroscopy suggested a disorder induced local symmetry lowering, even though x-ray diffraction results confirmed an average pyrochlore structure. Thus, the aim of this work is to investigate the low temperature stability of the fluoride pyrochlore structure of compounds belonging to both families by neutron powder diffraction and Raman spectroscopy.

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Keywords: pyrochlore, symmetry breaking, Raman scattering

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The Pseudo-Ternary Intermetallic System CaAg₂-CaZn₂-CaAl₂
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The three pseudo-binary intermetallic systems Ca(Ag_{1-x}Zn_x)₂, Ca(Ag_{1-x}Al_x)₂, Ca(Zn_{1-x}Al_x)₂, and the pseudo-ternary system CaAg₂-CaZn₂-CaAl₂, were examined by X-ray single crystal and powder diffraction. The CeCu₂-type structure, showed by both the CaAg₂ and CaZn₂ phases, is maintained in the whole Ca(Ag_{1-x}Zn_x)₂ system. The Ca(Ag_{1-x}Al_x)₂ system shows the structural sequence: CeCu₂-type ($x=0-0.1$), MgZn₂-type ($x=0.1-0.6$), MgNi₂-type ($x=0.7-0.9$), MgCu₂-type ($x=1$). A simpler sequence occurs in the Ca(Zn_{1-x}Al_x)₂ system: CeCu₂-type ($x=0-0.5$), MgNi₂-type ($x=0.6-0.8$), MgCu₂-type ($x=0.9-1$). Within the pseudo-ternary system, four regions occur, corresponding to the cited structural types: the three Laves phase types (MgCu₂, MgZn₂, MgNi₂) and the CeCu₂ type. The central composition Ca₃Ag₂Zn₂Al₂ belongs to the MgZn₂ type.

A structural map collecting the studied phases shows a combined influence of both the size factor and the electron concentration on the distribution of the structure types as a function of the phase composition. Considering the average atomic volume, a sharp volume increase (up to 6.5%) is observed in the regions showing the change from a Laves-phase-type to the CeCu₂-type structure, owing to the different geometrical space filling conditions.

Keywords: crystal chemistry and structure, intermetallic compounds, ternary alloys