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**Crystallosymmetric Structure and Evolution of the Mineral World**

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The generalized theory of symmetry in application to mineralogy should certainly treat a mineral as an entire functional system, embracing its outer and inner environments, links, properties, external fields. In geological terms, the problem that seems most important is how to transfer symmetry investigations from the mineral individual to the entire mineral world. We are developing crystallosymmetric analysis of complex systems now (N. P. Yushkin "Crystallosymmetric Analysis of Complex Mineral Systems", Syktyvkar, 1985 which opens the possibility to study polymineral objects, such as rocks, ores, geospheres, etc., in terms of symmetry and provides principally new information for the understanding of their nature. To characterize the crystalline state of substances in polymineral systems, we introduced the concept of crystallosymmetric structure of systems.

Each geologic system composed of minerals is characterized by a strictly definite crystallosymmetric structure expressed by the constant parameters of the mineral species distribution within ranks of the symmetry system (categories, syngonies, point groups).

On the basis of obtained results a law of the geologic evolution of crystallosymmetric structure of mineral systems has been formulated. In the process of cosmic and geologic evolution the crystallosymmetric structure of mineral systems undergoes complication and qualitative changes; it's manifested in the increase of entropy of all symmetry characteristics, as well as in replacement of originally predominant cubic and orthorhombic minerals by monoclinic ones; decrease in the mineral substance symmetry occurs alongside with high and even increasing external morphology symmetry of the Earth and other mineral bodies.

**Keywords: symmetry of minerals, crystallosymmetric structure, evolution of symmetry**

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**Borophosphate: Crystal Chemistry, Systematic and Synthesis**

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Borophosphate synthesis and characterization has been started only ~10 years ago. Significant contribution including first approach to structural chemistry [1] has been made in Germany. In our investigation among new borophosphates, $In[BP_2O_8].0,8H_2O$ relates to $M^{I} M^{II}(H_2O)_2[BP_2O_8].H_2O$ [1] and $Fe(H_2O)_2[BP_2O_8].H_2O$ [2], has framework of In, B and P tetrahedra and most successful zeolite properties.

New systematic [3] uses B:P ratio (as in [1]) and besides topology and symmetry analysis of structural building blocks. When B:P>1, B polyhedra in complex anion form structural blocks and its combination typical for the borates with the P tetrahedron in outside "decorating" (of high charge reason) or connecting role. When B:P~1, low degree of condensation B and P polyhedra is typical with the borate anions topology and the same P tetrahedra role. When B:P<1 (most of the compounds) structural block of equal topology and local symmetry *–4* with the central B tetrahedron and four apical P tetrahedra may be detected in all the structures. Block can be full or deficient protonated. The condensation degree determines the systematic with the ortho, soro, chain, ribbon, layer or framework borophosphate anion. The higher pH is at hydrothermal synthesis, the higher is the condensation degree of blocks; low pH (acid condition) assists protonation of blocks. Topology and symmetry analysis demonstrates that in despite of the diversity, borophosphate form a single class of compounds. This work was supported by RFBS, project 02-03-33316.

[1] Kniep R., Engelhard H., Hauf C., *Chem. Mater*, 1998, **10**, 2930. [2] Yilmaz A., Bu X., Kizilyalli M., Stuky G.D., *Chem. Mater*, 2000, **12**, 3243. [3] Ruchkina A., Belokoneva E.L., *Russ. J. Inorg. Chem*, 2003, **48**, 1812.

**Keywords: borophosphate, crystal chemistry and systematic, synthesis**

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**Crystallochemical Analysis of Halogenides and Chalcogenides of *d*-metals**

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A comparative crystallochemical analysis and classification are performed for 35 halogenides, 123 chalcogenides $M_y[TX_4]$ (T is *d*-metal), and 1573 binary compounds $A_xB_y$ using the program *IsoTest* of the *TOPOS* package. Two levels of structural relationship are considered: (i) 'grey' isomorphism, when a binary compound $A_xB_y$ relates to a ternary compound $M_y[TX_4]$ if some atoms M, T, or X are topologically equivalent; (ii) partial isotypism when a complex salt $M_y[TX_4]$ is considered as a quasi-binary compound $M_y[T]$ keeping the connectivity of initial net. The examples of 'grey' isomorphism for ternary compounds are found with $Tl_2Cl_4$, $In_2Br_4$, magnetite, cristobalite, and $C_3N_4$. Partial isotypism is much more frequent; the following binary compounds participate in such relations: CsCl, $NdS_2$, NiAs, FeB, $BaF_2$-HP, PtS, sphalerite, fluorite, $PoCl_2$, $BiF_3$ (gananite), $ReO_3$. Many of the found correspondences are typical also for other anhydrous inorganic salts: orthosilicates, orthogermanates, arsenates, sulfates, selenates, molybdates, perchlorates, periodates, nitrates, carbonates, and borates.

Topological analysis of ionic arrays shows that in a half of the halogenides and almost in all the chalcogenides there are arrays related to close packings. Using the data on uniformity of these arrays the conclusions are made about their significant structure-forming role.

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**Keywords: comparative analysis, classification, inorganic compounds**

**P.10.02.3**

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**Crystal Structure of Two Related Selenites**

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$M_3(SeO_3)_3{\cdot}H_2O$ for M= Mn,Co have been synthesized using mild hydrothermal conditions under autogeneous pressure. The crystal structure of both compounds have been solved from X-ray single crystal data in $P\bar{1}$ triclinic space group with Z= 2. The crystal structures of the $M_3(SeO_3)_3{\cdot}H_2O$ (M= Mn,Co) consist of a three-dimensional framework formed by $MO_6$ octahedra and $(SeO_3)^{2-}$ selenite anions with trigonal pyramidal geometry. Both structures show the existence of zig-zag chains linked through $M_2O_{10}$ dimeric units and $MO_6$ octahedra and are inter-changeable by the rotation of these dimers and octahedra and a corresponding change of edge/corner sharing connectivity.

Taking into account the results of the luminescence and diffuse reflectance spectroscopies, the Dq and Racah (B and C) parameters have been calculated by fitting the experimental frequencies to an energy level diagram for octahedral $d^5$ and $d^7$ high spin Mn(II) and Co(II) ion systems.

Magnetic measurements show the existence of antiferromagnetic interactions in these compounds.

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**Keywords: synthesis, selenites, crystal structure and properties**

**P.10.02.4**

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**Partial Substitution by Y, Pb or Bi in $Sr_8Ca_6Cu_{24}O_{41}$**

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$Sr_8Ca_6Cu_{24}O_{41}$ 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*:*F*222:-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 $Cu_2O_3$ zigzag chains and $CuO_2$ straight chains of $CuO_4$ 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 $Bi_2O_3$ further decrease the decomposition temperature of the phase.

**Keywords: cuprate, spin ladder compound, composite structure**

**P.10.02.5**

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**Influence of Al, Ga and In on the Crystal Structure of $ErGe_{2\pm x}$**

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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 ($RGe_{2\pm x}$).

The existence of the compounds $ErGe_{2.83}$, $Er_2Ge_5$, $ErGe_{1.83}$, $ErGe_{1.5}$, and $Er_3Ge_4$ 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 $Er_2Ge_5$, $ErGe_{1.83}$ and $Er_3Ge_4$ (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 $AlB_2$-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 $ErGe_{1.85}Al_{0.15}$ ($ZrSi_2$-type structure, Pearson symbol *oS*12, *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 $ZrSi_2$-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 $PrNi_2$-$PrAl_2$-$PrGe_2$ 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 $PrGe_2$-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 $\alpha$-$ThSi_2$-type structure and the ternary compounds PrAlGe ($\alpha$-$ThSi_2$-type structure) and $Pr(Ni,Ge)_{2-x}$ ($AlB_2$-type structure) were determined. For the solid solution with $AlB_2$-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 $AlB_2$-type structure ($a$ = 4.255(2), $c$ = 4.221(2) Å, $q_1$ = 0.169**b***, $q_2$ = 0.154**c***).

**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 isoestructural to the mineral pyrochlore $((NaCa)_2(NbTa)_2O_6(F/OH)$ form a populous family with more than 150 members. All of these compounds have a regular or distorted pyrochlore structure, which has the form $A_2B_2X_6X'$ (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: $A(M^{2+}{}_{1/2}M'^{3+}{}_{1/2})_2F_6$ (the $A_2X'$ sublattice is replaced by larger monovalent cations, such as $Cs^+$ and $Rb^+$) and $(A^{1+}{}_{1/2}A'^{2+}{}_{1/2})_2B^{2+}{}_2F_7$ or, in a more compact form, $AM^{2+}M'^{3+}F_6$ and $A^{1+}A'^{2+}B^{2+}{}_2F_7$, 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 if this work is to investigated 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 $CaAg_2$-$CaZn_2$-$CaAl_2$**

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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 psudo-ternary system $CaAg_2$-$CaZn_2$-$CaAl_2$ , were examined by X-ray single crystal and powder diffractometry. The $CeCu_2$-type structure, showed by both the $CaAg_2$ and $CaZn_2$ 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: $CeCu_2$-type (x=0-0.1), $MgZn_2$-type (x=0.1-0.6), $MgNi_2$-type (x=0.7-0.9), $MgCu_2$-type (x=1). A simpler sequence occurs in the $Ca(Zn_{1-x}Al_x)_2$ system: $CeCu_2$-type (x=0-0.5), $MgNi_2$-type (x=0.6-0.8), $MgCu_2$-type (x=0.9-1). Within the pseudo-ternary system, four regions occur, corresponding to the cited structural types: the three Laves phase types ($MgCu_2$ , $MgZn_2$ , $MgNi_2$) and the $CeCu_2$ type. The central composition $Ca_3Ag_2Zn_2Al_2$ belongs to the $MgZn_2$ 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 $CeCu_2$-type structure, owing to the different geometrical space filling conditions.

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