08.2-35 STRUCTURAL CHEMISTRY OF CYCLOPHOSPHATE ANIONS AND STRUCTURE OF THE FIRST DECAMETAPHOSPHATE, by M. Bagieu and J.C. Guitel, Laboratoire de Cristallographie, C.N.R.S., 166 X, 38042 - Grenoble Cedex, France.

Ring anions with the general formula $(P_nO_{3n})^{-n}$ are known for n = 3, 4, 5, 6 and 8. With the structure of the barium-zinc decametaphosphate $Ba_2Zn_3P_{10}O_{10}$, we describe the first example of a cyclophosphate with n = 10. The symmetry is monoclinic, space group Pn, with a = 21.738, b = 5.356, c = 10.748 Å, β = 99.647° and Z = 2. The refinement yielded R = 0.032 for 4698 intensities and 406 parameters.

The dimensions of the isolated rings found in this compound are about 11 x 10 Å ; they form arrays along b, linked by ZnO_4 tetrahedra ; such arrays are further connected by ZnO_6 and BaO_9 polyhedra.

Main geometrical features of the $(P_{10}O_{30})^{-10}$ group are compared with those observed in already described metaphosphates such as $Cu_2Li_2P_6O_{18}$, $Cr_2P_6O_{18}$, $Cr_3(NH_4)_2P_8O_{24}$ and numerous tetra- and trimetaphosphates. Comparison is also made with other X_nO_{3n} ring-anions, where X = Si, Ge and As.

08.2-36 X-RAY AND INFRA-RED SPECTRAL STUDIES OF $CsREP_4O_{12}$ CRYSTALS. By. I.I. Plyusnina, K. Byrappa and G.I. Dorokhova, Department of Crystallography and Crystal Chemistry, Moscow State University, Leninsky Gori, Moscow, USSR 117234.

The discovery of unusual spectral characteristics in the rare earth phosphates has attracted the attention of crystallographers, physicists and chemists. It has been found that these unusual spectral characteristics are connected with their internal structures. Among the rare earth phosphates the ultraphosphates and metaphosphates of rare earth elements are of great importance. The crystal chemistry of RE ultraphosphates has been studied in detail by many workers. But the investigations of the RE metaphosphates are incomplete in many aspects.

We have obtained $CsREP_4O_{12}$ crystals from highly concentrated phosphoric acid solutions. The X-ray study reveals that the $CsREP_4O_{12}$ crystals can be divided into five structural types. A brief description of the morphology of $CsREP_4O_{12}$ crystals with reference to the temperature of growth is given. Based on the structures of these crystals, they can be divided into three types viz. ring type, chain type and ribbon type. The crystal chemistry of $CsREP_4O_{12}$ crystals has been discussed in brief. We have determined the absorption peaks characteristic for all the three types in the IR-spectra taken in the range of 1800-400 CM^{-1}. It was found that the angle <OPO in the ring type is less than in the chain type. The splittings $\nu_{as}PO_2$ and ν_sPO_2 are higher for the chain type of CsRE phosphates ($\Delta\nu\approx200$ CM^{-1}) than for the ring type ($\Delta\nu\approx170$ CM^{-1}) and the ribbon type ($\Delta\nu\approx150$ CM^{-1}) of CsRE metaphosphates. Therefore, it can be considered that the ribbon type of CsRE metaphosphates are nearer to the ring type of CsRE metaphosphates in their <OPO values.

08.2-37 PLANAR Ca - PO_4 SHEET STRUCTURES.

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A number of calcium phosphates are known to have Ca-PO_4 chains constituting sheet-type structures, corrugated or planar. As part of a program to correlate the stability of these sheet-type structures with the nature of bonding, we have determined the crystal structures of $CaBr(H_2PO_4).4H_2O$ (I) and $CaI(H_2PO_4).4H_2O$ (II). Crystals of I are monoclinic, C2/c, Z = 4, a = 20.314(5), b = 6.558(1), c = 6.973(1) Å and β = 90.02(3)°. The structure was refined to R = 0.034. Crystals of II are monoclinic, B2/c, Z = 4, a = 21.416(4), b = 6.550(1), c = 7.000(1) Å and β = 91.03(2)°. The structure was refined to R = 0.032.

The two structures are nearly isomorphous despite the difference in space group. Both compounds have a planar sheet-type structure consisting of edge-sharing Ca-PO_4 chains. The interlayer contents, Br or I (X) and the water molecules form $X(H_2O)_6$ octahedra via O - H...X hydrogen bonds. The two types of sheets, Ca - PO_4 and X - H_2O, are held together by Ca... O ionic bonds and O - H...O hydrogen bonds. Relationship with other calcium phosphates with sheet-type structures will be discussed.

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08.2-38 A REDETERMINATION OF THE STRUCTURE OF α - POTASSIUM FLUOROPHOSPHATE. By Y.P. Mascarenhas and S.H. Pulcinelli. Instituto de Física e Química de São Carlos, 13560 São Carlos, S.P., Brazil.

The crystal structure of α-KPF_6 was determined by Bode & Clausan (1951, Z. Anorg. Chem. 265, 229-293) from powder data as cubic, s.g. Pa3, NaCl type, (P in 000, K in 0.5, 0.5, 0.5 and F in x = 0.137, y = 0.137, z = -0.068). This redetermination was undertaken in view of suspicion of disorder suggested by electrical conductivity measurements carried out in this department by M.F. de Souza and J.H. Gallo (M.Sc. thesis, 1979). Lattice constants and intensities were measured with an Enraf-Nonius CAD-4 automatic diffractometer using a small crystal with aproximate dimensions of 0.2, 0.3, 0.5 mm, graphite monochromated Mo Kα radiation. Cell dimension is a=b=c=7.71(2) Å . 128 unique reflections were collected and after the application of the acceptence criterion $I \geq 1\sigma(I)$, where σ was based on counting statistics, only 39 reflections were retained in the data set all of them with systematic absences corresponding to an F cell. The possible space groups are then F23, F432, F$\bar{4}$32 and Fm3m. In each of them we have K and P in special position 000 and 0.5, 0.5, 0.5 and F statistically disordered in the general position. Lorentz and polarization factors were applied but no absorption correction (μ (Mo K α)=15.42) was made. Using the atomic parameters from Bode and Clausen we tried to refine the structure in each of the above space groups by full-matrix least-squares method by minimization of $\Sigma\omega\,(k|F_o| - |F_c|)^2$. The best refinement was achieved in space group F432 with a final R = 0.093. Final atomic parameters are: P at 0,0,0 B_{iso}=3.45, K at 0.5,0.5,0.5 B_{iso}=5.12, F at 0.109, 0.165, -0.043 B_{iso}=4.94, site occupation = 0.25.

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