

THE INFLUENCE OF THE LATTICE ON CATION DISTORTIONI. D. Brown¹ V. S. Urusov²¹McMaster University Brockhouse Institute for Materials Research 1280 Main St. W. HAMILTON ONTARIO L8S 2M1 CANADA ²Dept of Crystallography and Crystal Chemistry, Moscow State University, 119899 Moscow, Russia.

Distorting the environment of a cation is well known to increase the average bond length, in effect expanding the coordination sphere. When a cation appears in a coordination sphere that is constrained to be too large, such a distortion increases the effective size of the cation, thereby helping to relax the stretched bonds. Where the distortion arises from electronic effects and is intrinsic to the cation (e.g., lone pair and Jahn-Teller distortions), the size of this expansion depends not only on the size of the distortion but also on its mode, that is, on the distribution of the bond lengths. The expansion of the coordination sphere in these cases is responsible for an increase in the lattice energy. Wherever possible, therefore, the lattice energy is minimized by choosing a mode that keeps this expansion to a minimum. For example, the Jahn-Teller theorem applied to octahedral Cu^{2+} requires a distortion with $4/mmm$ symmetry. Two modes are consistent with this symmetry, one with four short and two long bonds, and one with two short and four long bonds. The former is universally observed since it leads to a smaller expansion of the coordination sphere, hence a smaller increase in the lattice energy. A similar explanation accounts for the tendency of highly distorted octahedral V^{5+} environments to contain only one long bond since the fewer the number of long bonds, the smaller the increase in the size of the coordination sphere.

Keywords: CATION DISTORTION, BOND VALENCE, LATTICE ENERGY

PREPARATION AND CHARACTERIZATION OF BARIUM-LEAD FLUOROPATITES $\text{Ba}_{(10-x)}\text{Pb}_x(\text{PO}_4)_6\text{F}_2$

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Fluorapatite, $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$, crystallising in the hexagonal $P6_3/m$ space group, accepts a variety of cationic substitutions, whose affect textural and structural properties, and have great incidence on applications. For a better understanding of substitution possibilities between bivalent metals, a series of samples containing both barium and lead were prepared and characterised with a variety of analytical techniques. Synthesis was done adding, drop wise and during 3 hours, solutions containing variable proportions of barium and lead acetates, to a boiling and constantly stirred solution containing diammonium hydrogen phosphate and ammonium fluoride. The powdered phases, separated by filtration, was investigated by chemical analysis, IR spectroscopy and structural refinement by the Rietveld methods, using powder X-ray diffraction patterns. Chemical analysis reveals continuous solid solution between barium and lead fluorapatites, with the formula $\text{Ba}_{(10-x)}\text{Pb}_x(\text{PO}_4)_6\text{F}_2$ with x from 0 to 10. The (Ba+Pb)/P atomic ratios are close to 1.67, indicating stoichiometric apatites, without vacancies. These results were confirmed by Rietveld refinements. The lattice dimensions and the IR frequencies of the solid solutions decrease linearly with the atom % of lead. Furthermore, IR spectra show the absence of foreign anions like CO and H_2PO_4^- . The site occupancy factors of metal atoms indicate a clear preference of barium for a site (2) of the cell, around the screw six fold axes and F⁻ ions. These results stigmatize the interdependence of anionic and cationic substitutions in apatites, since in a parallel job on hydroxyapatites we found substitutions limited to 2 Pb atoms.

Keywords: FLUORAPATITES CATIONIC SUBSTITUTIONS RIETVELD REFINEMENTS

NOVEL LAYERED BISMUTH OXYHALIDES: A GEOMETRICAL APPROACH TO PREDICTION AND SYNTHESISD.O. Charkin¹ O.A. Dytyatiev¹ V.A. Dolgikh² P. Lightfoot³¹Moscow State University Dept. of Materials Sciences, Moscow State University, GSP-3, Vorob'evy Gory MOSCOW 119899 RUSSIA ²Department of Chemistry, Moscow State University, Moscow, Russia ³School of Chemistry, St.Andrews University, St.Andrews, Scotland

Multinary compounds of trivalent bismuth with structures featuring fluorite-related layers form a vast family of inorganic and hybrid organic-inorganic materials. Their crystal chemistry is unusually versatile, representing a wide field for targeted synthesis of compounds with novel crystal structures and applied properties. Earlier, we classified their structure types on the basis of 2D prototypes of the layers forming the structure. Starting from this, we predicted and successfully realized a new structure type of bismuth oxyhalides representing a sequence of fluorite- and CsCl-derived layers, as well as its intergrowths with structures of Sillen phases. Two questions arose: if other representatives of known structure types can exist and whether new intergrowth structures can be found in this family. Now we report results of our extensive searches for new bismuth oxyhalides with structures involving fluorite- and CsCl-derived layers. Using our 3D prototype approach to structure modeling, we obtained over 80 new compounds comprising several novel intergrowth structure types involving Aurivillius phases. Crystal structures of selected representatives were determined. We apply a semi-quantitative approach for describing crystal chemical boundaries of known structure types which is a useful tool for predicting new materials with desired crystal structures. We discuss influence of chemical composition and synthesis conditions on the structure of resulting compounds. We also predict new intergrowth structures and areas of compositions where they can be realized. A support from Russian Foundation for Basic Researches and INTAS under Grants No. 01-03-38006 and YSC-00-32 is acknowledged.

Keywords: BISMUTH OXYHALIDES, LAYERED COMPOUNDS, STRUCTURE PREDICTION

THE CUBIC FLUORITE-TYPE SUPERSTRUCTURE OF $\text{Y}_7\text{ReO}_{13}$

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$\text{Y}_7\text{ReO}_{13}$ crystallizes in space group $Fm-3m$ with $a = 10.472(1)$ Å. This structure can be derived from a fluorite-type structure ($\text{Y}_{0.875}\text{Re}_{0.125}\text{O}_{2-\delta}$) by the ordered distribution of the 32 cations in a unit cell with doubled axes as compared to the parent fluorite structure onto different crystallographic sites: Y on (4a) and (24d), Re on (4b). Oxygens occupy two (32f)-sites (x,x,x) with distortions from $x = 0.125$ and 0.625 to $x = 0.1355(9)$ for O1 and $0.606(2)$ for O2. The site-occupation factor for O2 is in agreement with 0.625 ($\delta = 0.375$). Therefore, only slightly more than half of the oxygens in the $[\text{ReO}_8]$ -cubes are occupied, indicating disordered $[\text{ReO}_4]$ -tetrahedra. This structure is isotopic with $\text{Ag}_7\text{NO}_{11}$ [1], which has even more deficiencies on the O2-site.

[1] I. Naray-Szabo, G. Argay, P. Szabo. Acta Cryst. 19, 180-4 (1965).

Keywords: $\text{Y}_7\text{ReO}_{13}$, FLUORITE-TYPE SUPERSTRUCTURE, INORGANIC CRYSTAL STRUCTURE