*Materials of Conferences*

## PREDICTION OF ISOVALENT SUBSTITUSHIONS OF $PB^{2+}$ IN $PBZR_3O_4F_6$ STRUCTURE

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The structure type $PbZr_3O_4F_6$ ($a \approx 2a$ (fluorite), $Z = 8$, space group of symmetry $Fm\text{-}3m$) is derived from the structure type $KY_3F_{10}$, which belongs to the group $A_2B_6X_{20\text{-}22}$ of family fluorite-like phases $\{A_{8-x}B_6C_yX_{n+2(y-x)}\}_m$ [1]. The feature of this family is the ability of iso- and heterovalent substitutions in the cation and anion sublattices, which offer the way to find new structures that can serve as a basis for creating materials with desired physical and chemical properties. The change of composition of chemical compounds within the unchanged structural type is associated with changes of the unit cell parameters and as a result reducing or increasing the energy density of the crystal lattice, which leads to the variation of some physical and chemical properties [2]. Modeling of crystal structures can significantly reduce the amount of experimental research in order to find promising new materials.

This article is described the options isovalent substitutions $Cd^{2+}$, $Ca^{2+}$, $Sr^{2+}$ and $Ba^{2+}$ cations of $Pb^{2+}$ cations in the $PbZr_3O_4F_6$ structure. $Cd^{2+}$, $Ca^{2+}$, $Sr^{2+}$ and $Ba^{2+}$ cations are able to form structures belonging to the family of fluorite-like phases $\{A_{8-x}B_6C_yX_{n+2(y-x)}\}_m$. To estimate the possibility of the formation of new structures the bond valence method was used that is widely used in modern chemistry of inorganic ionic compounds [3]. According to this method, the sum of the bond valences of each ion in the structure is equal to the absolute value of the charge of this ion (oxidation state):

$$|Z| = \sum s$$

The simulation results of the basic crystal structure $PbZr_3O_4F_6$ testify to the correctness of this concept [4]. The relative deviations of the calculated structure parameters from experimental parameters did not exceed 2 %.

The coordinates of the atoms of the structure $PbZr_3O_4F_6$ were used as a starting model for calculations. When modeling structures proposed in [5] function $\Phi$ was minimized, taking into account not only the cation-anion interaction, but anion-anion repulsion too:

$$\Phi = \sum(\Delta Z_i)^2 + \sum[B/(d_{X\text{-}X})^{12}]/2,$$

where $\Delta Z_i$ – the difference between the tabulated and calculated ion charge, $d_{X\text{-}X}$ – the anion-anion distance, $B$ – empirical constant. Our previous studies have shown that the cation-cation interactions can be neglected, since their inclusion does not affect the final result.

Calculation of the bond valence was executed by the exponential dependence of $s = \exp((R_o - d)/b)$ [3], where $s$ – the cation-anion bond valence, $R_o$ – empirical parameter that characterizes this relationship, $d$ – the interatomic distance, $b$ – empirical constant equal to 0,037 nm. The correctness of the obtained model of the structure was evaluated by the global instability index *GII* [3]:

$$GII = [\sum(d^2/N)]^{1/2},$$

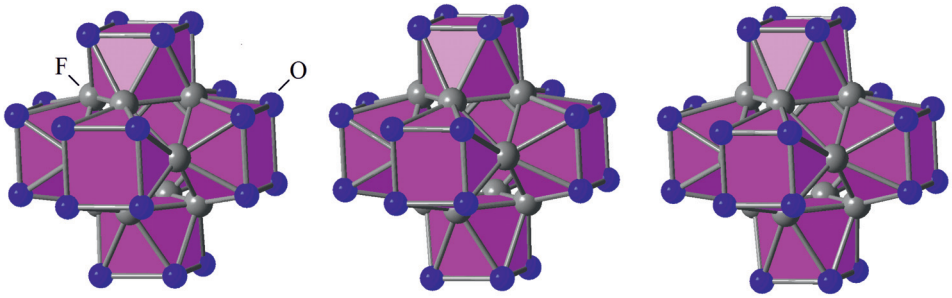
where $d$ is a difference between the tabulated and calculated charge for $N$ ions in the independent part of the unit cell. The values of the *GII* index less than 0,1 indicate the stability of the crystal structure.

The results of the simulation indicate the stability of structures $CaZr_3O_4F_6$ and $SrZr_3O_4F_6$ (Table).

The simulation results of the crystal structures $AZr_3O_4F_6$.

| Structure | *a*, nm | Coordinates of the atoms | | | Index *GII* | Absolute ion charge | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | *x*(Zr) | *x*(O) | *y*(F) | | $Zr^{4+}$ | $A^{2+}$ | $O^{2-}$ | $F^{1-}$ |
| $CdZr_3O_4F_6$ | 1,0792 | 0,2200 | 0,1226 | 0,1662 | 0,140 | 3,87 | 1,60 | 1,94 | 0,91 |
| $CaZr_3O_4F_6$ | 1,0715 | 0,2228 | 0,1232 | 0,1663 | 0,006 | 3,99 | 1,98 | 2,00 | 1,00 |
| $SrZr_3O_4F_6$ | 1,0896 | 0,2256 | 0,1143 | 0,1650 | 0,005 | 3,99 | 2,00 | 2,00 | 1,00 |
| $BaZr_3O_4F_6$ | 1,1232 | 0,2172 | 0,1104 | 0,1654 | 0,246 | 3,59 | 2,23 | 2,08 | 0,79 |

The theoretically calculated absolute values of the charges of the ions for these structures don't differ from the generally accepted values. The global index of instability *GII* has a small value of about 0.01, which indicates a possibility of their existence. The obtained interatomic distances are in the typical range for crystal structures containing these ions. The constructed of six square antiprisms $\{ZrO_4F_4\}$ structure-forming fragments – clusters $\{Zr_6O_{24}F_{12}\}$ in structures $CaZr_3O_4F_6$ and $SrZr_3O_4F_6$ don't differ from similar clusters $\{Zr_6O_{24}F_{12}\}$ in the basic structure $PbZr_3O_4F_6$ (Figure).




a) b) c)

Clusters $\{Zr_6O_{24}F_{12}\}$ in the structures $CaZr_3O_4F_6$ (a), $SrZr_3O_4F_6$ (b) and $PbZr_3O_4F_6$ (c)

The $CdZr_3O_4F_6$ and $BaZr_3O_4F_6$ structures are characterized by high values of the global instability index more than 0.1 for the first structure and more than 0.2 for the second structure, that indicate the inability to obtain these structures. The theoretical values of the charges of the ions forming the $CdZr_3O_4F_6$ and $BaZr_3O_4F_6$ structures differ substantially from the conventional values (Table).

Thus, the simulation of crystal structures $AZr_3O_4F_6$ ($A$ = Cd, Ca, Sr, Ba) belonging to the structural type $PbZr_3O_4F_6$ indicates the possible existence of crystal structures $CaZr_3O_4F_6$ and $SrZr_3O_4F_6$.

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