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Dedicated to the memory of Academician E.S. Fedorov (1853 – 1919)

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Polyfunctional materials based on β - $\text{Ca}_3(\text{PO}_4)_2$ structure type

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The structural features of β - $\text{Ca}_3(\text{PO}_4)_2$ (five crystallographic sites of calcium cations, the absence of central symmetry) allow various hetero- and isomorphic measurements in a wide range of compositions without noticeable changes in structures. Such materials provide the preparation of laser crystals, ferroelectric and antiferroelectric materials with high nonlinear optical activity, solid electrolytes, phosphors, thermoluminescent dosimeters. In some cases, these properties are combined in the same compound, for example, ferroelectric, luminescent and nonlinear optical properties, ionic conductivity of two divalent cations, which allows obtaining polyfunctional materials. Doping into the system of rare earth cations Ce^{3+} , Eu^{3+} , Dy^{3+} , Tb^{3+} , Tm^{3+} , Eu^{2+} , $\text{Eu}^{2+}/\text{Tb}^{3+}$, $\text{Tm}^{3+}/\text{Dy}^{3+}$, $\text{Eu}^{2+}/\text{Ce}^{3+}$, $\text{Tb}^{3+}/\text{Eu}^{3+}$, $\text{Eu}^{2+}/\text{Mn}^{2+}$ allows you to obtain materials with luminescence in different regions of the visible spectrum. In addition, the combination of the cations allows to obtain more efficient single-phase phosphors with ideal optical properties. For tuning the luminescence spectra in the β - $\text{Ca}_3(\text{PO}_4)_2$ matrix, additional cations are also introduced, such as Mg^{2+} , Zn^{2+} , Sr^{2+} , which isovalent replace calcium cations in the structure. In some cases, such substitution can radically change the properties to the opposite. So, we have shown, that the substitution of calcium cations in the small octahedral $M5$ site for in $\text{Ca}_9\text{R}(\text{PO}_4)_7$ with the formation of $\text{Ca}_8\text{MeR}(\text{PO}_4)_7$ ($\text{Me} = \text{Mg}, \text{Zn}$; $\text{R} = \text{REE}, \text{Y}$) is accompanied by properties changing.

The report substantiates the criteria for the contribution of various physicochemical factors to the formation of dipole moments (ferroelectricity) of the β - $\text{Ca}_3(\text{PO}_4)_2$ structural type. It is shown that the increase in nonlinear optical activity is due to the following factors: a) the presence of cations with the presence of cations with a lone pair of electrons (Pb^{2+} , Bi^{3+}); b) the placement of different cations in sites $M1$ and $M2$, which are connected by a pseudo-center of symmetry and / or a different distribution of two or more cations in sites $M1$ and $M2$; c) a large difference in the distances between $M1 - M3$ and $M2 - M3$ sites ($M3$ is in the pseudo-center of symmetry); d) splitting the $M4$ into two / three subsites $M4_1$, $M4_2$ and $M4_3$; e) the splitting of the $M3$ into $M3_1$ and $M3_2$. All these factors increase the nonlinear optical activity when a radius of introduced cations is more than 0.8 Å are. It is shown that the nonlinear optical properties of β - $\text{Ca}_3(\text{PO}_4)_2$ structure type compounds can be changed by an order by means of isovalent replacement of Ca^{2+} cations with Pb^{2+} or larger Ba^{2+} ions. A record value of nonlinear activity ($I_2\omega/I_2\omega(\text{SiO}_2) = 620$, $50 \pm 5 \mu\text{m}$) was obtained for $\text{Ca}_{5.6}\text{Pb}_{4.9}(\text{VO}_4)_7$. An increasing of Pb^{2+} in the $\text{Ca}_{10.5-x}\text{Pb}_x(\text{VO}_4)_7$ system leads to an increase in the oxygen-oxygen distances in the polyhedra and thereby increases the conduction windows and, as a result, the ionic conductivity. The lead cations in the structure increases the ionic conductivity by an order (800 K) for $\text{Ca}_{5.6}\text{Pb}_{4.9}(\text{VO}_4)_7$. This value is a record for compounds with the β - $\text{Ca}_3(\text{PO}_4)_2$ structure. It was found that the introduction of divalent and trivalent ions into the structure is accompanied by a decreasing in the ferroelectric-paraelectric phase transition temperature. Such changes in the temperature of the phase transition are associated with an increasing in the unit cell volume and, easier rotation of the tetrahedra and mobility of cations in the structure. The phase transition temperature of an antiferroelectric-paraelectric is always lower than the transition temperature of the ferroelectric-paraelectric. Replacing the Ca^{2+} by Pb^{2+} in $\text{Ca}_3(\text{VO}_4)_2$ results in a 30-fold increasing in the intensity of second-harmonic generation (SHG) and a significant ($\Delta T = 608 \text{ deg.}$) decreasing in the ferroelectric-paraelectric phase transition temperature. This fact is due to an increasing in the $M3 - \text{O}11$ and $M1 - \text{O}12$ distances in the structure and, as a result, with a lighter rotation of the VO_4 tetrahedron and splitting of the $M4$ site into three ($M4_1$, $M4_2$ and $M4_3$) and $M3$ into two ($M3_1$ and $M3_2$) subsites.

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