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# Pure, lithium- or magnesium-doped ferroelectric single crystals of $Ca_9Y(VO_4)_7$: cation arrangements and phase transitions

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The non-centrosymmetric vanadates $Ca_9R(VO_4)_7$ (*R* = rare earth elements, Bi, Y) [1] are isostructural to $\beta$-$Ca_3(PO_4)_2$ [2], and belong to the whitlockite mineral family [3]. These compounds are currently considered promising for white light emission LEDs, phosphors and light converters, for example [4]. Single crystals of $Ca_9Y(VO_4)_7$ (**1**), $Ca_9Y(VO_4)_7$:$Li^+$ (**2**) and $Ca_9Y(VO_4)_7$:$Mg^{2+}$ (**3**) were grown by the Czochralski method. Their chemical composition was analysed by ICP spectroscopy and their crystal structure was examined by single crystal X-ray analysis. The crystals are characterized by trigonal symmetry, space group *R*3*c*. Hexagonal unit-cell parameters are: $a$ = 10.8552(1) Å, $c$ = 38.0373(2) Å, $V$ = 3881.65(1) Å$^3$ for **1**; $a$ = 10.8570(1) Å, $c$ = 38.0161(3) Å, $V$ = 3880.77(4) Å$^3$ for **2**; $a$ = 10.8465(1) Å, $c$ = 38.0366(2) Å, $V$ = 3875.36(3) Å$^3$ for **3**. All crystals are characterized by $\beta$-$Ca_3(PO_4)_2$-type structure with statistical distribution of $Ca^{2+}$ and $Y^{3+}$ over *M*1, *M*2 and *M*5 sites in different ratios and with completely empty *M*4-cationsite. The impurity of $Mg^{2+}$ in structure **2** has been detected in octahedral *M*5 site. Ferroelectric phase transitions are evidenced by DSC and SHG. At about 1220 and 1300 K, they demonstrate phase transitions. Upon heating the symmetry of the crystal structure changes according to the scheme *R*3*c* → *R*-3*c* → *R*-3*m* and is restored during consequent cooling. The first of them is of ferroelectric and the second of non-ferroelectric nature. Even a small amount of impurities in $Ca_9Y(VO_4)_7$ structure is accompanied by a noticeable decrease in the temperature of the ferroelectric-paraelectric phase transition.

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