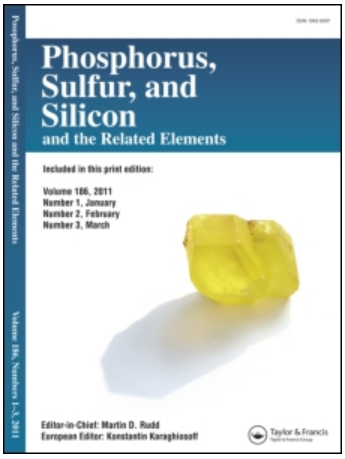

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STRUCTURAL CHANGES AND PHASE TRANSITIONS IN WHITLOCKITE-LIKE PHOSPHATES

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New compounds with a β-$Ca_3(PO_4)_2$ structure type were found in three systems: $Sr_{9+x}M_{1.5-x}(PO_4)_7$ (M = Mn, Fe, Co, Ni, Cu, and Cd; space group $R\bar{3}m$; Z = 3), $Sr_9R(PO_4)_7$ (R = Al, Sc, Cr, Fe, Ga, In, and Gd–Lu; space group $P2/c$, Z = 4), and $Sr_{9+2x}M_{1+x}A_{1-6x}(PO_4)_7$ (M = Mn, Ni, Cd; space group R3c and Z = 6 for A = Na, K; space group $P2/m$ and Z = 4 for A = Li). Crystal structures of these compounds were determined by time-of-flight neutron, synchrotron X-ray, and laboratory X-ray powder diffraction. Reversible polar-to-centrosymmetric phase transitions ($R3c \rightleftarrows R\bar{3}m$) were observed at high temperatures in $Ca_{3-x}Sr_x(PO_4)_2$ ($0 \le x \le 12/7$), $Ca_{10.5-1.5x}Fe_x(PO_4)_7$ ($0 \le x \le 1$), and $Ca_9R(PO_4)_7$. Solid solutions $Ca_{3-x}Sr_x(PO_4)_2$ ($13/7 \le x \le 16/7$) are centosymmetric with space group $R\bar{3}m$ at room temperature. These phase transitions were studied by high-temperature X-ray diffraction, second-harmonic generation, DSC, electric-conductivity and dielectric measurements.

Keywords: Crystal structure; phase transition; tricalcium phosphate; whitlockite

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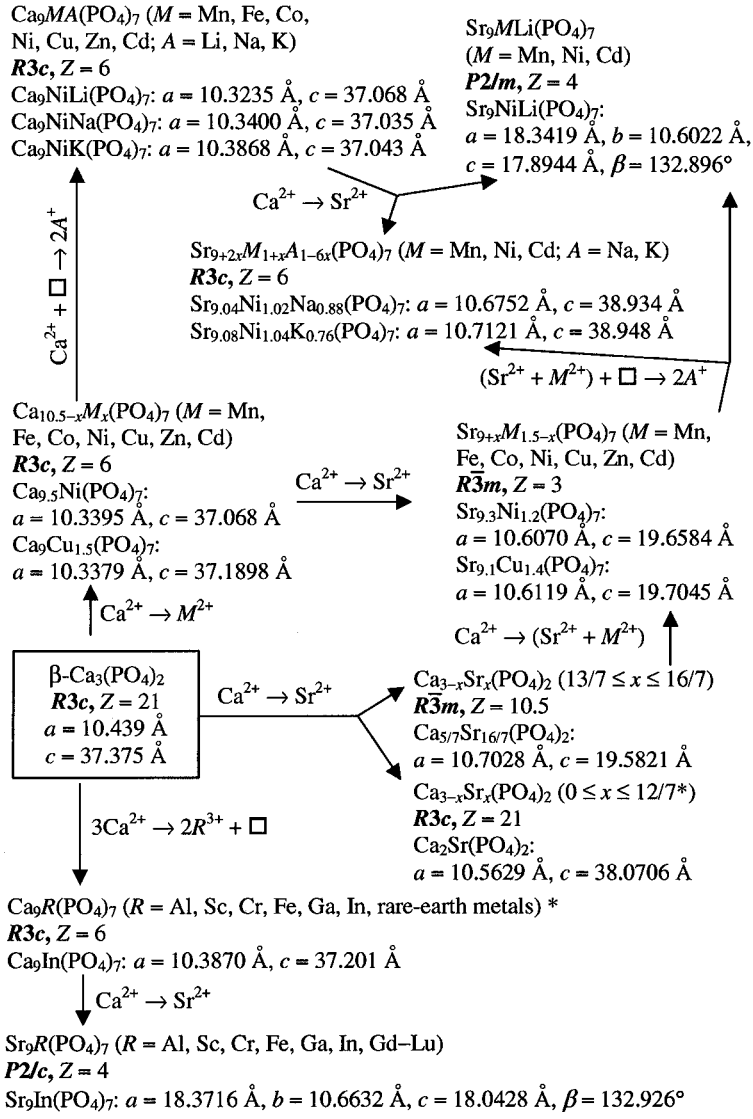

*High-temperature phase transitions ($R3c \rightleftarrows R\bar{3}m$) were found for these compositions.

FIGURE 1 Structural changes in the β-$Ca_3(PO_4)_2$-related compounds on the substitution of metals. □: vacancy.

$Ca_3(PO_4)_2$ and structural variations on it have been extensively studied for their applications as biomaterials,[1] luminescent materials,[2] and catalysts.[3] Detailed knowledge of structural transformations accompanying cationic substitutions is essential for these types of

applications. This paper deals with new structural variations of the phosphates related to β-$Ca_3(PO_4)_2$ and phase transitions in these compounds.

All the samples were synthesized by solid-state methods. We refined their structure parameters with time-of-flight neutron powder diffraction data measured on Vega at KENS, synchrotron X-ray powder diffraction (XRD) data taken on BL15XU at SPring-8, and laboratory XRD (SIEMENS-D500, Cu $K\alpha_1$) data by the Rietveld method using RIETAN-2000[4] and RIETAN-2001T. Phase transitions were investigated by high-temperature XRD (SIEMENS-D500, Cu $K\alpha$), second harmonic generation (SHG; Q-switch pulsed Nd:YAG laser operated at $\lambda_\omega = 1064$ nm; reference: polycrystalline SiO_2), DSC (Setaram DSC-111), electric-conductivity (frequency response analyzer Solatron 1260), and dielectric measurements.

Figure 1 presents structural changes of the β-$Ca_3(PO_4)_2$-related compounds on substitution of metals. In most cases, the substitution of Sr^{2+} for Ca^{2+} led to changes in the crystal symmetry of β-$Ca_3(PO_4)_2$ (space group $R3c$). Our Rietveld refinements revealed that the structural variations of β-$Ca_3(PO_4)_2$ exhibit different orientations of $P1O_4$ tetrahedra and different cation distribution in $M3$, $M4$, and $M6$ sites.[5]

The SHG and XRD measurements showed that solid solutions $Ca_{3-x}Sr_x(PO_4)_2$ ($0 \le x \le 12/7$) crystallize in space group $R3c$ with $a \approx 11$ Å and $c \approx 38$ Å, and that solid solutions $Ca_{3-x}Sr_x(PO_4)_2$ ($13/7 \le x \le 16/7$) belong to space group $R\bar{3}m$ with $a \approx 11$ Å and $c \approx 19$ Å. A reversible polar-to-centrosymmetric phase transition ($\beta \rightleftarrows \beta'$) was found at high temperatures for $Ca_{3-x}Sr_x(PO_4)_2$ ($0 \le x \le 12/7$) in the SHG (Figure 2a), DSC (Figure 3a), and electric-conductivity measurements (Figure 2b). The temperature of phase transitions $\beta \rightleftarrows \beta'$ in $Ca_{3-x}Sr_x(PO_4)_2$ decreased with increasing Sr content. A new modification, β'-$Ca_3(PO_4)_2$, was detected above 900 °C in the conductivity measurements (Figure 2b).

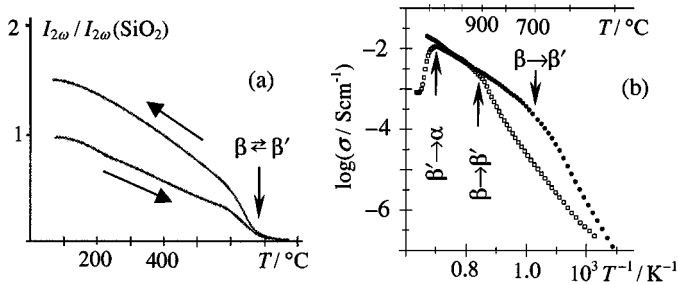

FIGURE 2 Temperature dependence of (a) the SHG signal for $Ca_2Sr(PO_4)_2$ and (b) the electric conductivity for $Ca_2Sr(PO_4)_2$ (black circles) and $Ca_3(PO_4)_2$ (squares).

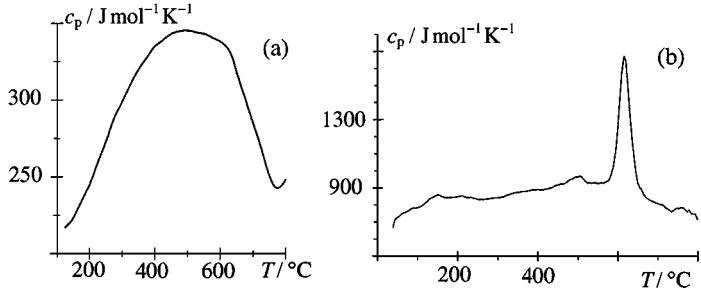

FIGURE 3 Dependence of the specific heat capacity on temperature for (a) $Ca_2Sr(PO_4)_2$ and (b) $Ca_9Fe(PO_4)_7$.

This phase transition was hardly observed in the DSC measurements; it gave a very broad exothermic peak (Figure 3a). In contrast with $Ca_{3-x}Sr_x(PO_4)_2$, the $\beta \rightleftarrows \beta'$ phase transitions in $Ca_9R(PO_4)_7$ (see Figure 1) and $Ca_{10.5-1.5x}Fe_x(PO_4)_7$ $(0 \leq x \leq 1)$ are characterized by sharp peaks in specific heat capacity versus temperature curves (Figure 3b). The dielectric measurements showed the $\beta \rightleftarrows \beta'$ phase transitions to have ferroelectric nature.

REFERENCES

[1] N. Rangavittal, A. R. Landa-Canovas, J. M. Gonzalez-Calbet, and M. Vallet-Regi, *J. Biomed. Mater. Res.*, **51,** 660 (2000).
[2] H. Donker, W. M. A. Smit, and G. Blasse, *J. Electrochem. Soc.*, **136,** 3130 (1989).
[3] A. Legrouri, J. Lenzi, and M. Lenzi, *React. Kinet. Catal. Lett.*, **65,** 227 (1998).
[4] F. Izumi and T. Ikeda, *Mater. Sci. Forum*, **321–324,** 198 (2000).
[5] B. I. Lazoryak, *Rus. Chem. Rev.*, **65,** 287 (1996).