Abstract

Influence of transition metal content on structure and thermal expansion of $Ca_{10.5-x}TM_x(VO_4)_7$ (TM=Co, Ni, Cu) orthovanadates

This thesis presents an investigation of the structure and thermal expansion of multicomponent oxides crystallizing in the whitlockite-β-$Ca_3(PO_4)_2$ structure type. Nature of these compounds offers an opportunity for wide modification of chemical compositions, allowing for the tuning of their properties through suitable substitution. Specifically, the present study focuses on three series of novel closely related compounds,
$Ca_{10.5-x}TM_x(VO_4)_7$ ($0 \leq x \leq x_{lim}$), where divalent transition metals (TM = Co, Ni, Cu) are substituted into $Ca_3(VO_4)_2$. These compounds were synthesized using solid state reaction method.

Upon substituting the transition metals, a clear decrease in lattice parameters a and c as well as the unit cell volume is found, consistent with previous studies on the effect of Co, Ni, Zn, and Cu ions on the crystal structure of β-$Ca_3(PO_4)_2$. The solubility limit (x_{lim}) was determined from the $V(x)$ dependence. It is found that the M5 site is the preferred site for TMs ions, as indicated by the refined occupancy.

The structures of these compounds remain stable over a wide temperature range (4-1150 K), showing no signs of either phase transition or decomposition.

Occurrence of the axial ratio fluctuations with temperature shows that the lattice expands anisotropically. The inflection temperature (the temperature at which the slope of the axial ratio changes) at high temperature tends to decrease as the content of transition metal increases. As the content of the given transition metals increases in each series of compounds, there is a corresponding decrease in volumetric thermal expansion at room temperature, while an increase is observed at the highest studied temperature. For all the investigated $Ca_{10.5-x}TM_x(VO_4)_7$ materials, significant changes in volumetric thermal expansion occur in the vicinity of the above mentioned inflection temperature, i.e. they correlate with the change of the anisotropy character. Thermal expansion anisotropy in the studied TM substituted crystals is markedly smaller as compared to rare earth substitutions.

Optoelectronics applications can benefit from the favorable characteristic of low thermal expansion anisotropy in studied crystals. The current findings indicate a potential for reducing the expansion in crystals that have been doubly substituted with both rare earth and transition metal elements, compared to crystals containing only rare earth elements.

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