

Ferroelectrics Vanadates as New Multi-Functional Materials

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Abstract. New $\text{Ca}_{10.5-x}\text{Pb}_x(\text{VO}_4)_7$, $0 \leq x \leq 5$ high-temperature ferroelectric based on $\text{Ca}_3(\text{VO}_4)_2$ is obtained in powders and ceramics form by solid-state method. Nonlinear optical properties of the whitlockite-type compounds increased with the substitution of Ca^{2+} by Pb^{2+} cations by an order of magnitude. It is found that ferroelectric Curie point goes linearly from 1367 K at $x = 0$ down to 751 K at $x = 5$ at rise of lead content. A maximum value of optical nonlinearity and the lowest temperature of ferroelectric-paraelectric phase transition was found for $\text{Ca}_{5.5}\text{Pb}_5(\text{VO}_4)_7$. Combination of low temperature transition with record non-linear optical activity makes its applicable in ion-exchange technology and useful for optical devices.

Introduction

Ability of whitlockite-type phosphates and vanadates to isovalent and heterovalent substitutions [1] makes them attractive for crystal community. Many technical desires can be achieved by means of properties modifying in a large family of ferroelectric phosphates and vanadates with the whitlockite-type structure [2].

The whitlockite-type crystal structure (sp. gr. $R3c$) has five cation sites $M1$, $M2$, $M3$, $M4$ and $M5$ [1] different in size and oxygen coordination and consists of isolated VO_4 tetrahedra connected with the MO_n polyhedra. The positions $M1$ – $M5$ are fully occupied Ca^{2+} cations whereas $M4$ and $M6$ sites are half-occupied and vacant, respectively. The specificity of the structure makes them applicable to substitutions of calcium cations by different cations with radii and charge variations without significant changes of the framework.

The first-ever in this family was calcium orthovanadate, $\text{Ca}_3(\text{VO}_4)_2$, classified as high-temperature ferroelectric [3]. Ferroelectric phase transition in $\text{Ca}_3(\text{VO}_4)_2$ single crystal was detected as a characteristic maximum of dielectric permittivity in the Curie point $T_c = 1383$ K. $\text{Ca}_3(\text{VO}_4)_2$ single crystals were grown by the Czochralski technique [4].

In this paper, SHG efficiency and dielectric properties of $\text{Ca}_{10.5-x}\text{Pb}_x(\text{VO}_4)_7$, $0 \leq x \leq 5$ solid solutions along with structural details of crystal structure are investigated.

Experimental Procedures

$\text{Ca}_{10.5-x}\text{Pb}_x(\text{VO}_4)_7$ ($0 \leq x \leq 5$) solid solutions with β - $\text{Ca}_3(\text{PO}_4)_2$ -type structure were prepared in air by a solid-state method from stoichiometric amounts of CaCO_3 (99.99%), PbO (99.8%), V_2O_5 (99.8%) at 1173 K ($x \leq 3$) and at 1073 K ($4 \leq x \leq 5$) for 100 h with intermediate grindings every 20 h followed by slow cooling in the furnace from high temperature to room temperature (T_R).

Powder X-ray diffraction (PXRD) patterns were collected on a Thermo ARL X'TRA powder diffractometer (CuK α radiation, $\lambda = 1.5418 \text{ \AA}$, Bragg–Brentano geometry, Peltier-cooled CCD detector) at T_R over the 10° - 70° 2θ range with a step of 0.02° .

Second-harmonic generation response of powder samples was measured in a reflection mode [5]. A Q-switch pulsed Nd:YAG Minilite-I laser operating at $\lambda_{\omega} = 1064 \text{ nm}$ was used as the radiation source (repetition frequency 15 Hz, repetition rate of 4 impulses/s, pulse duration 3 ns).

Dielectric constant, ϵ and ionic conductivity, σ were measured between 293-1273 K according to two-probe method at frequencies from 0.3 Hz to 1 MHz using a Novocontrol Beta-N Impedance Analyser with Probostar A cell.

Results and Discussion

$\text{Ca}_{10.5-x}\text{Pb}_x(\text{VO}_4)_7$ ($0 \leq x \leq 5$) solid solutions was obtained by substitution of Pb^{2+} cations for Ca^{2+} in $\text{Ca}_3(\text{VO}_4)_2$. The vanadates crystallize in $R3c$ space group of $\beta\text{-Ca}_3(\text{PO}_4)_2$ -type structure. The highest second harmonic signal ($I_{2\omega}/I_{2\omega}(\text{SiO}_2) = 600$) and the lowest temperature of ferroelectric-paraelectric phase transition ($T_c = 751 \text{ K}$) among the whitlockite-type related compounds are found for $\text{Ca}_{5.5}\text{Pb}_5(\text{VO}_4)_7$. The presence of reversible ferroelectric phase transitions in $\text{Ca}_{10.5-x}\text{Pb}_x(\text{VO}_4)_7$, $0 < x \leq 5$ is confirmed by data obtained from temperature dependence of SHG signal and dielectric measurements. The dependence of ferroelectric Curie point, T_c , on lead content, accordance to second harmonic generation response and dielectric temperature investigations, goes linearly down from $T_c = 1367 \text{ K}$ ($x = 0$) to 751 K ($x = 5$) where second harmonic generation response vanishes. The crystal structures are refined with the Rietveld method based on powder X-ray diffraction data. The properties are correlated with crystal structures of $\text{Ca}_{10.5-x}\text{Pb}_x(\text{VO}_4)_7$ ($0.5 \leq x \leq 2$). Rise of the optical nonlinearity in a wide range of substitution at $0 \leq x \leq 5$ indicates the preservation of stereochemical activity of Pb^{2+} lone electron pair. Thus, $\text{Ca}_{5.5}\text{Pb}_5(\text{VO}_4)_7$ can be considered as a multi-functional material with the combination of high nonlinear optical activity and ferroelectric properties.

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