TECHNICAL ARTICLE

Crystal structure refinement of new vanadates $Ca_{8-x}Pb_xCdBi(VO_4)_7$

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New $Ca_{8-x}Pb_xCdBi(VO_4)_7$ with the whitlockite-type structure were prepared by a standard solid-state method in air. Le Bail decomposition was used to determine unit-cell parameters. Structural refining was carried out by Rietveld's method. It is found that Bi^{3+} cations located partially in $M1$ and $M2$ sites along with calcium, while $M3$ site is settled in half by Pb^{2+}-ions. Second-harmonic generation demonstrate highest non-linear optical activity and along with dielectric investigations indicate polar space group $R3c$. © 2017 International Centre for Diffraction Data. [doi:10.1017/S0885715617000264]

Key words: crystal structure, whitlockite, non-linear optical activity, phase transition, Rietveld refinement

I. INTRODUCTION

Crystal chemistry tuning of dielectric and optical properties in whitlockite-like phosphate and vanadate systems makes them attractive for scientists (Liang *et al.*, 2010; Wu *et al.*, 2011; Zhang *et al.*, 2011) because of isovalent and heterovalent substitutions (Lazoryak, 1996). Cations location in the host lattice has a direct impact on many properties of whitlockite-like compounds. The whitlockite-like vanadates crystallize in structure with five cation sites $M1$, $M2$, $M3$, $M4$, and $M5$ (Yashima *et al.*, 2003) different in size and oxygen coordination. Varying of an occupation factor of the $M4$ site from zero to unity allows heterovalent substitutions. The $M5$ site has octahedral coordination and can be occupied by a large number of elements, such as Ca^{2+}, Cd^{2+}, transition metals in the oxidation states of 2+ and 3+, and small-radius rare earths ions.

An advanced material with ferroelectric, ionic conductivity, and non-linear-optical properties being $Ca_9Bi(VO_4)_7$ (Evans *et al.*, 2001; Lazoryak *et al.*, 2003). Highly polarizable asymmetric metal–oxygen bonds are formed by cations with a lone pair of electron (Bi^{3+}, Pb^{2+}, Tl^+, Te^{4+}). As a result increasing the non-linear optical activity of compounds usually occurs. Rise of bivalent metal concentration in $Ca_{9-x}M_xBi(VO_4)_7$ ($M^{2+} = Cd^{2+}$, Zn^{2+}) solid solutions leads to non-linear optical activities enhancement (Vorontsova *et al.*, 2004). Additional space for high-polarizable outer Bi^{3+} electrons is released because of occupancy $M5$ site by Cd^{2+} cations with small radius $[r_{VI}(Cd^{2+}) = 0.95$ Å] (Shannon, 1976). Thereby mean range $\langle M5–O \rangle$ in $Ca_9Bi(VO_4)_7$ decreases to $d_{\langle M5–O \rangle} = 2.298$ Å, while mean distances $\langle M5–O \rangle$ in $Ca_8CdBi(VO_4)_7$ are $d_{\langle M5–O \rangle} = 2.23$ Å. Additionally metal-oxygen distances increase in polyhedra $M1$, $M2$, and $M3$. The $M4$ site is vacant in compounds of such type (Benarafa *et al.*, 2000; Evans *et al.*,

2001; Vorontsova *et al.*, 2004). Widening of spare space in the whitlockite structure is caused in greater degree by introduction of larger cations Pb^{2+} $[r_{VIII}(Pb^{2+}) = 1.29$ Å (Shannon, 1976)] as compared with Bi^{3+}. It provides a retention rotating mobility of VO_4^{3-} tetrahedra at lower temperatures (Deyneko *et al.*, 2013a, 2013b) and, as a result, decreases the Curie points.

In this paper, structural details and an effect of crystal structure on the second-harmonic generation (SHG) efficiency and dielectric properties of $Ca_{8-x}Pb_xCdBi(VO_4)_7$ solid solutions are investigated.

II. EXPERIMENTAL

A. Synthesis of powders

Powders and ceramics of whitlockite-like structure solid solutions $Ca_{8-x}Pb_xCdBi(VO_4)_7$ at $0 \leq x \leq 2$ were prepared by solid-state method from stoichiometric mixtures of $CaCO_3$ (99.99%), PbO (99.8%), V_2O_5 (99.8%), CdO (99.8%), and Bi_2O_3 (99.8%). The raw materials were homogenized and reacted in Al_2O_3 crucibles in air at 1193 K during 150 h, and then cooled to room temperature, reground every 20 h.

B. Powder diffraction data collection and properties investigations

X-ray diffraction (XRD) patterns of powdered samples were collected at room temperature with Termo ARL powder diffractometer. The main details of the data collection are given in Table I. Lattice parameters were determined by the Le Bail decomposition (Le Bail *et al.*, 1988). To refine the structure Rietveld's method was applied with using the JANA2006 software (Dusek *et al.*, 2001; Petrícek *et al.*, 2014).

Optical SHG investigations were performed on graduated powders within electric furnace in one channel of optical installation, and 3-μm α-SiO_2 powder used as a standard in

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Formula $Ca_{6.5}Pb_{1.5}CdBi(VO_4)_7$
Space group: $R3c$
$Z = 6$
Lattice parameters
$a = b = 10.9052(3)$ Å
$c = 38.2764(1)$ Å
$\alpha = \beta = 90°$, $\gamma = 120°$
$V = 3942.11(2)$ Å^3
Experimental data
Temperature, 298 K; angular range, $10.000° \leq 2\theta \leq 87.112°$; step scan increment ($2\theta$), 0.01°
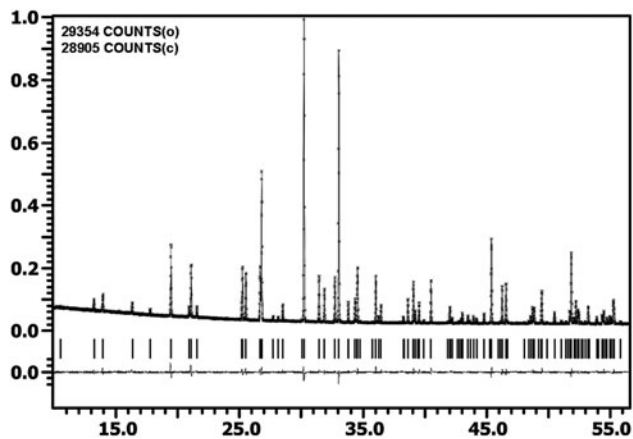Conventional Rietveld R-factors
$R_{wp} = 4.31\%$
$R_p = 3.2\%$
$R_{exp} = 3.37\%$

Figure 1. Observed, calculated and difference PXRD patterns for $Ca_{6.5}Pb_{1.5}CdBi(VO_4)_7$. Tick marks denote the peak positions of possible Bragg reflections.

the other channel. The both channels were identical and operated in the reflection geometry, as described in (Kurtz and Perry, 1968). In each channel, the SHG signal was excited by 1.064 μm radiation of Q-switched pulsed Nd:YAG laser (Minilite-*I*, $f = 15$ Hz). Generated in the samples green light of SH at $\lambda = 0.532$ μm was registered. Measured signal from the sample under investigation was calibrated in relation to quartz standard signal from the second channel, so value $Q = I_{2\omega}/I_{2\omega}(SiO_2)$ always presented quantitatively SHG activity of the powder in between 293 and 1100 K.

The dielectric parameters were measured between 293 and 1073 K by a two-probe method in frequency range from 0.3 Hz to 1 MHz using Novocontrol Beta-N Impedance analyzer equipped with Probostar A cell. Full reproducibility of $\sigma(T)$ curves in heating–cooling cycles indicated retention of quasi-equilibrium conditions in samples in all experiments.

III. RESULTS AND DISCUSSION

The XRD data for the systems $Ca_{8-x}Pb_xCdBi(VO_4)_7$ $(0 \leq x \leq 2)$ indicated single-phase whitlockite-like structures. Figure 1 displays a portion of the observed, calculated and difference XRD powder (PXRD) pattern. PXRD pattern is similar to those of other whitlockite-like compounds. PXRD pattern did not contain any impurity reflections. Atomic coordinates and distances were refined using the pseudo-Voigt profile function by the JANA2006 program. Unit-cell parameters and some numerical characteristics illustrating the quality of the structure refinements are presented in Table I.

We used fractional coordinates of $Ca_{8.5}PbCd(PO_4)_7$ in our initial structural model (space group $R3c$) (Deyneko *et al.*, 2013a, 2013b). At the first stage of structure refinement Cd^{2+} cation located in the $M5$ site [$6a$: 0 0 0, $g(Cd^{2+}) = 1$]. Successful refinement was produced through arranging Ca^{2+} and Pb^{2+} in $M3$, while Ca^{2+} and Bi^{3+} kept their locations in $M1$–$M2$ sites similar to other whitlockites (Lazoryak *et al.*, 2003). In connection with substitution scheme $(3Ca^{2+}) \rightarrow (2Ln^{3+} + \square)$ vacancies ($\square$) are generated and locate in $M4$ site. The fractional atomic coordinates, isotropic atomic displacement parameters, cation occupancies and main relevant interatomic distances for $Ca_{6.5}Pb_{1.5}CdBi(VO_4)_7$ are listed in Tables II and III.

This ionic distribution leads to the formation of enough space for lone-pair electrons to produce non-linear optical properties. The refinement of the $Ca_{6.5}Pb_{1.5}CdBi(VO_4)_7$

TABLE II. Structural parameters for $Ca_{6.5}Pb_{1.5}CdBi(VO_4)_7$.

Atom	site	x	y	z	U_{iso}	Occupancy
$M1$	18	0.7286	0.8630	0.4320	0.0057	0.805 Ca^{2+}/0.195 Bi^{3+}
$M2$	18	0.6117	0.8185	0.2346	0.0046	0.861 Ca^{2+}/0.139 Bi^{3+}
$M3$	18	0.1239	0.2721	0.3266	0.0168	0.5 Ca^{2+}/0.5 Pb^{2+}
$Cd5$	6	0	0	0	0.006	1
V1	6	0	0	0.2668	0.0204	1
V2	18	0.6835	0.8579	0.1349	0.0173	1
V3	18	0.6571	0.8497	0.0342	0.0106	1
O1	6	0	0	0.3114	0.021	1
O2	18	0.1468	0.1560	0.2558	0.021	1
O3	18	0.7266	0.9166	0.1774	0.0215	1
O4	18	0.7778	0.7802	0.1229	0.0215	1
O5	18	0.7177	1.0101	0.1133	0.0215	1
O6	18	0.5121	0.7416	0.1259	0.0215	1
O7	18	0.6001	0.9623	0.0440	0.0054	1
O8	18	0.5697	0.6838	0.0547	0.0054	1
O9	18	0.8393	0.9404	0.0456	0.0054	1
O10	18	0.6311	0.8244	−0.0110	0.0054	1

TABLE III. The main interatomic distances for $Ca_{6.5}Pb_{1.5}CdBi(VO_4)_7$.

$M1$	O2	2.534(1)
	O4	2.432(2)
	O5	2.490(2)
	O6	2.636(2)
	O6′	2.340(2)
	O7	2.480(2)
	O8	2.225(2)
	O10	2.368(1)
	$\langle M1\text{–O}\rangle$	2.438
$M2$	O2	2.418(1)
	O3	2.486(1)
	O4	2.432(2)
	O5	2.378(2)
	O7	2.800(2)
	O8	2.898(2)
	O9	2.582(2)
	O9′	2.309(1)
	$\langle M2\text{–O}\rangle$	2.538
$M3$	O1	2.639(5)
	O3	2.730(2)
	O4	2.565(2)
	O5	2.440(2)
	O7	2.421(2)
	O8	2.708(1)
	O10	2.747(2)
	O10′	2.666(1)
	$\langle M3\text{–O}\rangle$	2.615
$Cd5$	O6	$3 \times 2.304(2)$
	O9	$3 \times 2.323(2)$
	$\langle Cd5\text{–O}\rangle$	2.314
V1	O1	1.70(2)
	O2	$3 \times 1.707(2)$
	$\langle V1\text{–O}\rangle$	1.705
V2	O3	1.725(1)
	O4	1.690(2)
	O5	1.720(2)
	O6	1.688(1)
	$\langle V2\text{–O}\rangle$	1.706
V3	O7	1.672(2)
	O8	1.752(1)
	O9	1.775(1)
	O10	1.755(1)
	$\langle V3\text{–O}\rangle$	1.739
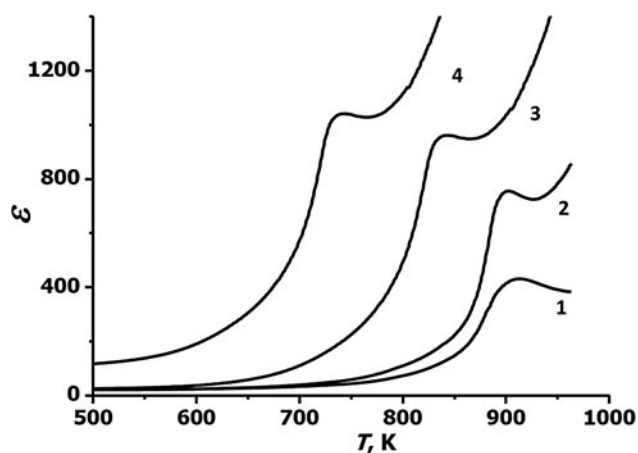
Figure 2. Temperature dependencies dielectric constant ε for $Ca_{8-x}Pb_xCdBi$ $(VO_4)_7$ [$x = 0.5$ (1), 1 kHz; 1 (2) 100 Hz, 1.5 (3) 1 kHz; 2 (4) 100 Hz].

structure leads to reasonable values of the R-factors, the interatomic distances, and the atomic displacement parameters U_{iso} of all atoms (Table II).

SHG analysis indicated higher non-linear optical activity of Pb^{2+}-containing compositions in comparison with $Ca_9Bi(VO_4)_7$ (Evans et al., 2001; Lazoryak et al., 2003). The highest SHG signal belongs to $Ca_{6.5}Pb_{1.5}CdBi(VO_4)_7$. Transition from paraelectric phase to centrosymmetric group attributed to structural transformation $R3c \leftrightarrow R\overline{3}\,c$. Ferroelectric phase transitions are confirmed by SHG and dielectric measurements. Curie temperature for $Ca_{8-x}Pb_xCdBi(VO_4)_7$ is between 730 and 900 K (Figure 2).

SUPPLEMENTARY MATERIAL

The supplementary material for this article can be found at https://doi.org/10.1017/S0885715617000264

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