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Article

$Cd_{1-x}Bi_x(Cd_{1+x}In_{1-x})VO_6$ ($0 \leq x \leq 0.14$): A New Polar Oxide with Second-Harmonic Generation

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The structure of the new polar oxide, Cd_2InVO_6, was determined by powder X-ray diffraction. Cd_2InVO_6 crystallizes in space group $P3_1$ with the unit cell parameters: $a = 12.218\,96(4)$, $c = 9.256\,75(4)$ Å. The Cd^{2+} and In^{3+} ions are statistically disordered in nine independent positions (M1−M9) with a certain level of site preference. M1−M3 form highly asymmetric oxygen-coordination polyhedra, which are similar to those formed by alkali or alkali-earth cations. M4−M9 are in distorted octahedral cavities. It is shown that M1−M3 are likely occupied mostly by Cd^{2+} while M4−M9 are extensively mixed by Cd^{2+} and In^{3+}. The structure is best described as a framework of interconnected M4−M9 distorted octahedra with the M1−M3 polyhedra off-framework and the three independent VO_4 tetrahedra filling the channels of the framework structure by corner-sharing with the MO_6 octahedra. The polar framework is composed of $M4O_6 \sim M9O_6$ octahedra in a five-connected net with the topology nomination (3^3, 6^3, 9^4). The Bi^{3+}-substituted compounds were also investigated with the rationale that the lone pair electrons of Bi^{3+} might enhance ferroelectricity. Single phase $Cd_{1-x}Bi_x(Cd_{1+x}In_{1-x})VO_6$ forms limited solid solutions ($0.02 \leq x \leq 0.14$). Ferroelectricity was observed for neither the parent nor the Bi^{3+}-substituted compounds, which suggest that the dipole moments are not switchable or too insignificant in magnitude. The powder second-harmonic generation measurements with 1064 nm radiation established that $Cd_{1-x}Bi_x(Cd_{1+x}In_{1-x})VO_6$ are type-1 phase-matchable materials for $x = 0$, 0.14 with 70 and 90 times the efficiency of α-SiO_2, respectively.

Introduction

Materials with polar structures are of great interest because polarity, the presence of a permanent electric dipole moment, may produce two important physical properties: pyroelectricity and ferroelectricity.[1−3] Pyroelectricity is a change in the magnitude of polarization on the crystal surface with change of external temperature, whereas in ferroelectric materials the direction of the dipole moments are susceptible to switching with application of an external electric field. The development of pyroelectricity in a material requires only a permanent dipole moment while for ferroelectricity the dipole moment must be switchable.

Crystallographically, the 230 space groups can be classified into 32 point groups, of which 10 are polar, including 1, 2, 3, 4, 6, *m*, *mm*2, 3*m*, 4*mm*, and 6*mm*.[4] Specifically, these 10 point groups define 69 space groups and the necessary conditions for a material to exhibit pyroelectricity or ferroelectricity is to crystallize in one of these 69 polar space groups.

The use of asymmetric structural building-blocks, such as distorted metal−oxygen polyhedra to achieve polar structures is a natural strategy. For example d^0 transition metal cations (e.g., Ti^{4+}, Nb^{5+}, W^{6+}), which are susceptible to second-order Jahn−Teller effects,[5] and lone-pair cations (e.g., Sb^{3+}, Se^{4+}, Pb^{2+}, Bi^{3+}) always prefer to be in asymmetric coordination environments. Yet there is no clear stipulation to predict a macroscopically polar structure constructed from locally asymmetric polyhedra. Only a few such cases have been carefully studied: Poeppelmeier and co-workers[6−10] synthesized and examined the crystallographically ordered transition-metal

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(1) Lang, S. B. *Phys. Today* **2005**, *58*, 31.
(2) Auciello, O.; Scott, J. F.; Ramesh, R. *Phys. Today* **1998**, *51*, 22.
(3) Halasyamani, P. S.; Poeppelmeier, K. R. *Chem. Mater.* **1998**, *10*, 2753.
(4) Hahn, T. *International Tables for Crystallography, Vol. A, Space Group Symmetry*; Kluwer Academic: Dordrecht, Holland, 2006; Vol. *A.*
(5) Albright, T. A.; Burdett, J.; Whangbo, M. H. *Orbital Interactions in Chemistry*; John Wiley and Sons: New York, 1984; Chapter 7.
(6) Maggard, P. A.; Stern, C. L.; Poeppelmeier, K. R. *J. Am. Chem. Soc.* **2001**, *123*, 7742.
(7) Well, M. E.; Norquist, A.; Arnold, F. P.; Stern, C. L.; Poeppelmeier, K. R. *Inorg. Chem.* **2002**, *41*, 5119.
(8) Maggard, P .A.; Nault, T. S.; Poeppelmeier, K. R. *J. Solid State Chem.* **2003**, *175*, 27.
(9) Izumi, H. K.; Kirsch, J. E.; Stern, C. L.; Poeppelmeier, K. R. *Inorg. Chem.* **2005**, *44*, 884.
(10) Marvel, M. R.; Lesage, J.; Baek, J.; Halasyamani, P. S.; Stern, C. L.; Poeppelmeier, K. R. *J. Am. Chem. Soc.* **2007**, *129*, 13963.

oxyfluorides $[MO_xF_{6-x}]^{n-}$ (M = d^0 transition metal, x = 1−3, and n = 2, 3) and determined that changes in the bond network lead to different crystal symmetries: polar or nonpolar. Halasyamani's group studied another series of analogues $A_2Ti(IO_3)_6$ (A = Li, Na, K, Rb, Cs, Tl) and ascribed the polarity of only the Li and Na phases to cation-size, coordination requirements, and bond valence concept arguments.[11] Generally, it is still a great challenge to design new oxides with polar structures.

Bosacka recently prepared a new oxide, Cd_2InVO_6, in air but reported no detailed structural information.[12] In this paper, we show from the analysis of the room temperature powder X-ray diffraction (PXD) data that Cd_2InVO_6 crystallizes in the polar space group $P3_1$. The structural feature motivated us to examine possible applicable properties of Cd_2InVO_6. The Cd^{2+} and In^{3+} ions are in highly asymmetric coordination environments, and the polar space group suggested the possibility of ferroelectric behavior. The Bi^{3+}-substituted compounds with the formula $Cd_{1-x}Bi_x(Cd_{1+x}In_{1-x})VO_6$ were also investigated with the rational that the lone pair electrons of Bi^{3+} might enhance ferroelectricity. However, single phases of $Cd_{1-x}Bi_x(Cd_{1+x}In_{1-x})VO_6$ with only $0.02 \leq x \leq 0.14$ could be prepared. Thus far, we did not observe ferroelectricity for neither the parent compound nor the Bi^{3+}-substituted phases, which suggests that the dipole moments are not switchable. The second-harmonic generation (SHG) measurements established that Cd_2InVO_6 is a type-1 phase-matchable SHG material with an efficiency of approximately 70 × α-SiO_2. The SHG efficiency is slightly enhanced to 90 × α-SiO_2 for $x = 0.14$. Further efforts are needed to prepare analogues of Cd_2InVO_6 with potentially multifunctional properties.

Experimental Section

A polycrystalline sample of Cd_2InVO_6 was prepared by standard solid state synthesis techniques. Stoichiometric amounts of CdO (Alfa Aesar 99.998%), In_2O_3 (Alfa Aesar 99.997%), and V_2O_5 (Alfa Aesar 99.995%) were ground thoroughly, pressed into a pellet, and treated for 10 h at 650 °C in air. The resultant powder was reground, repressed, and heated for 48 h (with two intermediate regrinding steps) at 850 °C. Bi^{3+}-substituted compounds can be obtained similarly. Typically, $Cd_{1-x}Bi_x(Cd_{1+x}In_{1-x})VO_6$ ($0 \leq x \leq 0.12$) can be obtained at 990 °C, while the sample with $x = 0.14$ can be only prepared at 980 °C. Below 980 °C, the product contains several impurity reflections, while above 980 °C, the pellet starts to melt.

PXD data for the structure determination were collected on a PANalytical X'Pert Pro Alpha-1 equipped with a PIXcel detector. Since the dielectric and polarization measurements did not indicate ferroelectric behavior, these data are discussed in the Supporting Information and will not be discussed further. Powder second harmonic generation (SHG) measurements were performed on a modified Kurtz-NLO system,[13] with a pulsed Nd:YAG laser of wavelength 1064 nm. A detailed description of the equipment and methodology has been published.[14] SHG efficiency has been shown to be strongly dependent on particle size;[13] thus, polycrystalline samples were ground and sieved into distinct particle size ranges (20−45, 45−63, 63−75, 75−90, 90−120, and >120 μm). Crystalline α-SiO_2 was also ground and sieved into the same particle size ranges to make relevant comparisons with known SHG materials. No index matching fluid was used in any of the experiments.

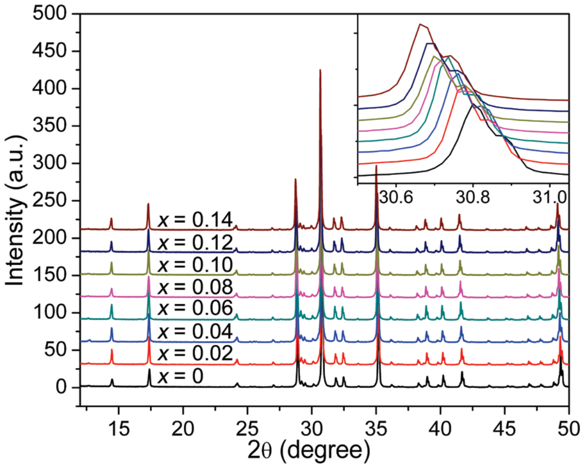

Figure 1. PXD patterns for $Cd_{1-x}Bi_x(Cd_{1+x}In_{1-x})VO_6$ ($0 \leq x \leq 0.14$) in the range of 12−50°. Zero shifts of 2θ for each pattern, which originated from the sample preparation for the X-ray diffraction measurements, are subtracted. The inset shows the shift of the strongest peak, indicating the expansion of the unit cell with increasing x.

Results and Discussion

Synthesis. The melting point of Cd_2InVO_6 is reported to be 1050 ± 10 °C in ref 12. The lowest synthesis temperature of Cd_2InVO_6 is ~675 °C, and it can easily form a single phase at 700 °C for 24 h. The resultant Cd_2InVO_6 is yellow, and the desity of the pellet is 80% of the calculated value (6.077 g cm^{-3}). An 85% condensed pellet can be achieved when heating at 1000 °C for 24 h.

Preliminary substitution attempts were made: for Cd^{2+} by Bi^{3+}, Pb^{2+}, Nd^{3+}, Ca^{2+}; for In^{3+} by Cu^{2+}, Sb^{3+}, Zn^{2+}, and Mn^{2+} either in air or dynamic reducing atmosphere, if a low valent state was aimed; and for V^{5+} by Si^{4+}, Ge^{4+}, and Ti^{4+}. Observable changes of the lattice parameters (from Le Bail refinements of PXD) indicate that only Bi^{3+} and Cu^{2+} can be substituted in a low concentration into Cd_2InVO_6. The specific formula, $Cd_{1-x}Bi_x(Cd_{1+x}In_{1-x})VO_6$ for the synthesis of the Bi^{3+} substitution is based on the structure analysis results, as will be discussed later. In Figures 1 and 2, the PXD patterns and related lattice parameters of $Cd_{1-x}Bi_x(Cd_{1+x}In_{1-x})VO_6$ ($0 \leq x \leq 0.14$) are plotted. The linear increase of the lattice parameters and volume with x in Figure 2 demonstrate the successful substitution of the significantly larger Bi^{3+} for Cd^{2+} as indicated in the formula and also confirms the purity of the substituted compounds. Although the synthetic temperature of the parent compound Cd_2InVO_6 is relatively low (700 °C), even a slight doping of Bi^{3+} ($x = 0.02$) requires 950 °C. The synthesis temperature of $Cd_{1-x}Bi_x(Cd_{1+x}In_{1-x})VO_6$ increases with increasing Bi^{3+} content, while in contrast, the melting point decreases. Thus the

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[11] Chang, H. Y.; Kim, S. H.; Ok, K. M.; Halasyamani, P. S. *J. Am. Chem. Soc.* **2009**, *131*, 6865.
[12] Bosacka, M. *Mater. Res. Bull.* **2009**, *44*, 2252.
[13] Kurtz, S. K.; Perry, T. T. *J. Appl. Phys.* **1968**, *39*, 3798.
[14] Ok, K. M.; Chi, E. O.; Halasyamani, P. S. *Chem. Soc. Rev.* **2006**, *35*, 710.

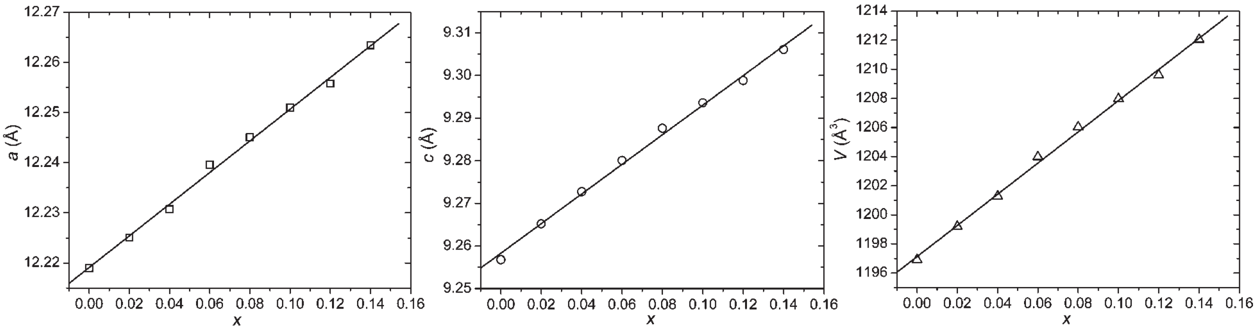

Figure 2. Cell parameters for $Cd_{1-x}Bi_x(Cd_{1+x}In_{1-x})VO_6$ ($0 \le x \le 0.14$) as a function of Bi^{3+} concentration (x). All the parameters were obtained from the Le Bail refinements on the PXD data collected at room temperature: 10−120°, 0.02°/step/10 s.

temperature window of formation becomes narrower, and the highest x we can achieve for Bi^{3+} is 0.14. A single phase compound $Cd_{1.75}Cu_{0.25}InVO_6$ was prepared at 800 °C for 12 h with a small impurity (< 3 wt %) and a refined cell volume (1186.7(1) $Å^3$), which is smaller than that of Cd_2InVO_6 (1196.899(9) $Å^3$) and consistent with the substitution of the smaller Cu^{2+} ion for Cd^{2+} (see Figure S1 in the Supporting Information).

The motivation for substituting transition metal ions in this polar phase, as alluded to earlier, was to induce either ferroelectricity (d^0) or ferromagnetism (d^n), or possibly both (multiferroicity). Since it was not possible to achieve substantial substitution of any of the transition metal ions, nor any of the other species tried, only the pure phase, Cd_2InVO_6 and its Bi^{3+}-substituted analogues will be discussed below.

Determination and Rietveld Refinement of the Crystal Structure. The majority of the strong reflections in the PXD of Cd_2InVO_6 can be indexed with a small trigonal unit cell with $a_s \sim 7.057$, $c_s \sim 9.257$ Å, which is very different from the reported monoclinic unit cell in ref 12. To confirm the correct unit cell, a series of tilt electron diffraction (ED) patterns were taken by rotating the crystal around the c^* axis as shown in Figure S2 in the Supporting Information. Surprisingly, the three-dimensional (3D) reconstructed reciprocal space by the program Trice indicated a larger unit cell with $a = \sqrt{3}a_s$ and $c = c_s$,[15] with which all the reflections in the PXD can be indexed. It is also evident that every third reflection is much stronger than the other two in the ED pattern along the [100] direction (Figure S2 in the Supporting Information), which is consistent with the fact that most of the strong reflections can be indexed with the small trigonal unit cell. This observation strongly indicated that the heavy atoms (Cd, In, and V) possess a pseudohigher symmetry, which is related to the smaller lattice; however, the real structure is more complicated because the light element (oxygen) disobeys this pseudosymmetry and demands a larger unit cell with $a = 12.218\,96(4)$, $c = 9.256\,75(4)$ Å.

The only extinction condition suggested by the ED patterns, $00l$, $l = 3n$, and also observed by PXD, is generated by a 3-fold screw along the c-axis and results in three choices for the space group: $P3_1$ (no. 144), $P3_112$ (no. 151), or $P3_121$ (no. 152).[4] Space group $P3_1$ is noncentrosymmetric and polar, while the other two are noncentrosymmetric but nonpolar. By careful examination of the ED patterns, the Laue class was determined as −3 or −31m, which excludes the space group $P3_121$. The SHG response cannot verify the actual space group, because all the above three can possess a nonlinear optical property. First, the lower symmetry $P3_1$ space group was used successfully for structure determination. However, considering indications of a pseudohigh symmetry, the structure that was refined in $P3_1$ was examined if it was close to a higher symmetry. As expected, the metal positions are close to the pseudohigh symmetry ($P3_121$ in the small trigonal cell) with a tolerance of about 0.4 Å, while the oxygen atoms are far away from any pseudo symmetry. Thus the final structure is conclusively the polar space group $P3_1$.

There are 9 metal (M = Cd or In), 3 V, and 18 O crystallographically independent atoms in the unit cell, all located in the general position of $P3_1$. The Cd and In with almost the same scattering factor for X-rays cannot be distinguished from PXD or from neutron diffraction, due to the high absorption coefficient of Cd for neutrons. For the Rietveld refinement of PXD data, we arbitrarily designated M1−M6 as Cd^{2+} and M7−M9 as In^{3+}. In fact, Cd^{3+} and In^{2+} may have different coordination behaviors and thus have some level of site preference, which will be discussed later.

Table 1 lists X-ray data collection conditions, crystallographic data, and results of the Rietveld analysis for Cd_2InVO_6. The metal atoms and some of the oxygen atoms were easily located by direct methods. A Monte Carlo based simulated annealing technique was applied with the TOPAS software package[16] to find the remaining oxygen atoms. The atomic coordinates and selected metal−oxygen bond distances are shown in Tables S1 and S2 in the Supporting Information, respectively. Figure 3 shows the final profile fitting for the PXD patterns. If the M−O bond distances below 3 Å are considered, Cd/In are coordinated by six or seven oxygen atoms in irregular polyhedral environments (see Table S2 in the Supporting Information and Figure 4). V atoms are all tetrahedrally coordinated. The shortest distances of M−M, M−V, and O−O are 3.29(1) Å (M1−M1), 3.22(2) Å (M6−V3), and

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(15) Zou, X. D.; Hovmöller, A.; Hovmöller, S. *Ultramicroscopy* **2004**, *98*, 187.

(16) TOPAS V2.1: General Profile and Structure Analysis Software for Powder Diffraction Data; Bruker AXS: Karlsruhe, Germany.

2.46(7) Å (O1−O4), respectively, which suggests that the structure model is chemically reasonable. There are a total of 30 independent atoms in the unit cell. Considering the very limited number of independent reflection peaks in the PXD, the parameters to be refined are too many. Therefore, soft restraints were applied during the final Rietveld refinement. For example, the thermal displacement factors for each element are correlated; the positions of O1, O4, and O9 are restricted in the finite ranges of the coordinates to control the bond distances of the V1O$_4$ tetrahedron. As shown in Table S1 in the Supporting Information, the errors of the atomic coordinates for oxygen atoms are relatively larger than those of the metal cations. This is an indication that the accuracy of the oxygen positions is strongly affected by the heavy metal atoms. Consequently some atoms may be slightly off from their real positions if all the atoms are allowed to refine without restraints. Therefore the soft restraints on the O1, O4, and O9 positions were applied.

Table 1. X-ray Data Collection Conditions, Crystallographic Data and Results of Rietveld Analysis for Cd$_2$InVO$_6$[a]

crystal data	
chemical formula	Cd$_2$InVO$_6$
M_r (g mol^{-1})	486.56
crystal system, space group	trigonal, $P3_1$
temperature (K)	293
a (Å)	12.218 96(4)
c (Å)	9.256 75(4)
V (Å^3)	1196.899(9)
Z	9
ρ (g cm^{-3})	6.077
radiation type	Cu $K\alpha_1$ λ = 1.540596 Å
diffractometer	PANalytical X'Pert Pro
data collection mode	reflection
scan method	step
2θ values (deg)	$2\theta_{\mathrm{min}}$ = 10.002, $2\theta_{\mathrm{max}}$ = 119.982, $2\theta_{\mathrm{step}}$ = 0.013
R factors and goodness of fit	R_p = 0.051, R_{wp} = 0.070, R_{exp} = 0.031, χ^2 = 2.30
number of data points	8461
number of parameters	113
number of constraints	10

[a] Computer programs used: *TOPAS*2.1 (Bruker, 2003).

Description of the Crystal Structure. Selected bond distances and the resultant bond valence sum (BVS) calculated for Cd/In are listed in Table S2 in the Supporting Information. On the basis of the calculated BVS values in Table S2 in the Supporting Information, there is qualitative evidence for site preference of Cd^{2+} in M1, M2, M3, M5, and M6, while M4, M7, M8, and M9 suggest mixed Cd/In occupation. Figure 4 illustrates that the coordination of MO$_6$ (or MO$_7$) polyhedra of M1−M3 are more asymmetric than those of M4−M9. The coordination of M1−M3 behaves similarly to that of alkali- or alkali-earth-oxygen polyhedra. On the basis of these considerations, it is likely that the M1−M3 sites are occupied mostly by Cd^{2+}, while Cd^{2+} and In^{3+} are

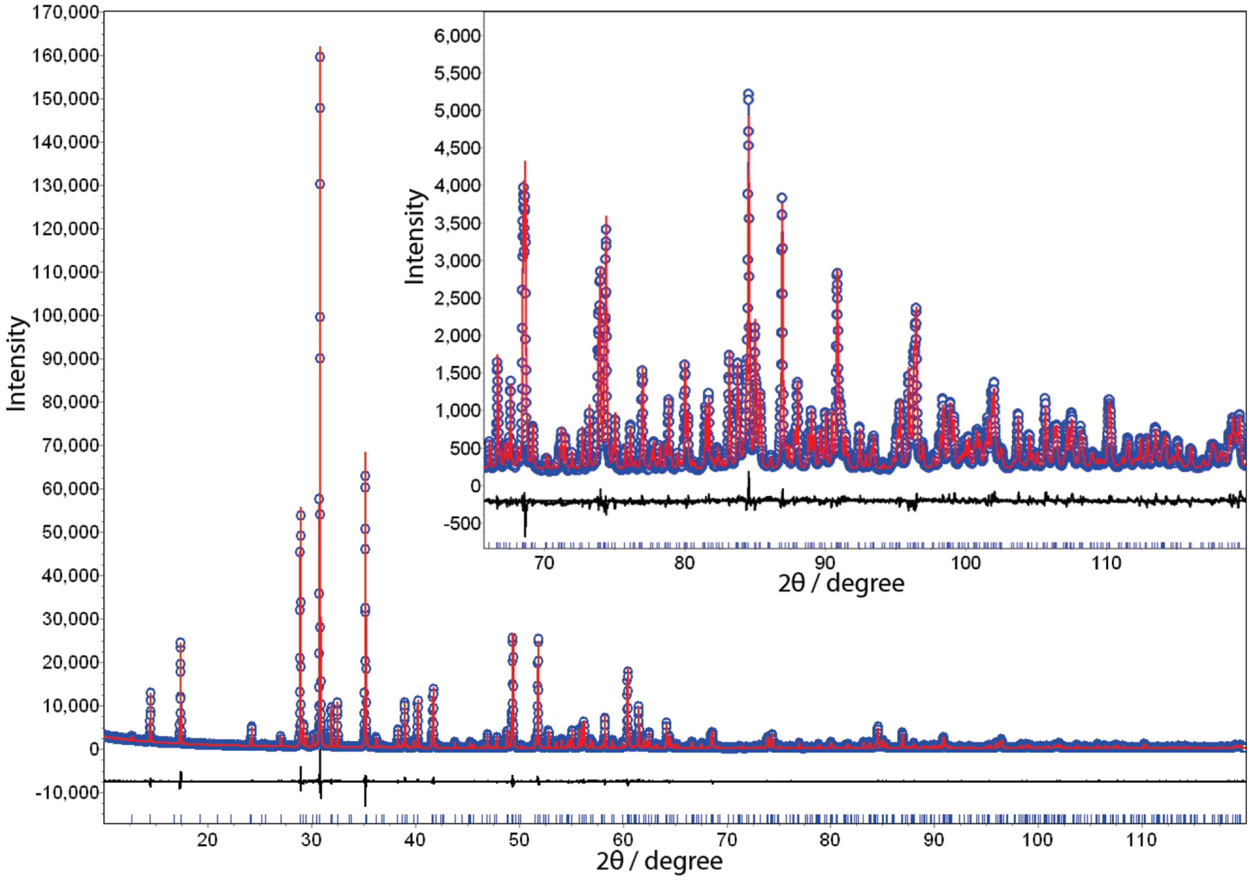

Figure 3. Rietveld plot of the powder X-ray diffraction pattern of Cd$_2$InVO$_6$. The symbol ○ represents the observed pattern and the solid line is the calculated pattern; the marks below the diffraction patterns are the expected reflection positions, and the difference curve is also shown below the diffraction curves. The inset shows the enlargement for the refinement at high angles.

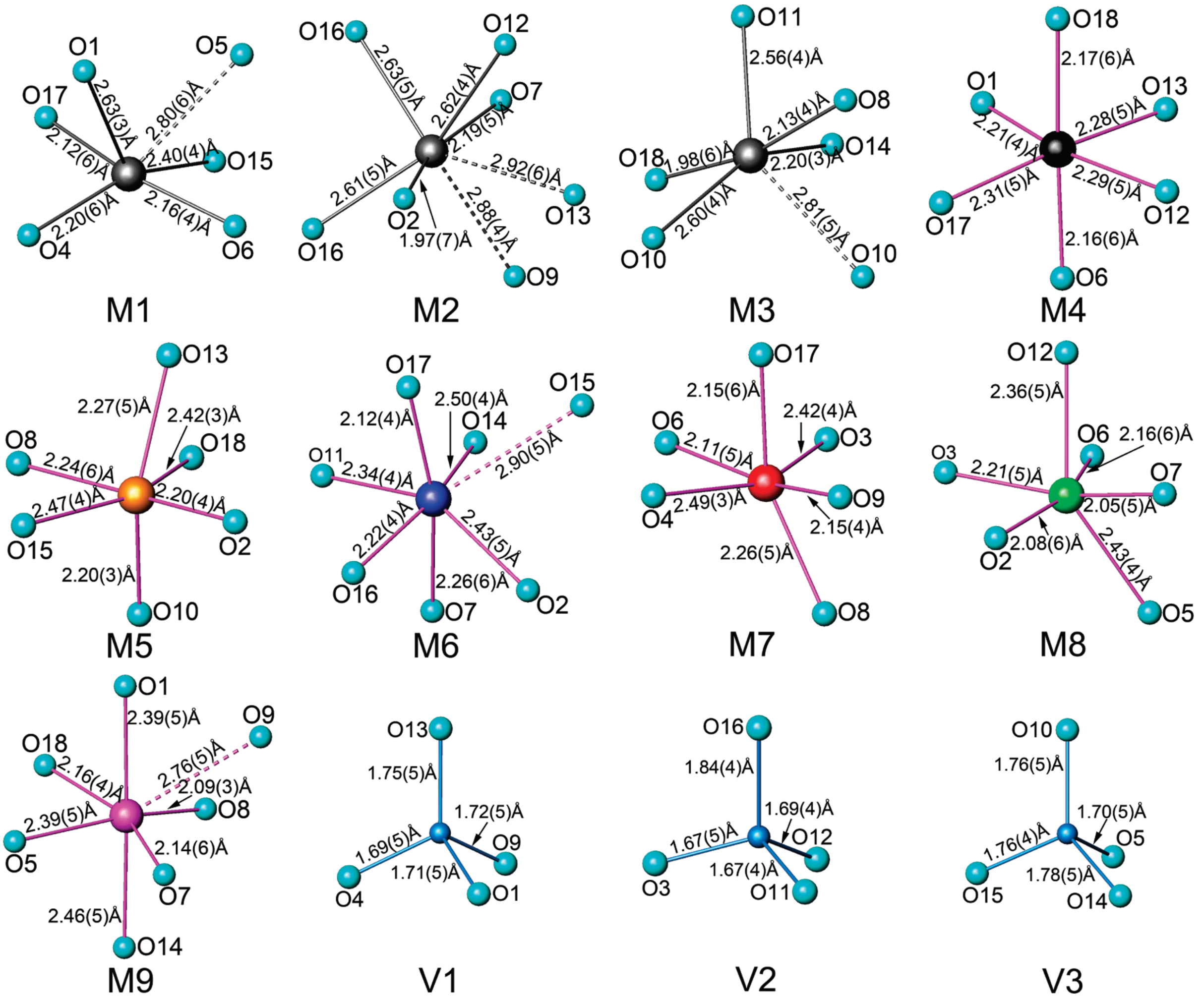

Figure 4. Coordination environments for all the independent metal atoms in Cd_2InVO_6. The M−O bonds with distances below 2.7 Å are shown as solid lines and those above 2.7 Å are shown as dashed lines.

extensively disordered in the M4−M9 positions. Rietveld refinements with several different models cannot convincingly determine the exact position of Bi^{3+} substitution. However, the effective ionic radius of Bi^{3+} argues for it to better fit in the sites primarily occupied by Cd^{2+}. The structure of Cd_2InVO_6 is evidently very complex. In order to describe the structure distinctly, the nine Cd/In sites were grouped into two types: M4−M9 forming the framework and M1−M3 as off-framework cations.

The three-dimensional framework composed of M4−M9-centered octahedra is shown in Figure 5a. Here for clarity, only M−O bonds below 2.7 Å are included. Thus, M4−M9 are six-coordinated in strongly distorted octahedral environments (also see Figure 4). Each MO_6 octahedron connects to five other MO_6 octahedra. For example, $M4O_6$ links to $M5O_6$, $M7O_6$, $M8O_6$, $M9O_6$ via edge-sharing and to $M6O_6$ by corner-sharing (Figure 5). There are in total 15 kinds of octahedron−octahedron connections: 9 edge-sharing with the M−M distances between 3.32(2) and 3.558(7) Å; 6 corner-sharing with M−M distances in the range of 3.60(1)−3.80(2) Å. As shown in Figure 5b, the topological connection of the framework is a pure five-connected net with a Schläli notation $(3^3, 6^3, 9^4)$[17] or named as *zfz* net in the Reticular Chemistry Structure Resource (RCSR) database.[18] The 3_1-screw axes are also evident in Figure 5b. This framework is built of six crystallographically independent M atoms, but M4−M9 are topologically equivalent nodes in this net. Along the *c*-direction, there are three different channels, where the VO_4 tetrahedra attach to the framework. As shown in Figure 6, the remaining negative charges of the framework are compensated by additional M1−M3 cations, which occupy the highly asymmetric cavities. It is suggested that the structural disordering of the Cd^{2+} and In^{3+} lead to the strongly distorted octahedral environments (see Figure 4). The structure appears to be highly strained, which may be the reason why substitutions cannot be easily achieved.

In the $P3_1$ space group, the unique polar axis is along the *c*-direction. In Cd_2InVO_6, each of the nine polyhedra are highly asymmetric, hence each can have a local dipole moment. However, only the *c*-component of the dipole moments will contribute to the total polarity according to space group $P3_1$. It is not possible by inspection of the

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(17) Koch, E.; Fischer, W. *Z. Kristallogr.* **1995**, *210*, 407.

(18) O'Keeffe, M.; Peskov, M. A.; Ramsden, S. J.; Yaghi, O. M. *Acc. Chem. Res.* **2008**, *41*, 1782.

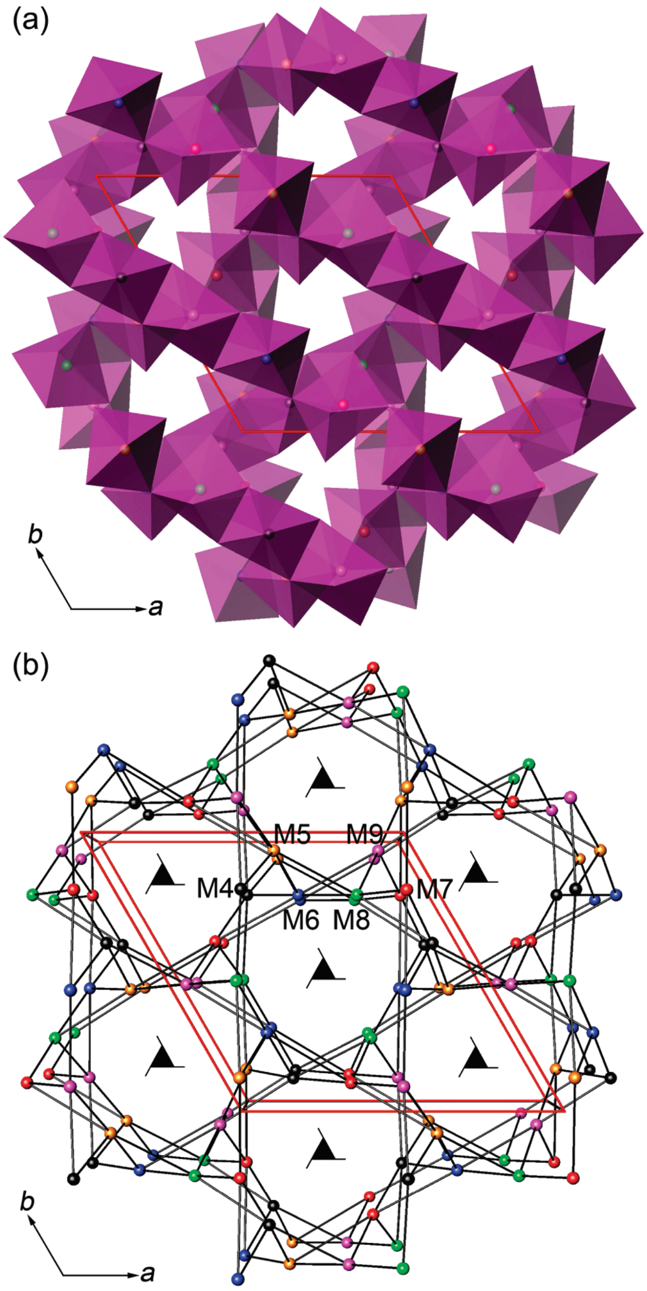

Figure 5. (a) The framework structure of Cd_2InVO_6 composed of M4∼M9 octahedra and (b) perspective view of the topology for the M4∼M9 network, where the 3_1-screw axes are also shown.

structure in Figures 4 and 5 to determine the direction and magnitude of the dipole moment in each of the nine polyhedra to obtain the total dipole moment and the relationship between the local moments and the macroscopic polarity.

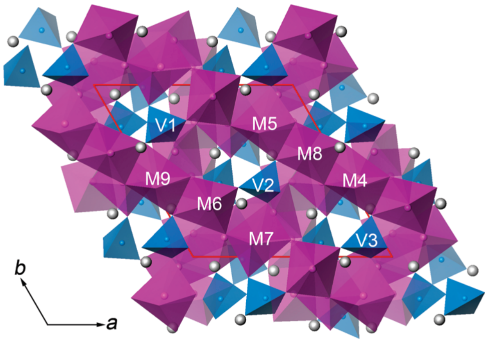

Figure 6. Overall structure of Cd_2InVO_6 along the *c*-direction. For clarity, M1−M3, M4−M9, and V1−V3 are shown as gray spheres, purple octahedra, and blue tetrahedra, respectively.

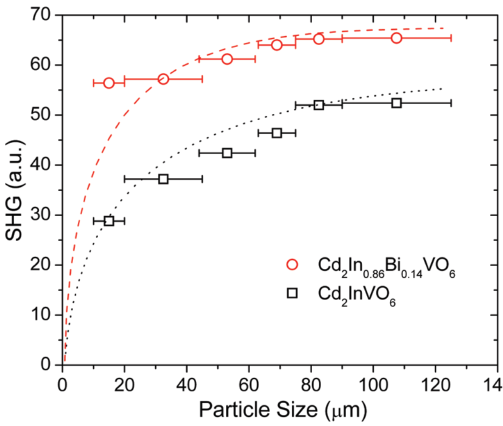

Figure 7. SHG phase-matching curves, particle size vs SHG efficiency, for Cd_2InVO_6 and $Cd_2In_{0.86}Bi_{0.14}VO_6$. Note that the solid line is drawn to guide the eye and is not a fit to the data.

Second Harmonic Generation. Since all polar space groups are piezoelectric, the $P3_1$ symmetry of the structure of Cd_2InVO_6 prompted the nonlinear optical property measurements. Figure 7 shows the SHG coefficient plots of Cd_2InVO_6 and that of the Bi^{3+}-substituted compounds, which are both apparently phase-matchable, with 70 and 90 times that of the coefficient of α-SiO_2 for a 45−63 μm particle size, respectively. It is established that polar, SHG chromophores in solid state materials can result from distorted polyhedra with a d^0 cation with a second-order Jahn−Teller effect,[19−21] polar displacement of d^{10} cation centers,[22] distortion from a stereochemically active lone pair of cations,[23,24] or borate π-orbital systems.[25,26] In Cd_2InVO_6, the major part of the SHG coefficient may originate from the Cd^{2+}- and In^{3+}-centered polyhedra, which are all strongly distorted. Recently, a similar case has been reported in another Cd^{2+}-rich compound, $Cd_4BiO(BO_3)_3$,[27] which is the first example of SHG with three-chromophore asymmetrical building units. In Cd_2InVO_6, the d^0 ion, V^{5+}, in a tetrahedral coordination could also contribute to the total SHG response. With a small amount

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(19) Ra, H. S.; Ok, K. M.; Halasyamani, P. S. *J. Am. Chem. Soc.* **2003**, *125*, 7764.
(20) Sykora, R. E.; Ok, K. M.; Halasyamani, P. S.; Albrecht-Schmitt, T. E. *J. Am. Chem. Soc.* **2002**, *124*, 1951.
(21) Chi, E. O.; Ok, K. M.; Porter, Y.; Halasyamani, P. S. *Chem. Mater.* **2006**, *18*, 2070.
(22) Inaguma, Y.; Yoshida, M.; Katsumata, T. *J. Am. Chem. Soc.* **2008**, *130*, 6704.
(23) Kim, S. H.; Yeon, J.; Halasyamani, P. S. *Chem. Mater.* **2009**, *21*, 5335.
(24) Phanon, D.; Gautier-Luneau, I. *Angew. Chem., Int. Ed.* **2007**, *46*, 8848.
(25) Sasaki, T.; Mori, Y.; Yoshimura, M.; Yap, Y. K.; Kamimura, T. *Mater. Sci. Eng.* **2000**, *30*, 1.
(26) Pan, S.; Smit, J. P.; Watkins, B.; Marvel, M. R.; Stern, C. L.; Poeppelmeier, K. R. *J. Am. Chem. Soc.* **2006**, *128*, 11631.
(27) Zhang, W. L.; Cheng, W. D.; Zhang, H.; Geng, L.; Lin, C. S.; He, Z. Z. *J. Am. Chem. Soc.* **2010**, *132*, 1508.

of Bi^{3+}, substitution for Cd^{2+}, the SHG response is enhanced by ~25%. Thus, the stereochemically active lone pair of Bi^{3+} in this polar structure has a strong SHG affect, although we could not determine exactly where the Bi^{3+} is located in the structure. Thus, $Cd_2In_{0.86}Bi_{0.14}VO_6$ is the second example to exhibit a nonlinear optical property with three chromophores.

Conclusions

$Cd_{1-x}Bi_x(Cd_{1+x}In_{1-x})VO_6$ ($0 \leq x \leq 0.14$) were synthesized by solid state reaction in air. The structure of Cd_2InVO_6 was determined by powder X-ray diffraction. It crystallizes in the polar space group $P3_1$ with 9 Cd/In, 3 V, and 18 O independent atoms per unit cell. M1~M3 sites are likely preferred by Cd^{2+} because of the highly asymmetric coordination environments, and M4~M9 positions are randomly occupied by a distribution of Cd^{2+} and In^{3+}, in distorted octahedral coordination. The framework composed of $M4O_6$−$M9O_6$ octahedra forms a five-connected net with the topology nomination (3^3, 6^3, 9^4). The channels of the framework along the *c*-direction are filled by VO_4 tetrahedra, sharing corners with MO_6 octahedra. The remaining negative charges of the framework are compensated by M1−M3 cations. The structure has a high level of distortion, indicated by highly irregular polyhedra. The polar properties of this new oxide structure, as expected by its $P3_1$ space group symmetry, are fundamentally interesting and potentially important for appplications. However, neither the $x = 0$ nor the $x = 0.14$ $Cd_{1-x}Bi_x(Cd_{1+x}In_{1-x})VO_6$ indicated ferroelectric behavior by dielectric and polarization measurements (see the Supporting Information). It appears that the dipole moments within Cd_2InVO_6 are either not switchable or too insignificant in magnitude. It is possible that in such a condensed and strained structure, the "flip" of the dipole vector cannot occur. Similarly, in $Cd_{0.86}Bi_{0.14}(Cd_{1.14}In_{0.86})VO_6$, the "flip" of the dipole moment due to the lone pair electrons to the opposite side of Bi^{3+} will involve a substantial rearrangement of metal−oxygen bonds, hence it is energetically not favorable; or even if the "flip" does occur, the magnitude of the switchable dipole is too small to lead to observable ferroelectricity. Evidence of the powder second harmonic effect in $Cd_{1-x}Bi_x(Cd_{1+x}In_{1-x})VO_6$ ($0 \leq x \leq 0.14$) is consistent with the polar space group symmetry. The powder second harmonic coefficients of $Cd_{1-x}Bi_x(Cd_{1+x}In_{1-x})VO_6$ with $x = 0$, 0.14 are 70 and 90 times that of α-SiO_2, respectively.

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Supporting Information Available: Atomic coordinates, selected metal−oxygen bond distances, PXD for $Cd_{1.75}Cu_{0.25}InVO_6$, ED patterns around the *c** axis, temperature dependence of dielectric permittivity for Cd_2InVO_6 and $Cd_{0.86}Bi_{0.14}(Cd_{1.14}In_{0.86})VO_6$, E-bias measurements and P(E)-measurements for $Cd_{0.86}Bi_{0.14}(Cd_{1.14}In_{0.86})VO_6$. This material is available free of charge via the Internet at http://pubs.acs.org.