The Structure, Vibrational Spectra, and Thermal Expansion Study of AVO$_4$ ($A=$Bi, Fe, Cr) and Co$_2$V$_2$O$_7$

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Abstract: Vanadate is an important functional material. It has been widely studied and applied in luminescence and photocatalysis. Vanadium compounds have been synthesized to investigate the thermal expansion properties and structure. Both BiVO$_4$ and Co$_2$V$_2$O$_7$ are monoclinic at room temperature, FeVO$_4$'s crystal structure is triclinic, and CrVO$_4$ is orthorhombic. The relatively linear, thermal-expansion, and temperature-dependent Raman spectroscopy results showed that the phase transition of BiVO$_4$ occurred at 200 to 300 $^\circ$C. The coefficient of thermal expansion (CTE) of Co$_2$V$_2$O$_7$ was larger than that of the monoclinic structure BiVO$_4$. The CTE of the tetragonal structure of BiVO$_4$ was $15.27 \times 10^{-6}$ $^\circ$C$^{-1}$ which was the largest CTE in our measurement results, and the CTE of anorthic structure FeVO$_4$ was $2.84 \times 10^{-6}$ $^\circ$C$^{-1}$ and was the smallest.

Keywords: vanadium; Raman spectroscopy; thermal expansion; crystal structure

1. Introduction

Due to the multivalent of vanadium, vanadate has rich physical and chemical properties. Vanadate is a kind of important functional material; it has been widely studied and applied in luminescence and photocatalysis. Vanadium compounds have been synthesized to investigate the thermal expansion properties and structure. Both BiVO$_4$ and Co$_2$V$_2$O$_7$ are monoclinic at room temperature, FeVO$_4$'s crystal structure is triclinic, and CrVO$_4$ is orthorhombic. The relatively linear, thermal-expansion, and temperature-dependent Raman spectroscopy results showed that the phase transition of BiVO$_4$ occurred at 200 to 300 $^\circ$C. The coefficient of thermal expansion (CTE) of Co$_2$V$_2$O$_7$ was larger than that of the monoclinic structure BiVO$_4$. The CTE of the tetragonal structure of BiVO$_4$ was $15.27 \times 10^{-6}$ $^\circ$C$^{-1}$ which was the largest CTE in our measurement results, and the CTE of anorthic structure FeVO$_4$ was $2.84 \times 10^{-6}$ $^\circ$C$^{-1}$ and was the smallest.

As a kind of transition metal oxide, FeVO$_4$ can be used as electrode materials for ion batteries and supercapacitors [8–11]. The compound materials of FeVO$_4$/BiVO$_4$ and FeVO$_4$/V$_2$O$_5$ has higher than pure FeVO$_4$ photocatalytic activity [12,13]. Chrome vanadate has three different crystal forms tetragonal, monoclinic, and orthorhombic structures [7]. The ambient-pressure stable polymorph of CrVO$_4$ is orthorhombic space group D$_{2h}^{17}$Cmcm-, with Z=4 at room temperature [14]. Cobalt vanadates and their composites have drawn a tremendous amount of attention because of their outstanding cycling stability [15,16]. The Co$_2$V$_2$O$_7$ was recently reported to exhibit amazing magnetic field-induced
magnetization plateaus and ferroelectricity, but its magnetic ground state remains ambiguous due to the fact of its structural complexity [17].

From the above discussion, we know that vanadium compounds have many structures, rich physical and chemical properties which makes them have potential application value in many aspects. Although there are many studies on the structure and application of vanadium compounds, the thermal expansion of materials has not been reported very intensively. It has been pointed out that ionic radius and electronegativity of the cations are important with respect to structure and phase transition temperature [18,19]. Herein, we have prepared some vanadate materials by a simple solid-phase sintering method, X-ray diffraction (XRD) was used to measure the structure of materials, Raman scattering was used to measure the lattice vibration, and dilatometers was used to measure the thermal expansion.

2. Experimental and Methods

The AVO$_4$ and Co$_2$V$_2$O$_7$ were synthesized by a solid-state method from Fe$_2$O$_3$ (≥99.0%), Bi$_2$O$_3$ (≥99.0%), Cr$_2$O$_3$ (≥99.0%), Co$_2$O$_3$ (≥99.5%), and V$_2$O$_5$ (≥99.0%). The raw materials were mixed according to stoichiometric amounts (1:1) of A$_2$O$_3$ and 2%-5% excess V$_2$O$_5$ of desirable material except (in order to compensate for the loss in the sintering process) and ground in a mortar for 2 h. Then, alcohol was poured over the raw material and grind again until dry. Lastly, it was pressed into tablets with a length of approximately 7 mm and a diameter of approximately 6 mm, followed by sintering at 750°C for 4 h and cooling naturally to room temperature.

The XRD measurements were carried out with an X'Pert PRO X-ray Diffractometer (Bruker D8, Bruker, Karlsruhe, Germany). Raman spectroscopy (Renishaw MR-2000 Raman spectrometer, Gloucestershire, UK) with a TMS 94 heating/freezing stage with an accuracy of ±0.1 °C was used to characterize the vibrational property of lattice. The linear thermal expansion coefficients were measured on dilatometers (LINSEIS DIL L76, Linseis, Selb, Germany), with heating and cooling rates of 5 °C/min.

3. Results and Discussion

3.1. Crystal Structure Analysis

Figure 1 shows the XRD patterns of as-prepared materials. Figure 1a is the pattern of BiVO$_4$, all diffraction peaks corresponded to BiVO$_4$ (PDF No. 01-083-1699) which means that the material crystals were in monoclinic structure space group I2/b, with Z = 4. The lattice constants of BiVO$_4$ were a = 5.196 Å, b = 5.094 Å, c = 11.703 Å and α = β = 90°, γ = 90.380°. Figure 1b is the pattern of CrVO$_4$, the primary diffraction peaks corresponded to CrVO$_4$ (PDF No. 00-038-1376, space group Amam) except for weak peaks indicated as “∇” for secondary phase Cr$_2$O$_3$ and “∗” for secondary phase V$_2$O$_5$ which could relate to the fact that the reaction time was much shorter than that reported in the literature (122 h). There was a second and third phase which could lead to some situations, such as internal stress, many cracks on the tablet, etc. The material crystals in orthorhombic structure with space group Amam from the primary diffraction peaks. The lattice constants of CrVO$_4$ are a = 5.567 Å, b = 8.210 Å, c = 5.975 Å. The pattern of FeVO$_4$ is shown in Figure 1c. As seen, the diffraction peaks are corresponding to FeVO$_4$ (PDF No. 00-038-1372, space group P-1) which crystal in anorhetic structure. The lattice constants of FeVO$_4$ are a = 6.720 Å, b = 8.059 Å, c = 9.256 Å, and α = 96.7°, β = 106.4°, γ = 101.6°. Figure 1d is the pattern of Co$_2$V$_2$O$_7$, all diffraction peaks corresponded to Co$_2$V$_2$O$_7$ (PDF No. 01-070-1189) with lattice constants a = 6.595 Å, b = 8.380 Å, and c = 9.470 Å which means that the material crystals were in monoclinic structure space group P21/c, with Z = 4.
was triclinic Figure 2d. For FeVO$_4$, there were 18 symmetrical inequivalent atoms in a one-unit cell, and all the atoms occupied the symmetry position 2i (Figure 2e). The total number of atoms in a unit cell was 36. The distance between the V atom and the O atom was different. The unit cell contained three symmetrical VO$_4$ tetrahedra and asymmetrical BiO$_6$ octahedra in one primitive cell of BiVO$_4$. The CrVO$_4$ crystal structure was orthorhombic (Figure 2c,d). The distance between the V and O atoms (approximately 1.63342 Å and 1.70978 Å) was shorter than that of BiVO$_4$, and the distances between the Cr and O atoms were 1.98422 Å and 2.04868 Å. It can be seen that there are four CrO$_6$ octahedra around each tetrahedron; however, each CrO$_6$ octahedron is not only connected with six tetrahedron vertices, but also connected with two other octahedron edges. The FeVO$_4$ crystal structure was triclinic Figure 2d. For FeVO$_4$, there were 18 symmetrical inequivalent atoms in a one-unit cell, and all the atoms occupied the symmetry position 2i (Figure 2e). The total number of atoms in a unit cell was 36. The distance between the V atom and the O atom was different. The unit cell contained three asymmetrical inequivalent VO$_4$ tetrahedra, two asymmetrical inequivalent FeO$_6$ octahedra, and one FeO$_5$ polyhedron [20] (Figure 2f). The CoV$_2$O$_7$ crystal structure was monoclinic Figure 2g, and all the atoms occupied the symmetry position 2i (Figure 2e). The total number of atoms in a unit cell was 44. The distance between the V atom and the O atom was different. The unit cell contained three symmetrical VO$_4$ of each tetrahedron and six asymmetrical CoO$_6$ octahedra (Figure 2h). It can be seen that each VO$_4$ tetrahedron was connected to four CoO$_6$ octahedra by the O atom; however, each CrO$_6$ octahedron was connected by the O atom to six VO$_4$ tetrahedras and shared a common edge with two other octahedral.

To visualize the coordination number associated with the structural transitions, crystal structures of monoclinic (BiVO$_4$, Co$_2$V$_2$O$_7$), triclinic (FeVO$_4$), and orthorhombic (CrVO$_4$) systems with polyhedral representation were drawn using a VESTA software as shown in Figure 2 (the “atomic coordinates” were obtained come from the joint conferences on pervasive computing (JCPC) references). The BiVO$_4$ crystal structure was monoclinic. From Figure 2a,b, Bi and V atoms occupied the symmetry position 4e, and O atoms occupied 8f. The distance between the V and O atoms was evenly distributed (approximately 1.68 Å and 1.785 Å); however, the distance of the Bi and O was very variable. There are six symmetry VO$_4$ tetrahedras and asymmetrical BiO$_6$ octahedra in one primitive cell of BiVO$_4$. The CrVO$_4$ crystal structure was orthorhombic (Figure 2c,d). The distance between the V and O atoms (approximately 1.63342 Å and 1.70978 Å) was shorter than that of BiVO$_4$, and the distances between the Cr and O atoms were 1.98422 Å and 2.04868 Å. It can be seen that there are four CrO$_6$ octahedra around each tetrahedron; however, each CrO$_6$ octahedron is not only connected with six tetrahedron vertices, but also connected with two other octahedron edges. The FeVO$_4$ crystal structure was triclinic Figure 2d. For FeVO$_4$, there were 18 symmetrical inequivalent atoms in a one-unit cell, and all the atoms occupied the symmetry position 2i (Figure 2e). The total number of atoms in a unit cell was 36. The distance between the V atom and the O atom was different. The unit cell contained three asymmetrical inequivalent VO$_4$ tetrahedra, two asymmetrical inequivalent FeO$_6$ octahedra, and one FeO$_5$ polyhedron [20] (Figure 2f). The CoV$_2$O$_7$ crystal structure was monoclinic Figure 2g; the total number of atoms in a unit cell was 44. The distance between the V atom and the O atom was different. The unit cell contained three symmetrical VO$_4$ of each tetrahedron and six asymmetrical CoO$_6$ octahedra (Figure 2h). It can be seen that each VO$_4$ tetrahedron was connected to four CoO$_6$ octahedra by the O atom; however, each CrO$_6$ octahedron was connected by the O atom to six VO$_4$ tetrahedras and shared a common edge with two other octahedral.
3.2. Thermal Expansion Property

Figure 3 shows the relative linear thermal expansion of BiVO$_4$, FeVO$_4$, and Co$_2$V$_2$O$_7$. It was found that the samples have different relative linear thermal expansion. For BiVO$_4$, there was a thermal expansion inflection point at about 237 °C which means that the material occurs phase transition at this temperature. The coefficients of thermal expansion (CTEs) were calculated as the average linear thermal expansion coefficient in terms of the slope of thermal expansion versus temperature. The CTEs were measured to be $(4.664 \pm 0.005) \times 10^{-6} \, ^\circ\text{C}^{-1}$ (25–235 °C) and $(15.40 \pm 0.002) \times 10^{-6} \, ^\circ\text{C}^{-1}$ (240–550 °C). For FeVO$_4$, there was a gradual change thermal expansion at approximately 400 °C,
the CTE of FeVO$_4$ was obtained to be $(2.751 \pm 0.004) \times 10^{-6} \, ^\circ\text{C}^{-1}$ from 20 to 350 °C and $(5.245 \pm 0.005) \times 10^{-6} \, ^\circ\text{C}^{-1}$ from 400 to 600 °C. Although both vanadium and iron are variable metals and thermal expansion is related to valence states [21], we prepared and measured the material in an air atmosphere, vanadium and iron should remain stable in the highest valence state. So, there should be no chemical expansion here. The thermal expansion of Co$_2$V$_2$O$_7$ was stable below 500 °C, and the CTE was $(9.230 \pm 0.004) \times 10^{-6} \, ^\circ\text{C}^{-1}$ from 20 to 500 °C. The inflection point above 500 °C is due to the softening of glass state above 500 °C which can be explained by the fact that Co$_2$V$_2$O$_7$ goes from the crystalline form to a glassy one. This phenomenon indicates that material intelligent stability exists with below 500 °C. Though the structure of Co$_2$V$_2$O$_7$ is similar to BiVO$_4$, their CTE is very different. This could come from the different ionic radius of Co$^{3+}$ (63 pm) and Bi$^{3+}$ (108 pm). The ionic radius of Co$^{3+}$ (63 pm) equals that of Fe$^{3+}$ (64 pm); however, they had the largest difference in CTE in this study. This was due to the different structures.

![Figure 3](https://example.com/figure3.png)

**Figure 3.** Relative length change of BiVO$_4$, FeVO$_4$, and Co$_2$V$_2$O$_7$.

Raman spectroscopy was applied to further demonstrate the existence of crystal. Raman spectra collected at room temperature is shown in Figure 4. The Raman spectra of BiVO$_4$, CrVO$_4$, FeVO$_4$, and Co$_2$V$_2$O$_7$ were in agreement with literature [10,20,22,23] and the spectra did not show the characteristic bands of V$_2$O$_5$. Hence, no effort was taken to consider the product selectivity in this work. For BiVO$_4$, the primitive cell contained 28 atoms (Figure 2) and, in principle, 81 vibrational modes were expected. The band at approximately 828 cm$^{-1}$ corresponded to stretching modes of V–O bonds, and there was no splitting which means that degeneracy occurs in the symmetric stretching vibration of VO$_4$ tetrahedron. The strongest peak of CrVO$_4$ and FeVO$_4$ was much higher, whereas the stretching modes of V–O give rise to intense bands, the difference in electronegativity of these metal (Bi, Co, Cr, and Fe). The Raman bands of FeVO$_4$ were much more than that of BiVO$_4$, CrVO$_4$ and Co$_2$V$_2$O$_7$, because the structure of FeVO$_4$ is triclinic, and all vibrations are nondegenerate. The 36 atoms in the unit cell had 105 vibrational modes among which 54 optical modes were Raman active $A_g$ modes, 51 were infrared active $A_u$ modes [23]. For all Raman spectra, the stretching modes of V–O combining M–O and V–O occurred above 650 cm$^{-1}$, and bending modes together with stretching modes appeared in the 630–420 cm$^{-1}$ region. The lower wavenumber bands were external modes from lattice, translational, and vibrational motions [24,25]. From a crystalline perspective, all catalysts were composed of V–O polyhedrons and other metal–oxygen polyhedrons.

In order to study the sudden change in thermal expansion of BiVO$_4$, the Raman spectroscopy dependent temperature of BiVO$_4$ is shown in Figure 5. The Raman bands became weaker and weaker with the increasing temperature which reflects the increase of the degree of disordering of the crystal structure. The relative intensity of 368 and 324 cm$^{-1}$ had obvious change at 200 °C, and
they disappeared at 300 °C; meanwhile, there was a new band at approximately 345 cm⁻¹. There was not only one change. The bands at 127 and 211 cm⁻¹ gradually became a wave packet; meanwhile, the 703 cm⁻¹ band disappeared, and the 828 cm⁻¹ band moved to 815 cm⁻¹, this might be caused by the bond expansion and weakening. All these mean that there was a phase transition between 200 °C and 300 °C. There was no change in the Raman spectra above 300 °C. The high temperature Raman spectra were in agreement with tetragonal structure which means that BiVO₄ crystal tetragonal as well [26]. Compared with Figure 3, we found that materials with high symmetry have larger CTE. The Raman band at 368 and 324 cm⁻¹ could inhibit the thermal expansion of material. It means that the thermal expansion property was related to the structure of the material.

![Figure 4. Raman spectra of BiVO₄, FeVO₄, CrVO₄, and Co₂V₂O₇.](image1)

![Figure 5. Raman spectra of BiVO₄ at temperature of 18, 50, 100, 200, 300, 400, and 600 °C.](image2)
4. Summary
Vanadium compounds were synthesized to investigate the thermal expansion properties and structure. The CTE of Co$_2$V$_2$O$_7$ was bigger than monoclinic structure BiVO$_4$ which means that the thermal expansion property was related to the ionic radius of metals. The CTE of the tetragonal structure of BiVO$_4$ was $15.27 \times 10^{-6}$ °C$^{-1}$ which was the biggest CTE in our measurement results, and the CTE of tetragonal structure FeVO$_4$ was $2.84 \times 10^{-6}$ °C$^{-1}$ which was the smallest. This indicates that the thermal expansion property was related to the structure of the material.

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