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Synthesis, crystal structure and nonlinear optical property of CsV_2O_5

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ABSTRACT

The new nonlinear optical crystal CsV_2O_5 has been synthesized by solid state reaction and characterized by single-crystal X-ray diffraction and thermogravimetric analysis. The crystal CsV_2O_5 crystallizes in the orthorhombic system with space *Ima*2 space group. It is a layered structure that is very flat and strongly parallel to c. The striking structural feature is that the V atom in single crystallographic site has two different valence states (V^{4+} and V^{5+}). The $[V_2O_5]_n$ layer consists of corner-linked tetrahedron. The six tetrahedrons lie very nearly in the same z-plane forming almost regular hexagons. The Kurtz powder SHG measurement, using 1064 nm radiation, showed that the second-harmonic generation efficiency of CsV_2O_5 is about six times that of KDP.

During the past two decades, the design and characterization study of second-order nonlinear optical (NLO) materials have become a hotspot for a lot of chemistry and physics scholars due to their wide commercial applications in laser frequency conversion, optical parameter oscillators, Q-switch signal processing and information storage [1,2]. Great progress has been made in searching for novel NLO crystals in inorganic oxides, organic crystals, polymers and organometallic compounds [3–5]. In general, vanadium may exist as V^0 (metallic), V^{2+}, V^{3+}, V^{4+} and V^{5+} depending on the synthesis procedure and chemical environment. Therefore, it can be the formation of many new structures, and has many interesting properties. Our interest in vanadium is based on its ability to form distorted tetrahedron, pentahedron, triangular pyramids, and octahedron. This type of distortion is prevalent in high-valent, d^0 transition metals owing to the symmetry-allowed mixing of a low-lying excited state (LUMO) with a nondegenerate ground-state molecular orbital (HOMO) [6–8]. This orbital mixing results in a distortion of the geometry of the metal centers along the *C*2, *C*3, or *C*4 axes [9,10]. Based on the above the new polar solids with large second-harmonic generation (SHG) responses can be prepared by combining distorted pentavanadium oxygen polyhedron and a large counterion , such as $ACa_9(VO_4)_7$ [11], $Ba_{1.5}VOSi_2O_7$ [12], $K_3V_5O_{14}$ [13], $Rb_3V_5O_{14}$ [14], and $A[(VO)_2(IO_3)_3O_2]$ ($A = NH^{4+}$, Rb, Cs) [15], which are of interest as a result of their nonlinear optical properties as well as their piezoelectric and pyroelectric properties.

The compound CsV_2O_5 with space group $P_{21/c}$ was reported and synthesized by two methods. The first kind is electrolysis of Cs_2O and V_2O_5 melt at high temperature [16], the second is the solid-state reaction of mixtures with appropriate molar ratios of $CsVO_3$, V_2O_3 and V_2O_5 in an evacuated silica tube [17]. It was a centrosymmetric structure and has no second-harmonic generation (SHG) responses. In this paper, we report the synthesis, structure, and nonlinear optical properties of no isomorphous phase of CsV_2O_5.

The brown single crystals of CsV_2O_5 were obtained by high-temperature solid-state reaction. The stoichiometric amounts of Cs_2CO_3(AR) and V_2O_5(AR) were weighed accurately. These mixtures were pressed into tablets and then placed in platinum crucible. Platinum was selected since it is essentially chemically inert in this system. The samples were gradually heated to 500°C for 15 h,held for 120 h, and then allowed to cool to about 100°C at a controlled temperature reducing rate of 10°C/h in the furnace in carbon monoxide atmosphere. Isomorphous phases of AV_2O_5(A = Na, K, Rb) were not obtained by the same method.

Single-crystal X-ray diffraction analysis [18] revealed that CsV_2O_5 crystallizes in the Ima2 space group [Table S1.S2] and displays a two-dimensional layer structure separated by Cs + cations (Fig. 1a). The EPR spectrum at 293 K (Fig. S1) shows V4+ signal with g = 1.95, suggesting that the synthesized sample is mixed-valence compounds. The calculated total bond valence for V is 4.528. This indicates that the V atoms is in an oxidation state of +4.5, and confirms that V site is really mix-valent. The striking structural feature is that the V atom in single crystallographic site has two different valence states (V^{4+} and V^{5+}). The layer character of this structure is very flat and strongly parallel to c. The $[V_2O_5]_n$ layer consists of corner-linked tetrahedron. As will be seen, the V atoms form four different bonds with O_1, O_2, O_3, and O_4 atoms, and form distorted tetrahedrons, V – O bond distances and O – V – O angles for tetrahedron are listed in table [S3.S4]. The tetrahedrons with apices pointing in the same direction along the c-axis are joined by sharing neighboring basal corners. The six tetrahedrons lie very nearly in the same z-plane forming almost regular hexagons (Fig. 1b). The tetrahedral sublattice was equally occupied by V^{4+} and V^{5+}. Each hollow space resulting from the six-ring configuration is occupied by a rubidium atom, placed

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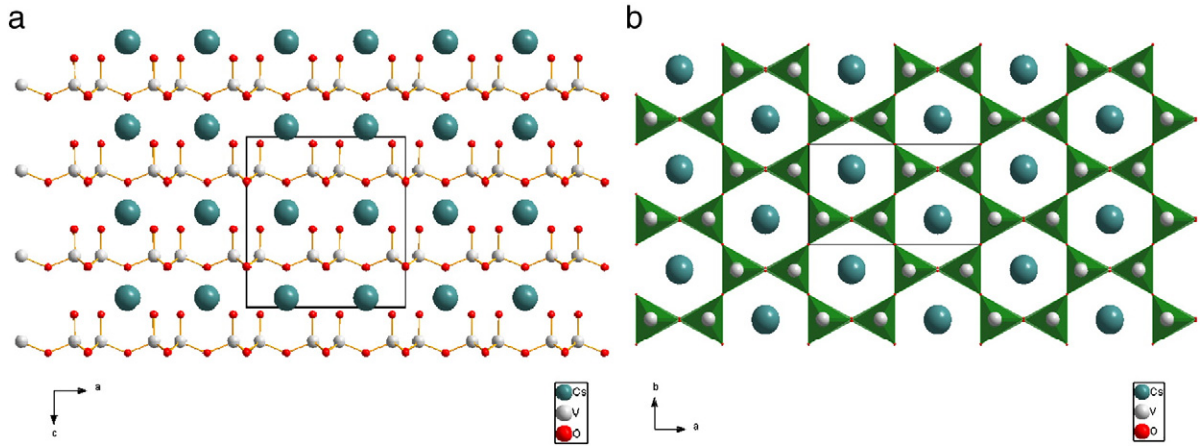

Fig. 1. View of the structure of CsV_2O_5, corner-connected VO_4 triangular pyramids interspersed with layers Cs ions (the green balls) is shown in projection down the [010] direction in (a) and the [001] direction in (b).

about half way between the layers. The interstitial Cs atom is nominally surrounded by 12 oxygens, six oxygens from the apex oxygen's of the tetrahedrons in the lower layer and six oxygens from basal corner of tetrahedrons in the layer above. This packing mode is favorable to the accumulation of microscopic second-order NLO coefficient and exhibits a relatively strong bulk NLO effect.

The experimental powdered X-ray diffraction (XRD) pattern of CsV_2O_5 agrees well with the simulated one based on the single-crystal X-ray data (Fig. 2), indicating that the sample of CsV_2O_5 is in a pure phase. But the diffraction intensity has some difference compared to the indexed and simulation pattern due to many factors such as the size of powder particulate, the control of the scanning conditions and the crystalline degree.

Thermogravimetric analysis (Fig. 3) shows that CsV_2O_5 can be thermally stable up to 700°C, and there isn't weight loss. The heating and the cooling DTA curves of CsV_2O_5 crystal show that crystal CsV_2O_5 melts congruently (Fig. 3). The melting point of the crystal is about 450°C, the CsV_2O_5 material begins to freeze about 410°C.

A preliminary SHG efficiency measurement of CsV_2O_5 has been carried out by the Kurtz–Perry method using polycrystalline samples at room temperature. In addition to identifying the materials with noncentrosymmetric crystal structure, it is also used as a screening technique to identify the materials with the capacity for phase matching. The SHG intensity from the material is measured as a function of particle size. The continuous increase of SHG intensity with increasing of particle size confirms the phase matching behavior of the material. An inverse relation between intensity and particle size confirms the non-phase matching behavior of the material.

With the 100 μm particle size, the intensity of the green light (frequency-doubled output: $\lambda = 532$ nm) produced by the CsV_2O_5 powder is about six times that of KDP powder, indicating that CsV_2O_5 six times the SHG efficiency of KDP. The curves (Fig. 4) of SHG signal as a function of particle size have been obtained, which are not consistent with phase-matching behavior. The continuous decrease of SHG with increasing of particle size [22,23] shows that CsV_2O_5 crystal is non-phase matching behavior.

In summary, a novel second-order NLO material of Cesium pentavanadium was synthesized by high-temperature solid-state reaction. The crystal CsV_2O_5 crystallizes in the orthorhombic system with Ima2 space group, namely a noncentrosymmetric (NCS) structure. The four O anions form the distorted tetrahedrons which lie very nearly in the same z-plane forming almost regular hexagons. This packing mode is favorable to the accumulation of microscopic second-order NLO coefficient and exhibits a relatively strong bulk NLO effect. The intensity of second harmonic generation effect is about six times as large as that of KDP. The melting point of CsV_2O_5 is about 398°C. It is possible for CsV_2O_5 to possess potential application as a new NLO crystal.

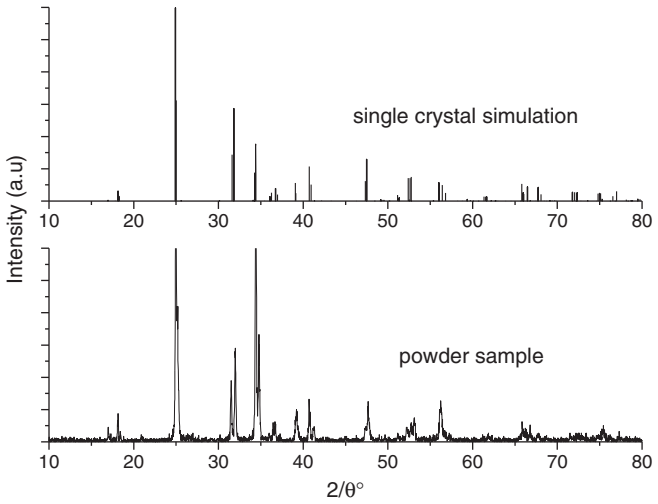

Fig. 2. The pattern of X-ray powder diffraction: (a) single crystal simulation pattern, and (b) powder sample pattern.

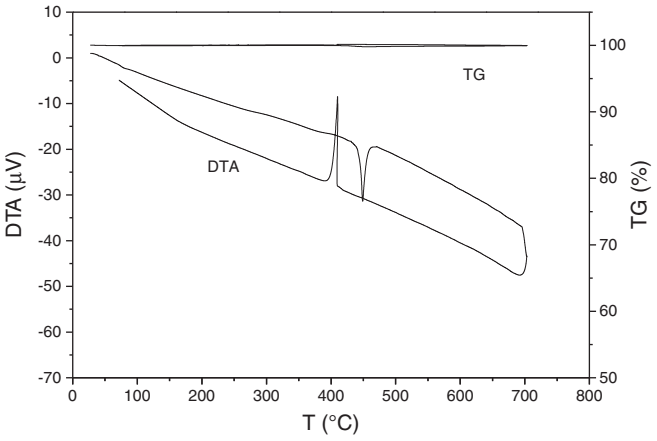

Fig. 3. TG and DTA curves of CsV_2O_5 crystal.

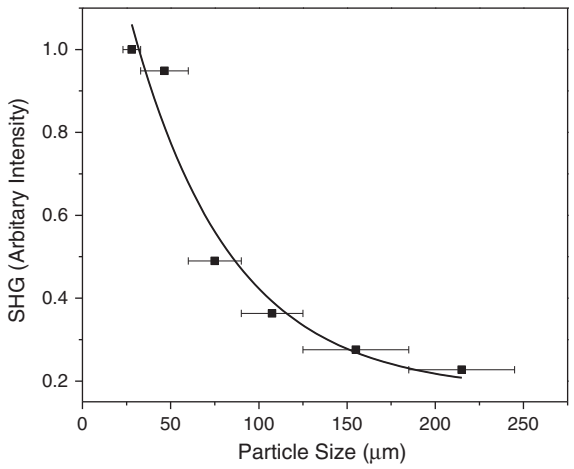

Fig. 4. Particle-size dependence of second-harmonic intensity for CsV_2O_5 powders. (The black curve is a fitting curve).

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.inoche.2012.10.023.

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