

Single crystal growth of $\text{Zn}_x\text{Cu}_{1-x}\text{V}_2\text{O}_7$ ($x = 0.05, 0.15$) by the vertical gradient freezing technique

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Abstract. Single crystals of $\text{Zn}_x\text{Cu}_{1-x}\text{V}_2\text{O}_7$ system with doping concentration of $x = 0.05$ and 0.15 were grown by the vertical gradient freezing technique. The crystal structures were confirmed by means of x-ray diffraction to be the beta phase of copper pyrovanadate, $\beta\text{-Cu}_2\text{V}_2\text{O}_7$, when the Zn concentration was as low as 0.05 , on the contrary to the previous studies on polycrystal samples. The Rietveld refinements on x-ray diffraction patterns showed that lattice constants were slightly increased, whereas the angle β was slightly decreased, when the doping concentration was decreased from $x = 0.15$ to 0.05 . θ - 2θ scan confirmed that the natural cleaved facet is crystallographic a -axis with FWHM around (200) peak of lower than 0.2° , suggesting a high quality of the obtained single crystals.

1. Introduction

Antiferromagnetic materials have attracted much interest in experimental condensed matter physics community due to their various intriguing magnetic phenomena such as spin Seebeck effect [1, 2], spin Hall effect [3] and multiferroics [4, 5]. Recent spin dynamics study on $\alpha\text{-Cu}_2\text{V}_2\text{O}_7$ surprisingly revealed nonreciprocal magnons arising from the breaking of spatial inversion and time reversal symmetry [6]. In addition, spin Seebeck effect [7] and spin-driven ferroelectricity [8] have also been reported in this system. Copper pyrovanadate, $\text{Cu}_2\text{V}_2\text{O}_7$, consists of two most stable phases i.e., α and β phases. The α phase of $\text{Cu}_2\text{V}_2\text{O}_7$ crystallizes in orthorhombic system with $a = 20.645\text{\AA}$, $b = 8.383\text{\AA}$, and $c = 6.442\text{\AA}$ [9], whereas the β phase crystallizes in monoclinic system (see Table 1 for lattice parameters). The structural phase transition temperature between the two phases were ambiguously reported to be 712° [10, 11] or below 550° [12], giving rise to difficulties in the phase control for single crystal growth [13]. However, the phase transformation can also be effectively controlled by substitution of nonmagnetic Zn^{2+} into magnetic spin-1/2 Cu^{2+} ions. Previous studies on polycrystal reported that the α - β phase transition in $\text{Zn}_x\text{Cu}_{1-x}\text{V}_2\text{O}_7$ occurred when $x \approx 0.15 - 0.2$ [10, 14]. Unfortunately, up to date, there has not been any report on single crystal growth of $\text{Zn}_x\text{Cu}_{1-x}\text{V}_2\text{O}_7$. Single crystal samples have always been ideal for studying the bulk properties, macroscopically and microscopically, of such materials.

In this paper, we report single crystal growth of $\text{Zn}_x\text{Cu}_{1-x}\text{V}_2\text{O}_7$ system with $x = 0.05$ and 0.15 by the vertical gradient freezing technique. The crystal structures of the obtained crystals, as well as their quality, were investigated using x-ray diffraction and analyzed by the Rietveld refinements.

2. Experiment

Starting materials of $\text{Zn}_x\text{Cu}_{1-x}\text{V}_2\text{O}_7$ with $x = 0.05$ and 0.15 in the form of powder were prepared by the standard solid-state reaction. Stoichiometric ratios of ZnO , CuO , and V_2O_5 were weighed and mixed thoroughly and calcined in the air between 550°C - 650°C with intermediate grindings until the homogeneous polycrystal samples were obtained.

The powder sample was loaded into a quartz tube where the bottom end was shaped into taper for seed selection during the crystalization. The quartz tube with powder sample inside was then hung inside the vertical furnace and slowly driven down by a DC motor through a natural vertical temperature gradient. The temperature gradient in this experiment was approximately 10°C at the position where the solid-liquid phase transition of $\text{Zn}_x\text{Cu}_{1-x}\text{V}_2\text{O}_7$ occurred, which is $\approx 780^\circ\text{C}$. The moving rate was approximately 2 cm/day . After 4 days of crystal growth, the sample was slowly cooled room temperature. The crystals were then brought out and extracted from the quartz tube by mechanical process.

Some small pieces of the obtained single crystals were collected and ground into powder for x-ray diffraction (XRD). The x-ray patterns were refined by the Rietveld method using FULLPROF [15]. A larger piece with clear cleave surface was used to determine the crystallographic direction of the cleaved facet by a θ - 2θ scan.

3. Results and discussion

The single crystals obtained from the vertical gradient freezing technique yielded as large as $1\times 1\times 1\text{ cm}^3$ as shown in Fig. 1(b) and (e) for $\text{Zn}_{0.05}\text{Cu}_{1.95}\text{V}_2\text{O}_7$ and $\text{Zn}_{0.15}\text{Cu}_{1.85}\text{V}_2\text{O}_7$, respectively. The crystals show clear cleaved facet [Fig. 1(c) and (f)] which was identified to be the crystallographic a -axis by the x-ray diffraction. The x-ray patterns around the cleaved facet of both samples are shown in Fig. 1(a) and (d). The Gaussian fits to the (200) Bragg peak (inset) yield the full-width at half-maximum (FWHM) as low as $0.12(1)^\circ$ and $0.10(1)^\circ$ for $x = 0.05$ and 0.15 , respectively, suggesting the high quality of the obtained crystals.

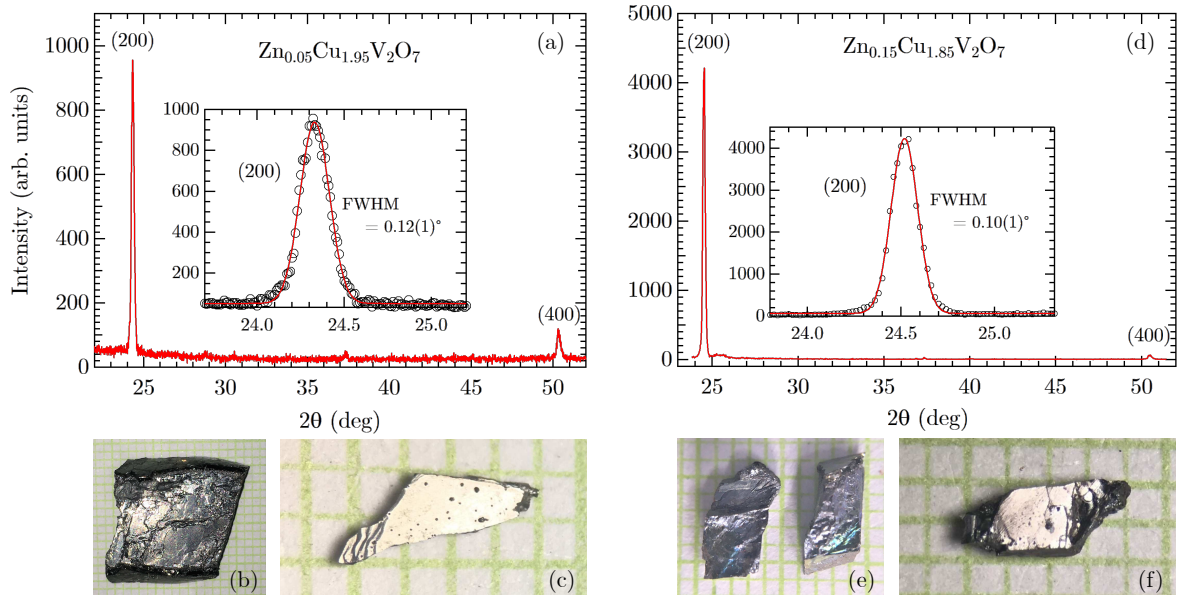


Figure 1. X-ray diffraction patterns showing θ - 2θ scans around the cleaved facet of (a) $\text{Zn}_{0.05}\text{Cu}_{1.95}\text{V}_2\text{O}_7$ and (d) $\text{Zn}_{0.15}\text{Cu}_{1.85}\text{V}_2\text{O}_7$. Insets show the Gaussian fit to the (200) peaks. The photographs of $\text{Zn}_{0.05}\text{Cu}_{1.95}\text{V}_2\text{O}_7$ and $\text{Zn}_{0.15}\text{Cu}_{1.85}\text{V}_2\text{O}_7$ are shown in (b) and (e) with the enlarged photographs showing the cleaved facet in (c) and (f), respectively.

In order to indentify the phase of the samples, small pieces of single crystals were collected and ground thoroughly into powder for the powder x-ray diffraction. The resulting XRD patterns, shown in Fig. 2, were refined by the Rietveld method with the structure of β - $\text{Cu}_2\text{V}_2\text{O}_7$ reported previously [16]. These results revealed that, in the Zn-doped single crystal samples, the structural transformation between the orthorhombic α phase and the monoclinic β phase started to occur as low as the doping concentration of $x = 0.05$. We note that our XRD on the powder sample of $\text{Zn}_{0.05}\text{Cu}_{1.95}\text{V}_2\text{O}_7$ i.e., starting material for single crystal growth, showed pure α phase without any trace of the β phase peaks (not shown here) which is consistent with those reported in Ref [10]. This is in contrary to the previous studies on polycrystal samples where the structural phase transition occurred at the doping concentration of $x \approx 0.15 - 0.2$ [10, 14], suggesting that the doping of Zn is more effective in single cryatals than in the polycrystal samples.

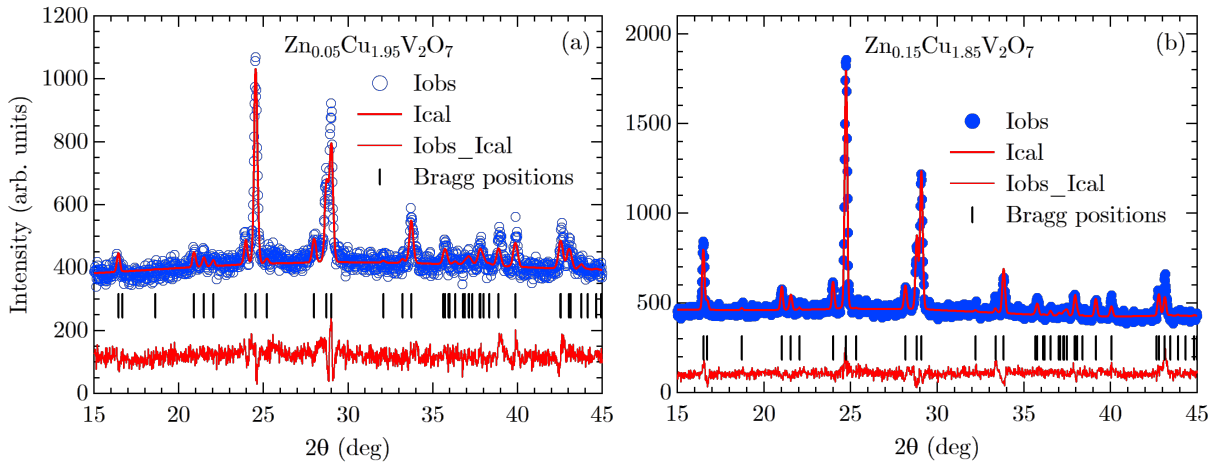


Figure 2. XRD patterns and the Rietveld refinements on the ground single crystals of (a) $\text{Zn}_{0.05}\text{Cu}_{1.95}\text{V}_2\text{O}_7$ and (b) $\text{Zn}_{0.15}\text{Cu}_{1.85}\text{V}_2\text{O}_7$.

Table 1 below summarizes the resulting refinement parameters from both samples. It can be seen that the crystallographic axes tend to increase, while the angle β tend to decrease, as the doping concentration was decreased. However, compared to the structure on the reported β - $\text{Cu}_2\text{V}_2\text{O}_7$, the lattice parameters of both samples are not substantially deviated from those values. We note that further study with lower doping as $0.01 \leq x < 0.05$ on the single crystal samples are required in order to study the structural phase transition on $\text{Zn}_x\text{Cu}_{2-x}\text{V}_2\text{O}_7$.

Table 1. Refined parameters from the powder x-ray diffraction of the ground crystals of $\text{Zn}_{0.05}\text{Cu}_{1.95}\text{V}_2\text{O}_7$ and $\text{Zn}_{0.15}\text{Cu}_{1.85}\text{V}_2\text{O}_7$ in comparison with the β - $\text{Cu}_2\text{V}_2\text{O}_7$.

	$\text{Zn}_x\text{Cu}_{2-x}\text{V}_2\text{O}_7$		β - $\text{Cu}_2\text{V}_2\text{O}_7$	
	$x = 0.05$	$x = 0.15$	Ref [10]	Ref [16]
$a(\text{\AA})$	7.7228(5)	7.6762(3)	7.718	7.6890
$b(\text{\AA})$	8.0605(8)	8.0558(5)	8.044	8.0289
$c(\text{\AA})$	10.145(1)	10.1040(6)	10.140	10.1065
$\beta(^{\circ})$	110.190(9)	110.360(6)	110.3	110.252
χ^2	1.5	1.6	-	-

4. Summary

We have been successfully able to grow single crystals of the $\text{Zn}_x\text{Cu}_{1-x}\text{V}_2\text{O}_7$ system with $x = 0.05$ and 0.15 by the vertical gradient freezing technique using a modified in-house furnace. The crystal structures of both samples are reminiscent of the β phase of $\text{Cu}_2\text{V}_2\text{O}_7$ despite the slightly different values of lattice parameters. Both samples are of good quality suggested by the x-ray diffraction on the cleaved facet, which is the crystallographic a -axis. The structural phase transition occurred as low as the doping concentration of $x = 0.05$ which is much lower than the values of $x \approx 0.15 - 0.20$ in previous studies suggesting a more effective doping in the single crystal samples. This study is beneficial for further magnetic properties study on the β phase structure of $\text{Cu}_2\text{V}_2\text{O}_7$ which was proposed to be an antiferromagnetic honeycomb lattice. We also note that lower substitution of the nonmagnetic Zn on the magnetic Cu ions is required in order to explore the structural phase transition between the α and β phase, as well as their magnetic properties, of $\text{Zn}_x\text{Cu}_{1-x}\text{V}_2\text{O}_7$ in single crystal samples.

5. Acknowledgement

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6. References

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