

Synthesis and Characterization of the Doped Orthoferrite $\text{HoFe}_{0.5}\text{V}_{0.5}\text{O}_3$

Josefa Gregorio, Lorena Aguirre, Jesus Perez, and Alejandro Zafra

Abstract

Based on published reports on the chemical substitution, or doping, of transition metal ions such as Cr^{3+} and Ni^{3+} into HoFeO_3 perovskite orthoferrites, we investigate the consequences of substituting V^{3+} into HoFeO_3 in order to create $\text{HoFe}_{0.5}\text{V}_{0.5}\text{O}_3$. Although HoVO_3 perovskite orthovanadates has been studied in the literature, other work has been done on examining whether a hybrid between the two can be achieved. We synthesized the new doped compound via solid state reaction and studied its physical characteristics using X-ray diffraction, electrical measurement, magnetic measurements, and heat capacity measurement.

Introduction

The magnetic properties of materials are largely determined by the orientation of the quantum mechanical spins of the electrons. The spins interact to form a net magnetic order, or in some cases disorder, which depends on variables including the material's chemical composition, molecular geometry, and the ambient temperature. For example, iron's ferromagnetic nature arises because the majority of its spins naturally align in the same direction [1]. Controlling the orientation of these spins can therefore lead to drastic changes in magnetic properties and offers application potential for consumer electronic devices. For instance, the alignment of spins can act as a memory state or can act as a sort of polarizer that valves electrical current on and off [2]. Whereas everyday electronic devices depend on electrical charge and current to perform computational operations, so-called spintronic devices would use the associated magnetic spins to perform these tasks, which could possibly lead to quantum computing and nanotechnology with increased processing speed, decrease in power consumption, and increased integration compared to today's semiconductor devices [3].

There has been recent interest in rare-earth orthoferrites because of their magnetic properties and potential to create new spintronic devices. They have a chemical compound form RFeO_3 , where R stands for rare earth ion, and have a distorted perovskite structure (**Fig. 1**) [3]. They contain two different magnetic ions, Fe^{3+} and R^{3+} . This indicates that there are three magnetic interactions R^{3+} - R^{3+} , R^{3+} - Fe^{3+} , and Fe^{3+} - Fe^{3+} , which induces various magnetic phase transitions [5]. The most notable interaction is a spin reorientation (SR) transition by which the most favorable magnetic spin configuration changes based on the temperature of the crystal. The orientation of the strong interacting spins of the R^{3+} - Fe^{3+} determines the temperature of the SR transition [5]. In the holmium (Ho) based orthoferrites (HoFeO_3), the SR transition temperature is approximately 50 Kelvin (K). The substitution of Cr^{3+} into the Fe-sites was reported to increase the SR transition temperature to 150 K [6]. However, when substituting Ni^{3+} , there was no noticeable effect on the SR transition temperature [7]. Since Cr and Ni are on the same row of the periodic table near Fe, we hypothesized that V^{3+} would also stabilize into the orthoferrite

structure. The literature shows that the orthovanadate HoVO_3 also has a SR transition at 40K and a Neel temperature transition at 110-114 K, where the magnetic order changes from antiferromagnetic to paramagnetic [8,9,10]. However, a doping between holmium-based orthoferrite and orthovanadate had yet to be reported into the literature. We therefore created the hybrid compound $\text{HoFe}_{0.5}\text{V}_{0.5}\text{O}_3$ in an attempt to observe a shift in either the SR transition temperature or the Neel transition temperature.

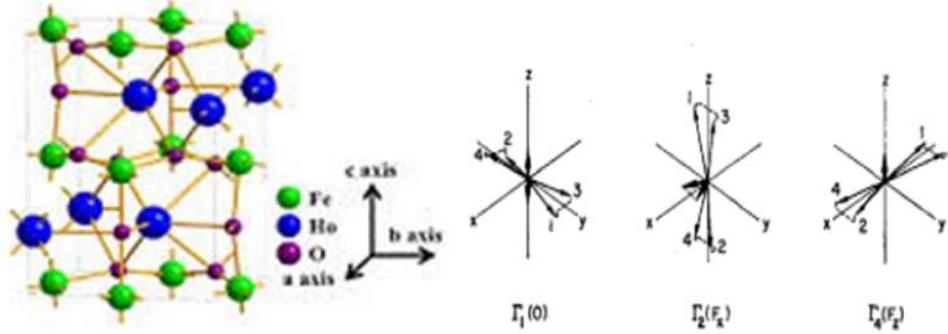


Fig. 1. The perovskite structure of orthoferrites (left) [4]. The neighboring interactions between the Fe sites dominate the order at lower temperatures, and the Fe-Ho interaction dominates at higher temperatures. Possible spin orientations for orthoferrites are shown in the right [3].

Chemical Synthesis

The polycrystalline compounds of the HoFeO_3 and $\text{HoFe}_{1-x}\text{V}_x\text{O}_3$ (where $x = 0.5$) were prepared by solid state reaction method using purity > 99.9% powders of Ho_2O_3 , Fe_2O_3 , and VO_2 as starting materials [5,6]. The proper stoichiometric ratios were weighed and ground via mortar and pestle. The mixtures were pressed into a pellet and underwent a heat treatment process. The compounds were annealed at 1200 C for 12 hours, re-ground, re-pressed, and annealed again at 1400 C for 24 hours [5].

Results and Discussion

Vibrating sample magnetometer (VSM), electrical transport option (ETO), and heat capacity (HC) measurements were performed on a Quantum Design VersaLab Physical Properties Measurement System. X-Ray diffraction measurements were performed on a Rigaku Mini. MATLAB software was used to process all the data.

X-ray Diffraction Measurement

X-ray diffraction is the experimental technique whereby X-rays are scattered off crystal structures in such a way as to create wave interference patterns that can be detected. Crystal planes reflect the X-rays in such a way as to create measurable interference peaks. Powder X-ray diffraction was performed on the $\text{HoFe}_{0.5}\text{V}_{0.5}\text{O}_3$ compound by recording reflected X-rays at angles from 12-90° around the sample. The pattern (**Fig. 2**) was then compared to the published diffraction patterns of HoFeO_3 [6] and VO_2 , [11] which was used to synthesize the new

compound. The comparisons show that the patterns do not well match with VO_2 [11] but do align with HoFeO_3 [6]. This suggests that the new compound does have an orthoferrite structure and that the vanadium was properly stabilized within it, meaning that we were successful in creating a new crystal compound. Table 1 compares some of the positions of peaks at various 2θ angles read off from the patterns.

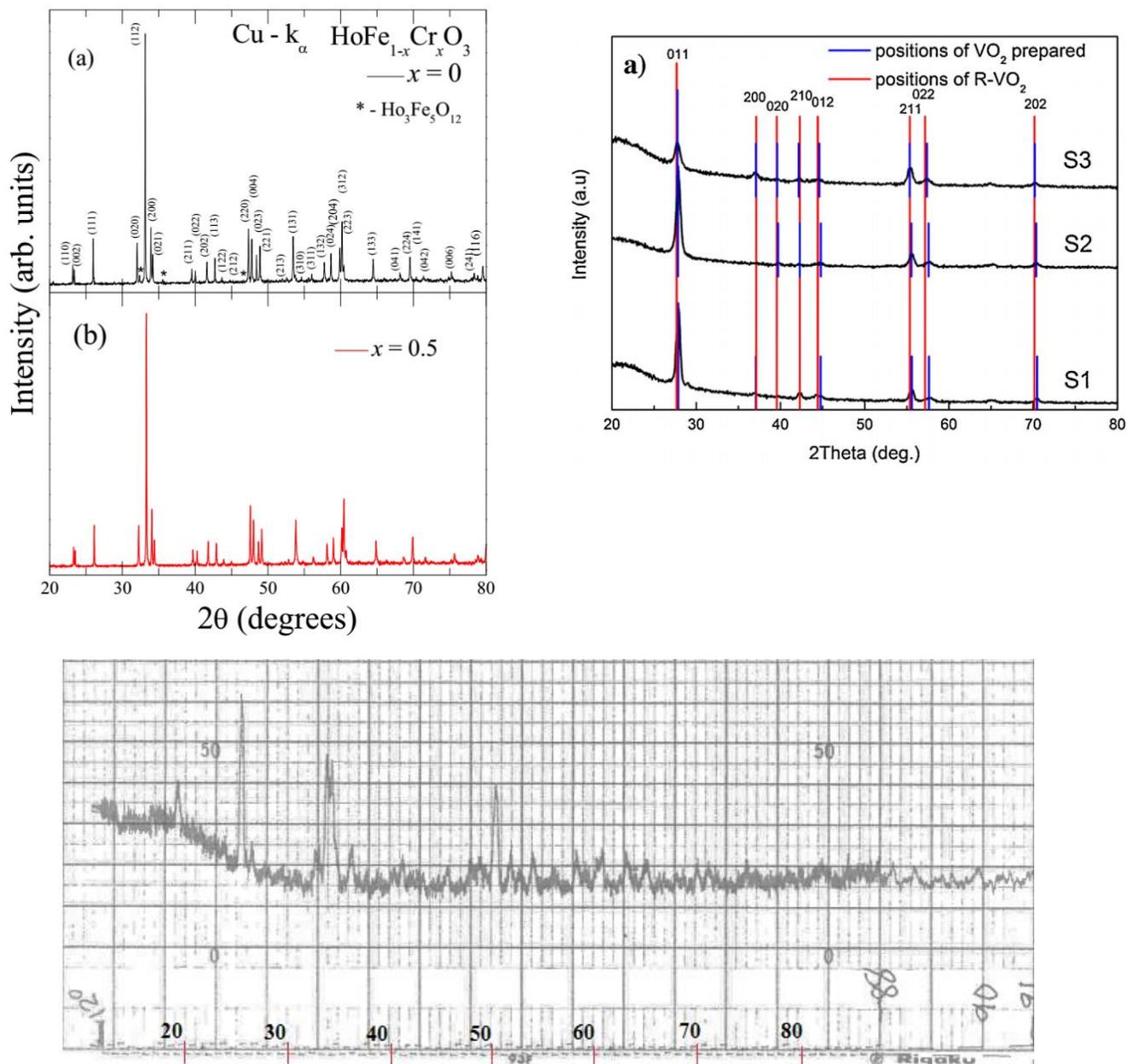


Fig. 2. Upper left: X-ray diffraction patterns for a) HoFeO_3 and b) $\text{HoFe}_{0.5}\text{Cr}_{0.5}\text{O}_3$ [6]. Upper right: X-ray diffraction pattern for VO_2 [11]. Bottom: Measured X-ray diffraction pattern for newly synthesized $\text{HoFe}_{0.5}\text{V}_{0.5}\text{O}_3$

<i>Table 1</i>	2θ (degrees)													Reference	
HoFe _{0.5} V _{0.5} O ₃		25.5		33	34		41	46	48	52	58.5	61	65		
HoFeO ₃	24	26		33			40		48	54		60			[8]
HoFe _{0.5} Cr _{0.5} O ₃	24	26		33	34		41		48	54		60	65		[8]
VO ₂			28			37	42	44		56	57			70	[11]

Table 1. Comparisons of dominant X-ray peak positions from **Fig. 2** showing little correlation of the newly synthesized compound to VO₂, suggesting that a new crystal has been stabilized.

VSM Measurement

The Vibrating Sample Magnetometer (VSM) measures the sample's magnetic moment by oscillating the sample in a fixed magnetic field, thereby inducing voltage in the VSM sense coils in accordance with Faraday's law of magnetic induction [12]. Magnetization vs. temperature (MvT) was recorded in the temperature range of 50 K – 300 K. **Fig. 3** shows the zero-field-cooled (ZFC) and field-cooled (FC) MvT data for the parent and V-based compound. An applied magnetic field is required to measure a magnetic response, but this field could also influence the net magnetic order of the system. Hence, the control sequence for the measurement begins with ZFC, the sample is cooled to 50 K in the absence of applied magnetic field. A magnetic field of 1000 Oe, which is approximately 20 times stronger than the magnetic field of a refrigerator magnet [13], is then applied, and the magnetic response of the sample is measured as the sample is warmed to 300 K. A “bump” in the magnetic moment is observable in both compounds, below 100 K [6]. This is associated with the SR transition, where the net total magnetic orientation rotates such that the peak moment value corresponds to maximum alignment with the applied magnetic field. The field is continued to be applied as the sample is then cooled for the FC measurement. Because the applied magnetic field has “locked” the behavior of the spins upon cooling, the FC measurement does not show the SR transition feature.

The SR transition in the doped compound is observed at a similar temperature to that of the parent orthoferrite compound. This suggests that the V substitution does not interfere with the Fe-Fe interactions in the crystal, which is reasonable considering that V has a smaller magnetic moment than Fe [6, 8]. Also, the data plotted as emu/g is the net magnetization per mass, which is an intrinsic property of the crystal. The lower overall values in the V-based compound in comparison to the parent compound is further evidence that we have stabilized a new crystal.

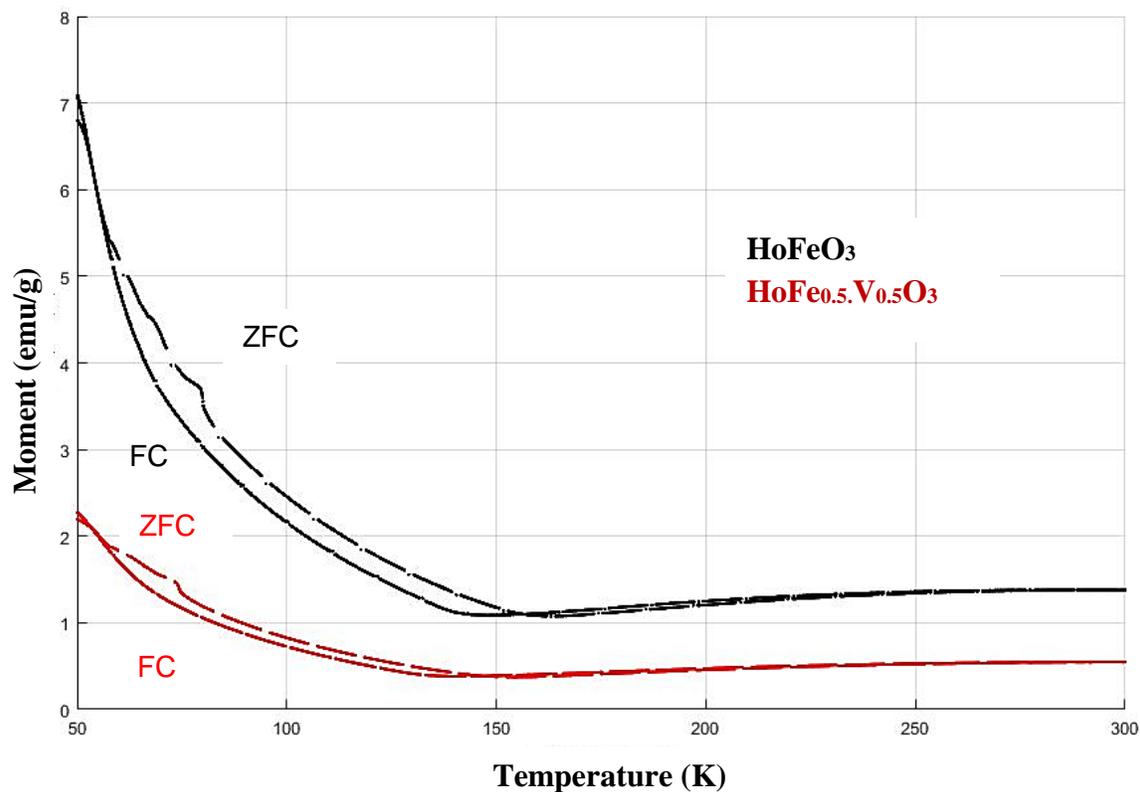


Fig. 3. Magnetization vs. temperature where the SR transition is seen in the zero field cool (ZFC) data below 100 K for both the parent and V-based compound. This graph indicates that that V-based compound is weaker because it has a smaller moment.

Heat Capacity Measurement

Heat capacity (HC) is the thermal energy required to change the temperature of a substance by 1 K. The sample is attached to a small heater system, and the temperature of the sample is measured during and after the application of a heat pulse. When plotting HC vs. temperature, a phase transition can be identified by a peak in the plot because the applied thermal energy goes into the chemical bonds to change the structure. This transition occurs in solid-liquid-gas phase, and it also occurs in crystalline structural transitions. We measured the HC of the $\text{HoFe}_{0.5}\text{V}_{0.5}\text{O}_3$ sample under an applied magnetic field of 1000 Oe from 50 K – 200 K (**Fig. 4**) to see whether the SR transition was observable. No such transition was observed, nor was any Neel transition observable in the HC data [8, 9]. This is not necessarily unexpected, since the heat capacity of a material depends on several vibrational interactions within the compound, and the signatures of the SR transition may very well be masked by these other vibrations.

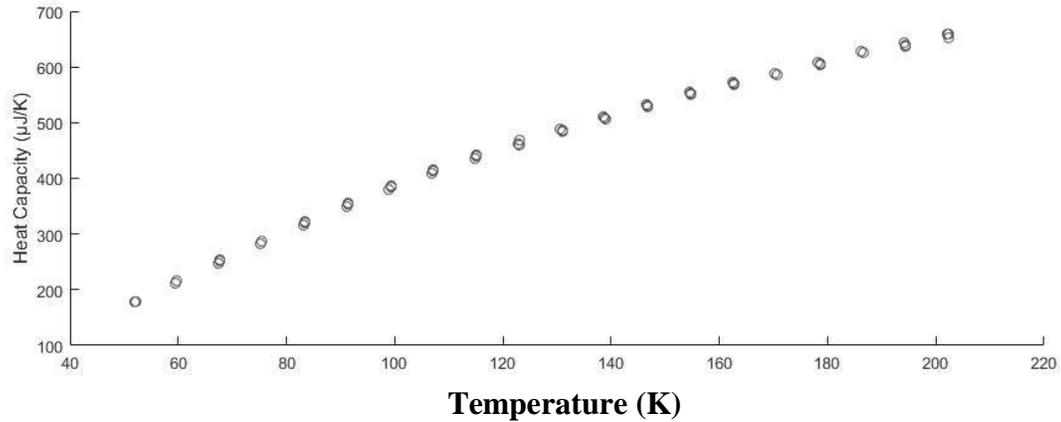


Fig. 4. Heat capacity in the temperature range 50-200 K with 1000 Oe applied magnetic field. No unusual physical characteristics are observed.

Heat capacity was also measured from 200 K to 388 K (**Fig.5**), which required a different instrument mounting. No magnetic field was applied. The data is noisy above 300 K, which unfortunately has been characteristic of our instrument. No sharp peaks are visible in the data, though whether a feature actually exists near 340 K requires further investigation. The $\text{HoFe}_{0.5}\text{V}_{0.5}\text{O}_3$ crystal was synthesized using VO_2 , and the presence of an impurity due to unreacted VO_2 is expected to result in a large HC peak near 340 K due to its phase transition between an electrically conducting and insulating state [11,12]. Due to the noise in the reading, this remains inconclusive without further investigation.

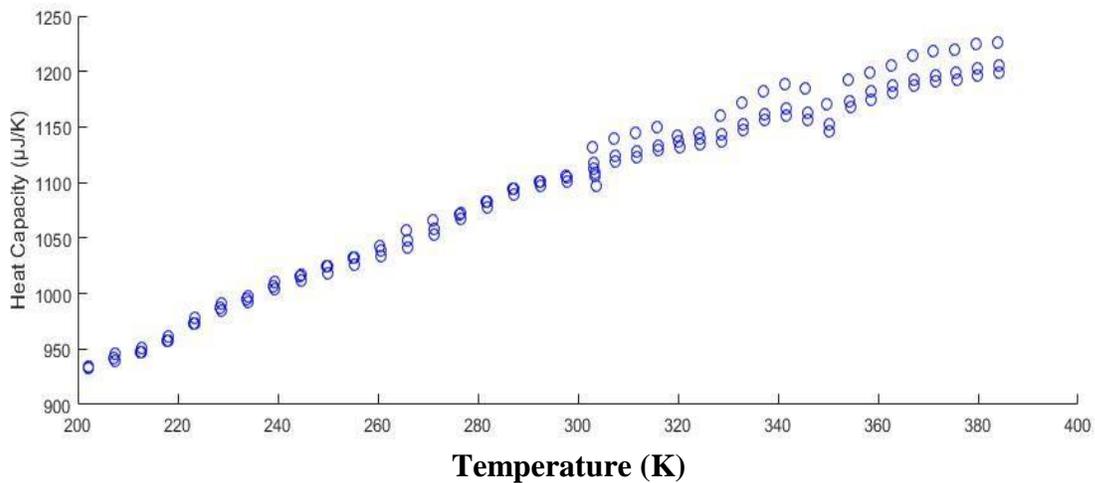


Fig. 5. Heat capacity at the temperature range 200-388 K. Although noisy, no strong phase transition can be observed at higher temperatures, which is in favor of the stabilization of the new crystal.

Resistivity Measurement

The electrical resistance of a material can reveal properties that include the nature of its charge carriers (e.g., free electrons), the scattering of these carriers, and interaction with the crystal lattice, as well as other possible behaviors especially under the presence of an applied magnetic field. Two platinum wires were attached to the sample using silver paint, and a measurement of the electrical resistance was performed using a lock-in amplifier, which is a low noise voltage measurement device. The $\text{HoFe}_{0.5}\text{V}_{0.5}\text{O}_3$ resistance was too high to be measured, indicating that the crystal is an insulator. It is significant to note that VO_2 does have a measurable resistance since it undergoes a metal-insulator transition at approximately 340 K [8,15], and by measuring such a high resistance for our sample, it offers further evidence, though not conclusively, that we have a new crystal and not simply an un-reacted mixture of HoFeO_3 and VO_2 .

Conclusion

We have synthesized a new compound $\text{HoFe}_{0.5}\text{V}_{0.5}\text{O}_3$ and have investigated its physical properties. The results of X-ray diffraction suggest that the crystal is a stabilization of vanadium within the HoFeO_3 structure, even though heat capacity measurements are inconclusive. However, our electrically insulating material exhibits a magnetic spin reorientation transition similar to that of HoFeO_3 but with smaller net magnetic ordering, which also suggests that we have stabilized a new crystal that incorporates the small magnetic moment of V within the Fe matrix. Further work will include performing more heat capacity measurements to resolve the noise issue, and varying the V doping ratios in order to investigate what physical and chemical properties lie hybrid between HoFeO_3 and HoVO_3 .

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