

Structural phase transitions of spinel compound $(\text{Fe}_{1-x}\text{Zn}_x)\text{V}_2\text{O}_4$

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Introduction

FeV_2O_4 has a normal spinel structure, in which Fe^{2+} and V^{3+} ions are located at the tetrahedral (A-site) and octahedral (B-site) sites, respectively. This compound has orbital degrees of freedom at both Fe^{2+} and V^{3+} ions and exhibits successive structural phase transitions from cubic to tetragonal ($a < c$) at 140 K, from tetragonal to orthorhombic at 110 K, and from orthorhombic to tetragonal ($c < a$) at 60 K for polycrystalline sample [1]. It was suggested that the possible scenario of the successive structural transition below 110 K is the competition and cooperation of Fe^{2+} and V^{3+} orbital, however, the origin is still unknown. In this study, we investigate the A-site substitution effect of Fe^{2+} by Zn^{2+} , which does not have orbital degrees of freedom, on the structural phase transition of FeV_2O_4 .

Experimental

The $(\text{Fe}_{1-x}\text{Zn}_x)\text{V}_2\text{O}_4$ powder samples were prepared by heating the mixture of high purity Fe, Fe_2O_3 , ZnO and V_2O_3 in an evacuated sealed quartz tube. The powder diffraction experiments were performed using a high-resolution diffractometer installed at a beam line of BL-6C station. A wavelength of incident beam used was 1.20 Å. A flat Si(111) crystal analyzer was used in order to improve the angular resolution. The temperature dependence of the profile patterns around 111, 400 and 440 reflection was measured using 2θ scanning mode.

Results and discussion

Figure 1 shows the temperature dependence of powder diffraction profiles of the $(\text{Fe}_{1-x}\text{Zn}_x)\text{V}_2\text{O}_4$ in the 2θ range around 400 reflection, where the indices of Bragg reflections are based on the cubic structure. For $x = 0.1$ (Fig. 1(a)), the single peak is split into two peaks (tetragonal-HT phase with $c/a < 1$) at 110 K, and split into three peaks (orthorhombic phase) at 90 K, and then becomes two peaks (tetragonal-LT phase with $c/a > 1$) at 60 K with decreasing temperature. This successive structural transition is similar to that observed in FeV_2O_4 . The transition temperature of cubic-to-tetragonal-HT and tetragonal-HT-to-orthorhombic is lower than that of FeV_2O_4 , however, that of orthorhombic-to-tetragonal-LT is almost the same as that of FeV_2O_4 . For $x = 0.2$ (Fig. 1(b)), the clear structural transition of the cubic-to-tetragonal-HT transition is not observed, which is attributed to weakening the cooperative Jahn-teller effect of Fe^{2+} due to the substitution of Zn^{2+} at A-site. The orthorhombic phase appears below ~80 K, and it becomes tetragonal-LT phase below ~60 K. For $x = 0.3$ (Fig. 1(c)), the structural transition seems to be from cubic to directly

tetragonal-LT, i.e., neither tetragonal-HT nor orthorhombic phase appears, which is surprising result. The detailed analysis such as the lattice constant are now in progress.

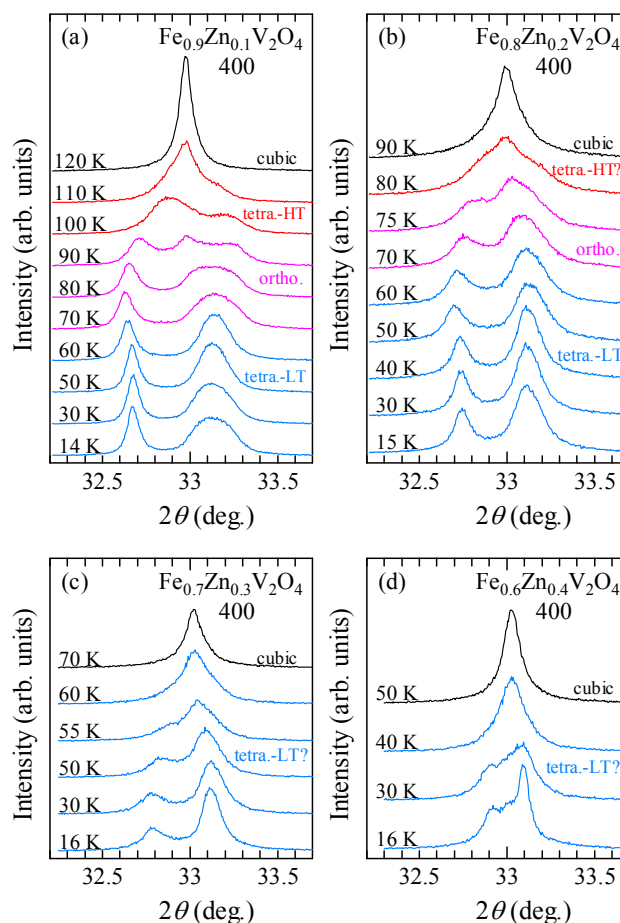


Fig. 1. Temperature dependence of powder X-ray diffraction patterns of $(\text{Fe}_{1-x}\text{Zn}_x)\text{V}_2\text{O}_4$ on heating in the 2θ range around 400 reflection for (a) $x = 0.1$, (b) $x = 0.2$, (c) $x = 0.3$ and (d) $x = 0.4$.

References

- [1] T. Katsufuji et al., J. Phys. Soc. Jpn. 77, 053708 (2008).

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