

Charge ordered microdomains in Cr doped AlV_2O_4

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We examined effect of the Cr doping on the stable charge ordering (CO) in the spinel compound AlV_2O_4 , which shows a metal-insulator transition accompanying the formation of the CO structure at 700K, by transmission electron microscopy. It is found that large CO domains in AlV_2O_4 changed drastically into the CO microdomains with the size of 10-20nm in $\text{AlV}_{2-x}\text{Cr}_x\text{O}_4$ with $x=0.125$. On the other hand, it is revealed that the introduction of the surplus oxygen (δ) into AlV_2O_4 destroys the stable CO structure with the modulation vector of $q=1/2[111]$ and induced new modulated structure with the modulation vector of $q=1/3[110]$.

Key words: Spinel compound, charge ordering, Cr doping effect, transmission electron microscopy

1. INTRODUCTION

Spinel compounds have the chemical composition AB_2O_4 and crystallize in the cubic, face-centered space group $\text{Fd}\bar{3}\text{m}$, where A and B atoms are metals located on the tetrahedral and octahedron sites, respectively, as shown in Fig.1(a). The B metal atom in the spinel structure forms an infinite three-dimensional lattice of corner-sharing tetrahedral. In particular, spinel structure involves both a triangle lattice and a *Kagome* lattice, on which geometrical spin configuration gives rise to some anomalous magnetic properties.[1,2] On the other hand, in case of spinel compounds with mixed-valence ions such as Fe_3O_4 and CuIr_2S_4 , the CO structure appears in the low-temperature phase.[3,4]

According to the recent work by Matsuno et al., the AlV_2O_4 compound with mixed-valence takes place a structural phase transition from the high-temperature cubic phase (space group: $\text{Fd}\bar{3}\text{m}$) to the low-temperature rhombohedral one ($\text{R}\bar{3}\text{m}$) around 700K with a thermal hysteresis.[5] Simultaneously, the charge ordering (CO) transition occurred, which is coupled with the appearance of the rhombohedral phase around 700K on cooling. It is pointed out from x-ray diffraction experiment that the CO structure in AlV_2O_4

is characterized as a unique spatial configuration of three $\text{V}^{2.5+3\delta}$ ions and one $\text{V}^{2.5-\delta}$ ion, which are separated from four $\text{V}^{2.5+\delta}$ ions on the tetrahedron.[5] Note that δ represents the magnitude of a deviation from the average valence ($\text{V}^{2.5+}$) of the V ion in AlV_2O_4 . One possible origin of the appearance of the stable CO structure in AlV_2O_4 is discussed in terms of the “charge frustration”. [6] Furthermore, the recent magnetic and electric measurements revealed that the substitution of Cr ions for V ones in AlV_2O_4 suppressed the appearance of the stable CO structure. [6]

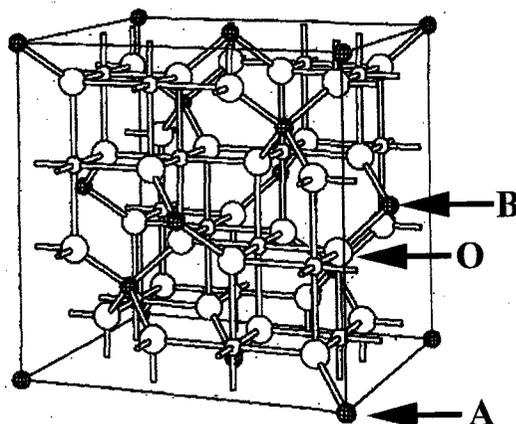


Figure 1: Crystal structure of spinel compounds. In AlV_2O_4 , A and B corresponds to Al and V ions, respectively.

In this paper, we clearly demonstrate how the stable CO in AlV_2O_4 is destroyed by both the substitution of the Cr ions for the V ones and the introduction of the surplus oxygen by means of the transmission electron microscopy. As the Cr concentration (x) is increased, the superlattice spots at the $1/2\ 1/2\ 1/2$ -type positions, which characterize the CO structure, change into the diffuse scatterings around the $1/2\ 1/2\ 1/2$ -type positions. Real-space images related to the CO structure clearly shows fine mixture of the CO and charge disordered microdomains with the size of 10-20nm. On the other hand, the surplus oxygen destroyed the stable CO structure with the modulation vector of $q=1/2[111]$ and induced new modulated structure with the modulation vector of $q=1/3[110]$.

2. EXPERIMENTAL METHOD

We prepared polycrystalline samples of both $\text{AlV}_2\text{O}_{4+\delta}$ and $\text{AlV}_{2-x}\text{Cr}_x\text{O}_4$ with $x=0.0, 0.075, 0.1125, 0.125$ and 0.20 by standard solid-state reactions. The observation was carried out by using the JEM-2010 transmission electron microscopy (TEM) at room temperature. Changes in the CO structure by both the Cr substitution and the introduction of the surplus oxygen were investigated by obtaining both various electron diffraction (ED) patterns and real-space images related to the CO structure. In particular, the microstructures related to the CO structure in $\text{AlV}_{2-x}\text{Cr}_x\text{O}_4$ were obtained by using the superlattice spots characterizing the CO structure. Note that indexes in the ED patterns are based on the high-temperature cubic spinel structure with the space group of $Fd3m$. Physical properties in $\text{AlV}_{2-x}\text{Cr}_x\text{O}_4$ such as resistivity, magnetic susceptibility and specific heat have been reported in our previous paper. [6] Here, variations of the microstructure due to the CO structure by both the Cr substitution and the introduction of the surplus oxygen were carefully investigated.

3. RESULTS AND DISCUSSION

To characterize the crystal structure of the CO phase appearing below 700K, we carefully examined various ED patterns in the CO structure of AlV_2O_4 and

it is found that the CO structure is characterized by the presence of the superlattice spots at the $1/2\ 1/2\ 1/2$ -type positions, in addition to the fundamental spots due to the cubic spinel structure with the space group of $Fd3m$. As a result, a complete reciprocal lattice in the CO phase of AlV_2O_4 was obtained. From our careful analysis of the ED patterns, it is concluded that the CO phase in AlV_2O_4 has a rhombohedral structure with the space group of $\overline{R3m}$.

In order to clarify how the stable CO structure in AlV_2O_4 is destroyed by the Cr substitution, changes in intensities of the superlattice spots at the $1/2\ 1/2\ 1/2$ -type positions were examined by obtaining ED patterns along the various $[110]$ -type zone axes. Figure 2 shows typical ED patterns with the incident beam parallel to the $[110]$ direction, which were obtained at room temperature. The CO structure of AlV_2O_4 is characterized by the presence of the superlattice spots with rather strong intensity at the $1/2\ 1/2\ 1/2$ -type positions, as evident in Fig. 2(a). Thus, we prepared some $\text{AlV}_{2-x}\text{Cr}_x\text{O}_4$ compounds with several Cr concentrations and examined carefully changes in intensities of the CO superlattice spots at room temperature. Figures 2(b) and 2(c) show ED patterns at room temperature obtained in the $\text{AlV}_{2-x}\text{Cr}_x\text{O}_4$ compounds with $x=0.125$ and 0.20 , respectively. As clearly can be seen in Fig. 2(b) obtained from the $\text{AlV}_{2-x}\text{Cr}_x\text{O}_4$ compound with $x=0.125$, there exist the CO superlattice spots with weak intensity in the ED pattern with the incident beam parallel to the $[110]$ direction. As the Cr concentration (x) was increased, it is found that intensities of the CO superlattice spots became weaker and changed into diffuse scattering at $[1/2\ 1/2\ 1/2]$ -type positions along $[111]$ and $[-1-11]$ directions, as shown in Fig. 2(c). The coherent length estimated from the half-width of the superlattice spots in Fig. 2(c) were about 10~20 nm.

In order to elucidate variations of microstructures related to the CO by the Cr substitution, we carefully examined dark-field images obtained by using the superlattice spots due to the CO at room temperature. Figure 3 shows typical microstructures obtained in AlV_2O_4 and Cr-doped AlV_2O_4 . In the CO phase of

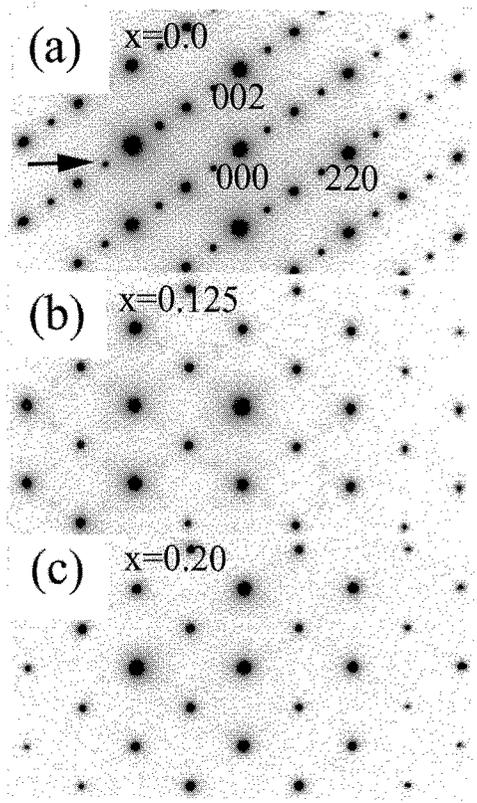


Figure 2: Electron diffraction patterns at room temperature in (a) $x=0.0$, (b) $x=0.125$, (c) $x=0.20$, respectively. The beam incidence is parallel to the $[1-10]$ direction.

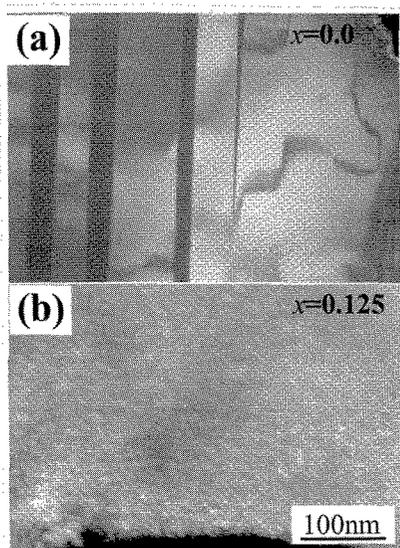


Figure 3: Microstructures related to the charge ordered state in (a) $x=0.0$ and (b) $x=0.125$, respectively. The images were obtained at room temperature.

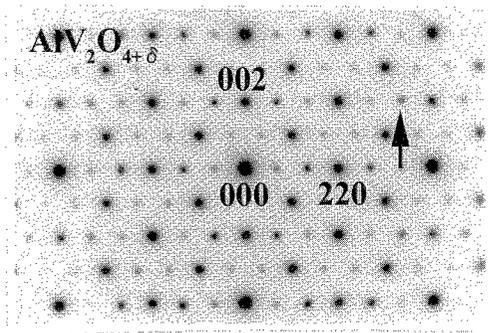


Figure 4: (a) Electron diffraction pattern obtained at room temperature in $\text{AlV}_2\text{O}_{4-\delta}$.

AlV_2O_4 , large CO domains, together with the rhombohedral twin structure, are formed below the CO transition temperature of 700K, as shown in Fig. 3(a). On the other hand, it is found that the large CO domains in AlV_2O_4 change drastically into the CO microdomains with the size of 10~20 nm in $\text{AlV}_{2-x}\text{Cr}_x\text{O}_4$ with $x=0.125$. Figure 3(b) is a typical microstructure related to the CO obtained in $\text{AlV}_{2-x}\text{Cr}_x\text{O}_4$ with $x=0.125$ at room temperature. The sparkle regions with the bright contrast correspond to the CO microdomains and, on the other hand, the regions with the dark contrast should be regarded as the charge disordered microdomains. This implies that the CO state in $\text{AlV}_{2-x}\text{Cr}_x\text{O}_4$ with $x=0.125$ is characterized as a fine mixture of the CO and the charge disordering microdomains with the size of 10-20 nm.

We investigated effect of the introduction of the surplus oxygen in $\text{AlV}_2\text{O}_{4+\delta}$ on the CO structure. It was found that the stable CO structure characterized by the presence of the superlattice spots at the $1/2[111]$ positions disappeared and new modulated structure with the modulation vector of $q=1/3[110]$ were formed. Figure 4 displays the ED patterns obtained in $\text{AlV}_2\text{O}_{4+\delta}$ at room temperature. As indicated by an arrow in Fig.4, new superlattice spots at the $(1/3\ 1/3\ 0)$ -type positions can be seen clearly. From these experimental results obtained in this work, both the Cr substitution and the surplus oxygen have strong influence on the stable CO structure appearing around 700K, accompanying the structural phase transition from the cubic phase to the

rhombohedral one.

4. SUMMARY

We investigated the stability of the CO structure in AlV_2O_4 by both the substitution of the Cr ions for the V ones and the introduction of the surplus oxygen. The stable CO structure with the long-ranged coherence rapidly destroyed and changed into the short-ranged CO in the case of the Cr substitution. The real space images reveal the fine mixed state of the charge ordered and the charge disordered microdomains with the size of 10-20nm. On the other hand, the surplus oxygen destroyed the CO structure and induced the new modulated structure with the modulated vector of $q=1/3[110]$.

5. ACKNOWLEDGEMENT

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