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The stabilization of the highest oxidation states of transition metals under oxygen pressures: TiNiO_3 , a new Ni(III) perovskite—comparison of the electronic properties with those of TNiO_3 (T = rare earth and Y)

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Abstract

The crystal structure and the magnetic properties of TiNiO_3 have been characterized and compared with those of TNiO_3 (T = rare earth and Y). The electronic structure of Ni(III) has been investigated by Mössbauer spectroscopy. Through these analyses, the effects of the A-site ion on structural distortion, magnetic behaviour and electronic structure of Ni(III) in a perovskite have been discussed.

1. Introduction

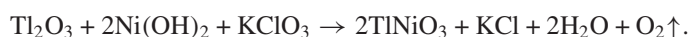
Since $\text{TNi}^{\text{III}}\text{O}_3$ perovskites (T = rare earth and Y) were first prepared under high-pressure conditions [1], much effort has been devoted to understand their structural and electronic properties [2]. Except for LaNiO_3 , all the $\text{TNi}^{\text{III}}\text{O}_3$ perovskites present a thermally driven metal–insulator (MI) transition. The transition temperature, T_{MI} , rises systematically as the rare-earth size becomes smaller [3]. For the large-rare-earth compounds (T = Pr, Nd, Sm and Eu), the crystal symmetry remains orthorhombic across T_{MI} . Below T_N , these compounds show an unusual antiferromagnetic order due to antiferromagnetic coupling of ferromagnetic Ni bilayers along the (111) direction in the pseudocubic lattice [4]. On the other hand, recent neutron diffraction studies for small rare-earth nickelates, TNiO_3 (T = Ho, Y, Er, Tm, Yb and Lu), have indicated a slight monoclinic distortion leading to the $P2_1/n$ space group at $T < T_{MI}$. Such a structural distortion implies two different Ni–O bonds resulting from a partial charge disproportionation of Ni(III): $2\text{Ni}^{3+} \rightarrow \text{Ni}^{(3+\alpha)+} + \text{Ni}^{(3-\alpha)+}$ [5, 6].

Recently we prepared a new Ni(III) perovskite, TiNiO_3 [7]. A post-transition-metal ion, Ti^{3+} , which has fully occupied 4f and 5d orbitals ($[\text{Xe}]4f^{14}5d^{10}6s^0$), is good to use in investigating the electronic effect of A-site cations. In this work, a comparative study was

performed on structural and magnetic properties for TiNiO_3 and TNiO_3 ($T = \text{rare earth or Y}$). Additionally, in order to examine whether the Ni(III) is disproportionated in the TiNiO_3 lattice as in TNiO_3 ($T = \text{Ho} \rightarrow \text{Lu}$), ^{57}Fe Mössbauer spectroscopy measurements for ^{57}Fe -doped TiNiO_3 were carried out.

2. Experimental details

The perovskite, TiNiO_3 , was prepared under high-pressure–high-temperature (HP–HT) conditions with a ‘belt’-type apparatus. The appropriate amount of Ti_2O_3 and $\text{Ni}(\text{OH})_2$ was mixed with an oxidizing agent, KClO_3 . The mixture was encapsulated in a gold tube with a diameter of 3 mm and heated at 700°C for 2–3 min under 7.5 GPa. The reaction expected in the HP–HT procedure is the following;



A ^{57}Fe -doped TiNiO_3 sample was prepared from Ti_2O_3 , $\text{Ni}_{0.98}\text{Fe}_{0.02}\text{O}$ and KClO_3 under similar pressure and temperature conditions. The precursor, $\text{Ni}_{0.98}\text{Fe}_{0.02}\text{O}$, was prepared by dissolving appropriate amounts of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and ^{57}Fe in 1 M nitric acid, and then precipitating in aqueous KOH (3 M) solution, washing with distilled water and drying at 300°C . After the HP–HT reaction, all the samples were quenched, washed with distilled water to remove the co-produced potassium chloride and then dried at 120°C .

The final products were characterized by powder x-ray diffraction (Philips PW 1050 diffractometer using graphite-monochromated $\text{Cu K}\alpha$ radiation). DC magnetic susceptibility was measured by a SQUID magnetometer (Quantum Design MPMS) in the temperature range from 5 to 300 K at 10 000 G after zero-field cooling. The ^{57}Fe Mössbauer spectra were recorded using a conventional constant-acceleration Mössbauer spectrometer. The radiation source $^{57}\text{Co}(\text{Rh})$ was kept at room temperature. All isomer shifts refer to the $\alpha\text{-Fe}$ absorber at 300 K.

3. Results and discussion

The x-ray diffraction profile for TiNiO_3 could be indexed using a primitive orthorhombic unit cell (space group $Pbnm$) with lattice parameters $a = 5.2549(1) \text{ \AA}$, $b = 5.3677(1) \text{ \AA}$, $c = 7.5620(2) \text{ \AA}$ [7]. The symmetry reduction from orthorhombic to monoclinic was not detected on the powder x-ray diffraction patterns. To compare the structural distortion for TiNiO_3 with those for isostructural series, TNiO_3 , the lattice parameters (a , b , c) are plotted as a function of the radius of T^{3+} ion (figure 1). We adopt the ionic radii ($\text{CN} = 8$) proposed by Shannon [8] for a comparison. For all orthonickelates except for TiNiO_3 , the lattice parameters change systematically with respect to the ionic radius of T^{3+} . The two lattice parameters a , c decrease gradually with decreasing rare-earth-ion size, while the b -parameter is nearly constant. The continuous variations give interpolated curves allowing us to predict the lattice distortion for the corresponding compound. However, a , b and c for TiNiO_3 deviate from these curves by +0.14, -0.13 and +0.22, respectively. In particular, c for TiNiO_3 is similar to that for SmNiO_3 although the Ti^{3+} ion is much smaller than the Sm^{3+} one. As a consequence, TiNiO_3 has a large unit-cell volume (213.3 \AA^3), which is comparable to that of YNiO_3 .

According to previous work [7], the twelve Ti-O bonds in TiNiO_3 are classified into approximately three groups (four short, four medium and four long distances), while in TNiO_3 ($T = \text{rare earth or Y}$) the T-O bonds fall into two groups of eight short and four long distances. The deviation in TiNiO_3 from the monotonic variation in structure for other nickelates might be caused by such a different coordination of Ti^{3+} ions.

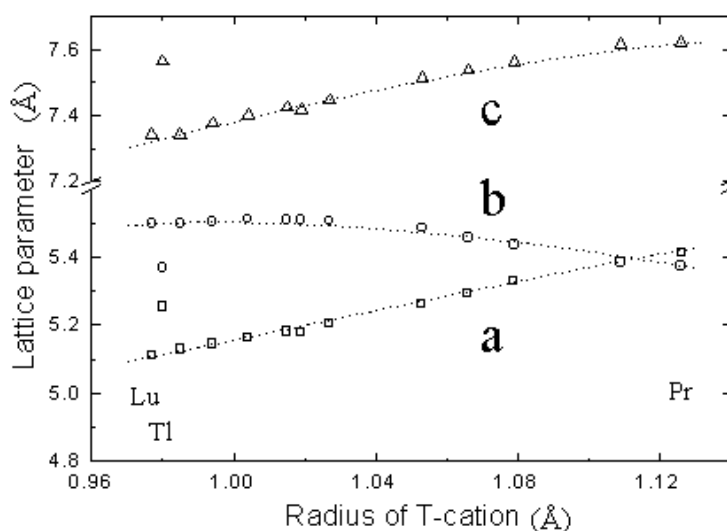


Figure 1. The relation between the ionic radius of the T cation and lattice parameters for TlNiO_3 and TNiO_3 [2, 6] ($T = \text{rare earth and Y}$).

The strongly covalent Tl–O bond also significantly affects the magnetism. TlNiO_3 has the lowest T_N (104 K) among all the nickelate perovskites, although the superexchange Ni–O–Ni angle (147.6°) is very similar to that observed in YNiO_3 (Ni–O–Ni angle $\approx 147.3^\circ$ and $T_N = 153$ K) [5].

In spite of such anomalous character of TlNiO_3 in structure and magnetism, it is found that the T_N -values for all orthornickelates including TlNiO_3 are strongly correlated with their crystallographic axial ratio, $c/a\sqrt{2}$. As shown in figure 2, the value of $c/a\sqrt{2}$ increases gradually on going from PrNiO_3 to LuNiO_3 and it is largest for TlNiO_3 in spite of the relatively large Tl^{3+} ionic size. This fact cannot be explained by A-site cation size alone. Moreover, a clear relation between the T_N -values and the corresponding ratio, $c/a\sqrt{2}$ is found for the various orthornickelates. T_N for all orthornickelates including TlNiO_3 decreases with increasing the value of $c/a\sqrt{2}$, all the points of T_N falling on a line within an error limit of 10 K.

This fact may be related to the electronic density around the A-site cation. The highly polarized electron density of the A-site cation was observed in several rare-earth perovskites [9, 10], which is due to the proximity of the rare-earth unfilled d and f states to their filled states. As the atomic number increases, the energy gap to neighbouring levels decreases, so the electron density would be redistributed via structural change. This effect is the most significant for TlNiO_3 due to the small energy gap between the filled 5d orbital and empty 6s one of Tl^{3+} . The strongly polarized Tl–O bonds might induce an elongation of the unit cell in the direction perpendicular to the mirror plane in the orthorhombic perovskite structure. It could also contribute to decreasing the Ni–O bond strength, leading to low T_N -values for TlNiO_3 in spite of the relatively large Ni–O–Ni superexchange angle compared to those for rare-earth orthornickelates. Consequently, the dependence of T_N on $c/a\sqrt{2}$ shows how the nature of the A-site cation affects the Ni–O bond in perovskite structure.

The electronic structure of Ni(III) in TlNiO_3 was probed by ^{57}Fe Mössbauer spectroscopy after replacement of a small amount (2%) of Ni by ^{57}Fe in the corresponding lattice. The participation of ^{57}Fe in the TlNiO_3 lattice was confirmed by magnetic measurement: T_N -values and magnetic susceptibilities χ_M were slightly modified by iron doping ($T_N = 94$ K for

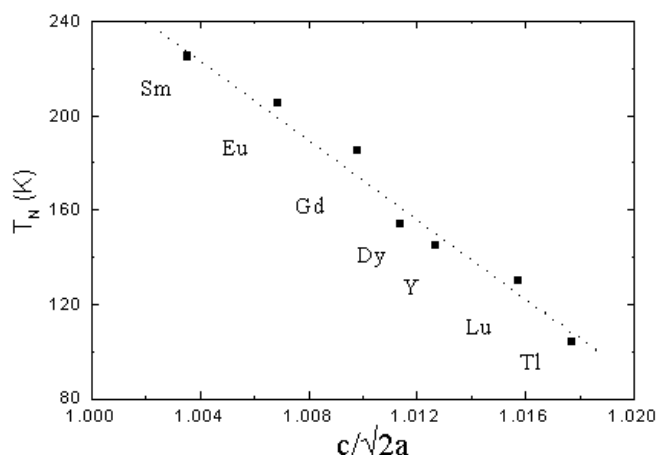


Figure 2. Evolution of T_N on the crystallographic axial ratio, $c/a\sqrt{2}$, for TlNiO_3 and TlNiO_3 [2, 6] (T = rare earth and Y).

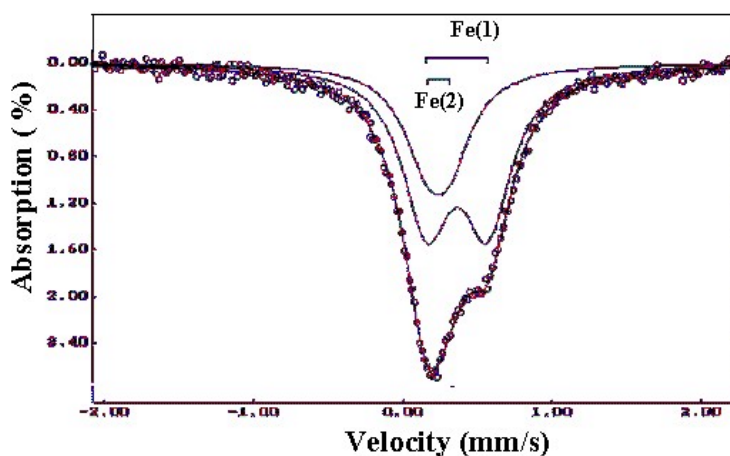


Figure 3. Mössbauer spectra for $\text{TlNi}_{0.98}\text{Fe}_{0.02}\text{O}_3$ at 300 K. (This figure is in colour only in the electronic version)

$\text{TlNi}_{0.98}\text{Fe}_{0.02}\text{O}_3$, $T_N = 104$ K for TlNiO_3). The Mössbauer spectra of $\text{TlNi}_{0.98}^{57}\text{Fe}_{0.02}\text{O}_3$ can be resolved into two quadrupole doublets (figure 3) which underlines that Fe ions are simultaneously stabilized in two non-equivalent crystallographic positions. These Fe sites are characterized by different values for the isomer shift δ and the quadrupole splitting Δ (table 1). The isomer shift values for these two kinds of iron ion, Fe(1) and Fe(2), reflect two different degrees of covalency in Fe–O bonds, suggesting a partial disproportionation phenomenon: $2\text{Fe}^{3+} \rightarrow \text{Fe}^{(3+\alpha)+} + \text{Fe}^{(3-\alpha)+}$. This result is consistent with the recent neutron diffraction analysis of small rare-earth nickelates (Ho–Lu and Y) which indicates the reduction in lattice symmetry from orthorhombic ($Pbnm$) to monoclinic ($P2_1/n$) driven by two independent crystallographic positions: Ni(1) O_6 and Ni(2) O_6 [5].

Considering that an increase of the formal oxidation state of Fe^{n+} cations leads to isomer shift reduction, the δ_2 -value would correspond to a nickel site characterized by a higher

Table 1. Mössbauer parameters for $\text{TiNi}_{0.98}\text{Fe}_{0.02}\text{O}_3$.

T (K)	Fe site	δ (mm s ⁻¹)	Δ (mm s ⁻¹)	Γ (mm s ⁻¹)	A (%)
300	Fe(1)	0.36(1)	0.40(1)	0.31(1)	67(2)
	Fe(2)	0.23(1)	0.18(1)	0.30(1)	33(2)

oxidation state $[\text{Ni}^{(3+\alpha)+}]$ and the δ_1 -value to a nickel site with a lower oxidation state $[\text{Ni}^{(3-\alpha)+}]$. The quadrupole splittings for the two types of iron, $\Delta_2(\text{Fe}^{(3+\alpha)+}) < \Delta_1(\text{Fe}^{(3-\alpha)+})$, are also in agreement with the neutron diffraction results which revealed that $\text{Ni}^{(3-\alpha)+}\text{O}_6$ octahedra might be more distorted than $\text{Ni}^{(3+\alpha)+}\text{O}_6$ ones [6]. Mössbauer studies on other rare-earth nickelates are in progress [11].

4. Conclusions

Although individual lattice parameters for TiNiO_3 deviate from the trends observed in other TiNiO_3 ($T = \text{rare earth and Y}$), the ratio $c/a\sqrt{2}$ for all the orthonickelates including TiNiO_3 shows a linear dependence on T_N . This relation shows how the electronic effect of the A-site ion affects the structural distortion and Ni–O bond strength in perovskite structure. The ^{57}Fe Mössbauer spectrum for ^{57}Fe -doped TiNiO_3 , which is resolved into two quadrupole doublets, supports the existence of two different crystallographic sites of Ni in the strongly distorted perovskite lattice.

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