Phase Transition of Ln$_3$IrO$_7$ (Ln=Pr, Nd, Sm, Eu) and its Low-Temperature Structure

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Ternary lanthanide iridium oxides Ln$_3$IrO$_7$ (Ln=lanthanides, M=Nb, Mo, Ru, Sb, Ta, Re, Os, Ir) have been extensively studied. They have a defect-fluorite structure. The relationship to the fluorite structure is as follows. The fluorite structure is well described with the space group Cmcm. The results for the specific heat measurements showed that only the structure for Pr$_3$IrO$_7$ is actually applied for such space group, and the other compounds were not the case. The results for the specific heat and differential thermal analysis (DTA) indicated that the phase transitions have been observed for any of these Ln$_3$IrO$_7$ compounds. Another topic for Ln$_3$IrO$_7$ is that detailed magnetic and thermal investigations on the ruthenium-, iridium- and osmium containing members of the Ln$_3$IrO$_7$ family show low-temperature structural phase transitions. However, the low-temperature structures are, in most cases, not known, or different structures were presented for the same compounds.

As for Ln$_3$IrO$_7$ compounds, Vente et al. reported the synthesis and their crystal structures. They reported that Ln$_3$IrO$_7$ (Ln=Pr, Nd, Sm, and Eu) compounds are isomorphous, and their structures were described with the same space group Cmcm. Our X-ray diffraction and neutron diffraction measurements showed that only the structure for Pr$_3$IrO$_7$ is actually applied for such space group, and the other compounds were not the case. The results for the specific heat and differential thermal analysis (DTA) indicated that the phase transitions have been observed for any of these Ln$_3$IrO$_7$ compounds. However, the low-temperature structures have not yet been known. Concerning the magnetic properties, only the Nd$_3$IrO$_7$ showed an antiferromagnetic transition at 2.6 K.

In this study, we re-examined the structure and thermal properties for the Ln$_3$IrO$_7$ compounds. After checking the existence of the phase transition in these compounds, we performed the X-ray diffraction measurements in order to determine their low-temperature crystal structures. The relationship between the high- and low-temperature structures was discussed.

1. Introduction

Metal oxides of the general formula Ln$_3$MO$_7$ (Ln=lanthanides, M=Nb, Mo, Ru, Sb, Ta, Re, Os, Ir) have been extensively studied. They have a defect-fluorite structure. The relationship to the fluorite structure is as follows. The fluorite unit cell for oxides has the composition $M^4+O^8$. If the four tetravalent metal ions are replaced by three trivalent ions (Ln) and one pentavalent ion (M), one oxide-vacancy is formed per fluorite cell. Due to the significant differences in radii between the Ln$^{3+}$ and M$^{4+}$ ions, cation ordering occurs on the metal sites and the oxide-vacancy orders on the anion sites. In 1979, Rossel first determined the crystal structure for La$_3$NbO$_7$. It is well described in the orthorhombic space group Cmcm. The M$^{4+}$ ion is coordinated with six oxygen ions, forming a MO$_6$ octahedron. These octahedra share corners forming one-dimensional chains which are oriented along the c-axis. The same space group Cmcm has been applied for Ln$_3$RuO$_7$ (Ln=La-Gd), $^{2,13}$ Ln$_3$ReO$_7$ (Ln=Pr, Nd, Sm-Tb), $^{14,16}$ Ln$_3$OsO$_7$ (Ln=Pr, Nd, Sm-Gd), $^{15,17,18}$ Ln$_3$TaO$_7$ (Ln=La-Nd), $^{19,23}$ Ln$_3$IrO$_7$ (Ln=Pr, Nd, Sm, Eu), $^{24,25}$ Pr$_3$NbO$_7$, and Pr$_3$SbO$_7$. $^{22}$ For Ln$_3$TaO$_7$ (Ln=Y, Sm-Ho), $^{19,23}$ Ln$_3$SbO$_7$ (Ln=Y, Dy, Ho), $^{19,26}$ Dy$_3$ReO$_7$, and Gd$_3$NbO$_7$, the space group C222, has been applied. The structures are basically similar. One-third of the Ln cation is 8-coordinated and lie in [0 0 1] rows which alternate with parallel rows of corner-linked MO$_6$ octahedra within slabs parallel to [1 0 0]. The remaining Ln cations lie between these slabs in a fold-coordinated. On the other hand, the structure for Ln$_3$MoO$_7$ (Ln=La-Nd, Sm, Eu) is well described with the different space group $P_{2_1}2_12_1$, and the one-dimensional MO$_6$ alignment is the same for the structures with the space groups Cmcm and C222, but the zig-zag chains of the corner-sharing MO$_6$ octahedra are parallel to the b-axis in this case.

Due to this unique crystal structure and possible related magnetic properties, many studies have been performed, especially for the magnetic properties of compounds containing Ru$^{4+}$ ion at the M-site because of its largest possible spin (S=3/2). $^{2,12}$ However, there was scant evidence for the expected one-dimensionality in the magnetic susceptibility. This is due to the fact that the magnetism due to the Ln$^{3+}$ ion tends to dominate when it is magnetic, but even in the La compounds; features due to one-dimensional effects were not evident in the susceptibility data. In 2002, Greedan et al. reported that the presence of one-dimensional intra-chain correlations was manifested in the magnetic susceptibility data in the form of broad maxima at ~18 K for the La$_3$RuO$_7$ and ~110 K for the La$_3$OsO$_7$ compounds.

Another topic for Ln$_3$MO$_7$ is that detailed magnetic and thermal investigations on the ruthenium-, iridium- and osmium containing members of the Ln$_3$MO$_7$ family show low-temperature structural phase transitions. However, the low-temperature structures are, in most cases, not known, or different structures were presented for the same compounds.

As for Ln$_3$IrO$_7$ compounds, Vente et al. reported the synthesis and their crystal structures. They reported that Ln$_3$IrO$_7$ (Ln=Pr, Nd, Sm, and Eu) compounds are isomorphous, and their structures were described with the same space group Cmcm. Our X-ray diffraction and neutron diffraction measurements showed that only the structure for Pr$_3$IrO$_7$ is actually applied for such space group, and the other compounds were not the case. The results for the specific heat and differential thermal analysis (DTA) indicated that the phase transitions have been observed for any of these Ln$_3$IrO$_7$ compounds. However, the low-temperature structures have not yet been known. Concerning the magnetic properties, only the Nd$_3$IrO$_7$ showed an antiferromagnetic transition at 2.6 K.

In this study, we re-examined the structure and thermal properties for the Ln$_3$IrO$_7$ compounds. After checking the existence of the phase transition in these compounds, we performed the X-ray diffraction measurements in order to determine their low-temperature crystal structures. The relationship between the high- and low-temperature structures was discussed.

2. Experimental

2.1 Sample preparation

As starting materials, lanthanide oxides Ln$_2$O$_3$ (Ln=Nd, Sm, Eu) and Pr$_2$O$_3$, and iridium metal powders Ir were used. They were weighed in an appropriate metal ratio and were ground in an agate mortar. The mixtures were pressed into pellets and then heated in an oxygen atmosphere up to 1473–1523 K at a rate of 0.5 K min$^{-1}$, held at this temperature for 12 h, and then cooled down to room temperature at the same rate. After several intermediate regrindings and repelletizing,
this heating procedure was repeated again. The heating in an oxygen atmosphere was necessary to avoid the formation of pyrochlore-type compounds \( \text{Ln}_2\text{IrO}_5 \) (\( \text{Ln} = \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu} \)) in which the \( \text{Ir}^{4+} \) ions are present.30

2.2 X-ray diffraction analysis

Powder X-ray diffraction profiles were measured using a Rigaku Multi-Flex diffractometer with Cu Kα radiation equipped with a curved graphite monochromator. The data was collected by step-scanning in the angle range of \( 10^\circ \leq 2\theta \leq 120^\circ \) at a \( 2\theta \) step-size of 0.02°. The X-ray diffraction data were analyzed by the Rietveld technique, using the programs RIETAN2000.31

2.3 Specific heat and DTA measurements

Specific heat measurements for \( \text{Ln}_2\text{IrO}_5 \) were performed using a relaxation technique by a commercial heat capacity measuring system (Quantum Design, PPMS) in the temperature range of 1.8–400 K. The sintered sample in the form of a pellet was mounted on a thin alumina plate with Apiezon for better thermal contact.

DTA measurements were performed with a TG-DTA 2000S (Mac Science) over the temperature range of 300–800 K. As a standard material, α-Al₂O₃ was used and the rates of heating and cooling were both controlled at 10 K min⁻¹.

3. Results and discussion

3.1 Preparation and crystal structure

We have successfully prepared a series of compounds \( \text{Ln}_2\text{IrO}_5 \) (\( \text{Ln} = \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu} \)) in an oxygen atmosphere. Figure 1 shows their X-ray diffraction (XRD) profiles and the fitting by the Rietveld analysis. Vente et al. reported that the crystal structures for \( \text{Ln}_2\text{IrO}_5 \) (\( \text{Ln} = \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu} \)) were orthorhombic with the space group Cmcm. Following them, we also refined the structures with the same space group. The fitting results by the Rietveld analysis shown in Fig. 1 appear to indicate that the structures for \( \text{Ln}_2\text{IrO}_5 \) (\( \text{Ln} = \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu} \)) were refined with the space group Cmcm and the goodness of the fit (S) was below 1.30 for all the compounds. However, the detailed X-ray diffraction profiles in the low 2θ angles (the inset of Fig. 1) indicate that some additional diffraction lines which cannot be fitted with the Cmcm space group appeared at 2θ=22° and 25° for \( \text{Pr}_2\text{IrO}_5 \) (\( \text{Ln} = \text{Nd}, \text{Sm}, \text{Eu} \)).

Figure 2 shows the temperature dependence of the specific heat for \( \text{Pr}_2\text{IrO}_5 \) and \( \text{Nd}_2\text{IrO}_5 \). Specific heat anomalies corresponding to the first-order phase transitions were observed at 261 K and 342 K for \( \text{Pr}_2\text{IrO}_5 \) and \( \text{Nd}_2\text{IrO}_5 \), respectively. For \( \text{Sm}_2\text{IrO}_5 \) and \( \text{Eu}_2\text{IrO}_5 \), corresponding anomalies were observed in the DTA measurements, i.e., the endothermic peaks during heating were found at 420 K for \( \text{Sm}_2\text{IrO}_5 \) and 485 K for \( \text{Eu}_2\text{IrO}_5 \). We consider that this transition is due to the phase transition. The transition temperature \( (T_p) \) increased with a decreasing Ln ionic radius (Pr→Eu). Only the \( \text{Pr}_2\text{IrO}_5 \) has a high-temperature structure at room temperature (\( T_p = 261 \) K). Therefore, \( \text{Nd}_2\text{IrO}_5 \), \( \text{Sm}_2\text{IrO}_5 \) and \( \text{Eu}_2\text{IrO}_5 \) should show a phase transition when the temperature is increased above room temperature.

We performed high-temperature XRD measurements for \( \text{Nd}_2\text{IrO}_5 \) in the temperature range of 298–550 K. Figure 3 shows the XRD profiles in the low 2θ range measured at 298 and 400 K. The XRD profile measured at 298 K has some weak diffraction lines (for example, at 2θ=22° and 25°) which cannot be assigned with the space group Cmcm. When the temperature was increased above 342 K, such diffraction lines disappeared and the XRD profile was successfully refined with the space group Cmcm. The same situation was observed in the temperature dependence of the XRD profiles for \( \text{Sm}_2\text{IrO}_5 \) and \( \text{Eu}_2\text{IrO}_5 \). The high-temperature structure for \( \text{Ln}_2\text{IrO}_5 \) is well described with the space group Cmcm, and this structure has been observed for most of the \( \text{Ln}_2\text{MO}_5 \) type.
As for oxygen atoms, the structure features chains of vertex-shared IrO₆ octahedra running along the c-axis. In the high-temperature structure, the phase distortion, and the average Ir–O distances are not affected by the transition temperature. On the other hand, the Ir–O distances are not affected by the phase distortion, and the average Ir–O distances are not affected by the transition temperature. The remaining two-thirds of the neodymium cations, Nd2 and Nd3, exist in two crystallographically unique sites. The remaining two-thirds of the neodymium cations, Nd2 and Nd3, exist in two crystallographically unique sites.

Figure 4 shows the low-temperature structure of Nd₃IrO₇ as well as its high-temperature structure. Similar to the high-temperature structure, the structure features chains of vertex-shared IrO₆ octahedra running along the c-axis. In the high-temperature structure, the chains of vertex-shared IrO₆ octahedra connect to the chains of edge-sharing NdO₆ pseudo-cubes via pairs of equatorial IrO₂ oxygen atoms. In the low-temperature structure, the vertex-shared IrO₆ octahedra are tilted greatly. The tilting of the IrO₆ chains caused one of the equatorial oxygen atoms to rotate away from the neodymium cation. This resulted in the reduction of the coordination number of the associated Nd²⁺ from 8 to 7. The Nd–O bond length 0.275 nm, which is included in the NdO₆ pseudo-cube at 400 K (Nd₁oO₁o, space group Cmcm) extends to 0.311 nm at 298 K (Nd₁mO₂m with space group P2₁/n). The Nd–O bond length 0.275 nm, which is included in the NdO₆ pseudo-cube at 400 K (Nd₁oO₁o, space group Cmcm) extends to 0.311 nm at 298 K (Nd₁mO₂m with space group P2₁/n). The Nd–O bond length 0.275 nm, which is included in the NdO₆ pseudo-cube at 400 K (Nd₁oO₁o, space group Cmcm) extends to 0.311 nm at 298 K (Nd₁mO₂m with space group P2₁/n).

The analysis of the X-ray diffraction data measured below the transition temperature showed that all additional diffraction peaks could be indexed to a primitive monoclinic cell. Refinement in the P2₁/n space group of the structural model yielded satisfactory results. Trial refinements in other space groups resulted in physically unreasonable displacement parameters, as well as high residual factors, R. The refinement atomic coordinates and lattice parameters for the low-temperature structure of Nd₃IrO₇ with those for the high-temperature structure are compiled in Table 1. The high-temperature structure is described in the orthorhombic space group Cmcm with 2 independent neodymium positions (Nd₁o, Nd₂o, where the subscript “o” means orthorhombic), one unique iridium site (Ir₁o), and 3 independent oxygen atom positions (O₁o, O₂o, O₃o). The low-temperature structures are best described in the primitive monoclinic space group P2₁/n with 3 independent neodymium positions, 2 unique iridium sites, and 7 independent oxygen atom positions. Due to this transition (orthorhombic→monoclinic), Ir₁o transforms into Ir₁m and Ir₂o (where the subscript “m” means monoclinic), Nd₁o transforms into Nd₁m, Nd₂o transforms into Nd₂m and Nd₃m. As for oxygen atoms, O₁o, O₂o, and O₃o transform into O₂m, O₃m, O₄m and O₅m, (O₆m and O₇m), and O₁m, respectively.

**Table 1. Crystal Structure Data for Nd₃IrO₇**

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</table>

Note: \( R_{wp} = \sum w_{ij}(f_{ij} - f_{ij}^0)^2 / \sum w_{ij} \) and \( R_{F} = \sum |F_{o} - F_{c}| / \sum F_{o} \).

The same \( \beta \) values were given for Nd, Ir, and O atoms, respectively.

On the other hand, the Ir–O distances are not affected by the phase distortion, and the average Ir–O distances are not affected by the phase distortion, and the average Ir–O distances are not affected by the phase distortion, and the average Ir–O distances are not affected by the phase distortion, and the average Ir–O distances are not affected by the phase distortion. For each of the five series of Ln₃MO₄ compounds, the phase tran-
Fig. 4. Crystal structures of Nd$_3$IrO$_7$. (a) high-temperature structure, Cmcm; (b) low-temperature structure, P$_2_1/n$. The relationship between the monoclinic unit cell (the low-temperature structure) and the orthorhombic unit cell (the high-temperature structure) are also indicated.

Fig. 5. Phase transition temperature for Ln$_3$MO$_7$ (M = Mo, Ru, Re, Os, Ir) against the ionic radius of Ln$^{3+}$. Transition temperatures decreased by increasing the ionic radius of Ln$^{3+}$, i.e., it is clear that the phase transition of Ln$_3$MO$_7$ is clearly influenced by the size of the Ln$^{3+}$ cation. Each transition temperature within a series is separated by approximately the same temperature interval except for the case of Ln$_3$MoO$_7$. The trend of the transition temperature against Ln$^{3+}$ radius for Ln$_3$MoO$_7$ is different from those for Ln$_3$MO$_7$ (M = Ru, Re, Os, Ir). The reason for this may be related to the difference in their high-temperature structures, that is, the Ln$_3$MoO$_7$ (Ln = La–Eu) exists in P$_2_1_2_1_2_1$ structure, whereas the other Ln$_3$MO$_7$ (M = Ru, Re, Os, Ir) exists in the Cmcm structure.

4. Summary
Lanthanide iridates Ln$_3$IrO$_7$ (Ln = Pr, Nd, Sm, and Eu) were formed in the orthorhombic superstructure of cubic fluorite with the space group Cmcm. These compounds show a phase transition at 262, 342, 420, and 485 K for Ln$_3$Pr, Nd, Sm, and Eu, respectively. At low temperatures, they crystalize in a monoclinic structure with the space group P$_2_1/n$.

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References


