Hexagonal Rare Earth-Iron Mixed Oxides (REFeO\(_3\)): Crystal Structure, Synthesis, and Catalytic Properties

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The rare earth-iron mixed oxide (REFeO\(_3\)) is an attractive material in fields such as electronic, magnetic, and catalytic research. Generally, orthorhombic REFeO\(_3\) (o-REFeO\(_3\)) with a perovskite structure is better known than hexagonal REFeO\(_3\) (h-REFeO\(_3\)), because o-REFeO\(_3\) is thermodynamically stable for all RE elements. However, h-REFeO\(_3\) has a very interesting crystal structure in which a RE and Fe layer are alternately stacked along the c-axis in the unit cell; nevertheless, synthesis of the h-REFeO\(_3\) belonging to metastable phase can be problematic. Fortunately, solution-based synthetic methods like solvothermal or coprecipitation synthesis have recently enabled the selective synthesis of h-REFeO\(_3\) and o-REFeO\(_3\) with comparative ease. Although the electronic and magnetic properties of h-REFeO\(_3\) have typically been evaluated, recent research has also revealed excellent catalytic properties that enable environmental cleanup reactions such as hydrocarbon or CO oxidation. This mini-review introduces a synthetic method for controlling the crystal structure between orthorhombic and hexagonal REFeO\(_3\) and the catalytic performance of h-REFeO\(_3\)-based materials.

Keywords: solvothermal method, coprecipitation method, catalyst, perovskite structure, hexagonal structure

INTRODUCTION

REFeO\(_3\) (RE: rare earth) with a RE/Fe ratio of 1 are largely relevant to the perovskite structure, a structure in which RE ions are basically replaced with 1/4 of cubic close-packed oxygen ions, and Fe ions occupy all octahedral gaps formed from the remaining oxygen ions. REFeO\(_3\) having a perovskite structure have been applied in various fields from electronic devices to catalysts. On the other hand, hexagonal REFeO\(_3\) is known to exist as a metastable phase, but the synthetic method is very complex. Interestingly, the crystal structure has a unique coordination state for Fe\(^{3+}\) ion and is different from that of the perovskite-type REFeO\(_3\); that is, Fe\(^{3+}\) ions in hexagonal structure have trigonal bipyramidal coordination, although Fe\(^{3+}\) ions in α-Fe\(_2\)O\(_3\), Fe\(_3\)O\(_4\), or perovskite-type REFeO\(_3\) generally prefer octahedral or tetrahedral coordination. Therefore, hexagonal structure has a potential which provokes an interesting property for the above applied fields. In particular, novel catalysts composed on abundant base metal as Fe ion have been recently desired to replace the use of precious metals, such as Pt or Pd; the catalyst design based on a unique crystal structure is considered to be necessary to dramatically improve the catalytic performance of Fe-based material.

First, the relationship between RE elements and hexagonal structure is introduced, based on a general perovskite structure. Considering that each ion is in contact within the perovskite structure, the following equation is true: \((r_{A} + r_{O}) = \sqrt{2}(r_{B} + r_{O})\), where \(r_A\), \(r_B\), and \(r_O\) represent the ionic radii of the A cation as RE ion, B cation as Fe ion, and oxygen ion, respectively. Therefore, the perovskite structure is generally considered to be a stable phase, when the tolerance factor,
$t = \frac{[(r_A + r_O)]}{\sqrt{2(r_B + r_O)}}$ is close to 1 (Schneider et al., 1961; Woodward, 1997; Li et al., 2004). Regarding the relationship between RE elements and tradition metal ions, the tolerance factor decreases with decreasing ionic radius of the RE element (Kumar et al., 2011); that is, the perovskite structure becomes less stable. However, for REFeO₃, the orthorhombic phase is thermodynamically stable for all RE elements, and the trend is different from a general trend observed in REMnO₃ (Figure 1A); orthorhombic REMnO₃ (o-REMN0₃) with a perovskite structure and the space group of Pbnm is preferentially formed for RE elements with small ionic sizes (La–Dy), while hexagonal REMnO₃ (h-REMN0₃) with P6₃cm is obtained for RE elements with small ionic sizes (Ho–Lu and Y) (Figures 1B,C). As the ionic size of an Fe³⁺ ion is almost the same as that of an Mn³⁺ ion, the difference in the electronic configuration of d orbitals between Fe³⁺ and Mn³⁺ ions may contribute to the stability of the hexagonal phase. In other words, because h-REFeO₃ is a thermodynamically unstable phase, it is relatively poorly studied compared with o-REFeO₃.

By controlling the synthetic route, h-REFeO₃ composed from RE ions with a smaller ionic radius than Er or Y have been obtained. The space group of h-REFeO₃ has been reported as P6₃cm with a YMnO₃ structure type or P6₃/mmc with a YAI0₃ structure type (Li et al., 2008; Kumar et al., 2009; Magome et al., 2010). The crystal structure belonging to P6₃cm is very similar to that to P6₃/mmc, except for a slightly more distorted crystal structure in the former than in the latter. Actually, the oxygen layer has a zigzag structure in the P6₃cm structure. In either space group, h-REFeO₃ has a unique crystal structure other than the coordination state of Fe³⁺ ion; RE and Fe layers are alternately stacked along the c-axis. REFe₂O₄ or RE₂Fe₃O₇, represented by the chemical formula RE₂Fe₉₊1O₃ₙ₊₁, are known as hexagonal phase-related materials (Malaman et al., 1976; Qin et al., 2009; Bourgeois et al., 2012; Lauffer et al., 2014), and the coordination environment of Fe ions is a trigonal bipyramidal structure similar to the structure of h-REFeO₃. REFe₂O₄ has a hexagonal layer structure with the space group of R₃m, which is formed by the alternate stacking of two layers with compositions of REO₃/2 and Fe²⁺Fe³⁺O₅/2 (Figure 1D). The Fe layer consists of two triangular shets of corner-sharing FeO₃ trigonal bipyramids. RE₂Fe₇O₁₇ can be transcribed to REFe₂O₄(REFeO₃), and the structures of the REFe₂O₄(REFeO₃)ₙ phases are described by alternately stacking REFe₂O₄ and hexagonal REFeO₃ blocks along the c-axis direction (Figure 1E).

When h-REFeO₃ is viewed as an applied material, its layered structure composed of RE and Fe layers along the c-axis is very attractive for multiple purposes, from electric to catalytic applications. In fact, LuFe₂O₄ has shown excellent oxygen storage properties because its hexagonal-related structure has unique structural flexibility accompanied by “topotactic transition” during the oxygen intercalation/de-intercalation process (Hervieu et al., 2014). In this transformation, the original cation ordering in the hexagonal structure is maintained without any intermixing between RE and Fe ions. This mini-review therefore presents the method for controlling the crystal structure of h-REFeO₃ and o-REFeO₃ and discusses the catalytic properties of h-REFeO₃.
**SOLVOTHERMAL METHOD**

Because \( h\)-REFeO\(_3\) is a metastable phase, a unique synthesis method is typically required. Among existing methods, a solvothermal method is effective for controlling the hexagonal and orthorhombic phases. In this method, synthesis of inorganic material is achieved by reaction in a liquid medium at high temperatures in a closed vessel (autoclave) (Demazeau, 1999; Cushing et al., 2004). Therefore, the traditional solvothermal method is a hydrothermal method in which water is used as the solvent. Since the last three decades, alcohol or glycol has been used as a solvent in the solvothermal method (Fanelli and Burlow, 1986; Das et al., 2008), with various metal oxides or mixed oxides with unique morphology or ultrafine nanoparticles have been reported.

Inoue et al. found that \( h\)-REFeO\(_3\) nanoparticles composed of RE with a smaller ionic radius than Er can be obtained through a non-aqueous solvothermal reaction of RE acetate with Fe acetylacetonate in 1,4-butanediol at 300°C (Figure 2; Inoue et al., 1997). It should be noted that crystal growth in the c-axis direction in \( h\)-REFeO\(_3\) is drastically suppressed during solvothermal synthesis, resulting in the formation of nanoparticles with a particle size of approximately 20 nm and a well-formed hexagonal plate-like morphology. It was found that \( h\)-YbFeO\(_3\) and \( o\)-YbFeO\(_3\) can be controlled by the choice of reaction conditions and the starting material for the solvothermal reaction (Hosokawa et al., 2009). Interestingly, when RE chloride (RE = Sm-Yb) and Fe acetylacetonate are used for the solvothermal reaction in 1,4-butanediol in the presence of hexamethylenediamine, monodisperse particles of \( o\)-REFeO\(_3\) (crystallite size: about 80 nm) are formed. It is suggested that \( o\)-YbFeO\(_3\) has a larger crystallite size than solvothermally-synthesized \( h\)-YbFeO\(_3\), which indicates that crystal nucleation is more difficult for \( o\)-YbFeO\(_3\) than \( h\)-YbFeO\(_3\).

High-resolution transmission electron microscopy (TEM) of Yb\(_2\)Fe\(_4\)O\(_{10}\) revealed that three or more YbFeO\(_3\) layers are inserted between the YbFeO\(_2\) layers (Matsui et al., 1979), suggesting that the REFe\(_2\)O\(_4\) phase with Fe\(^{3+}\) and Fe\(^{2+}\) species may act as a nucleus for \( h\)-REFeO\(_3\). The result indicates that the existence of Fe\(^{2+}\) ions plays an important role in the formation of \( h\)-REFeO\(_3\). The solvothermal reaction in 1,4-butanediol causes reductive conditions because of the reducing ability of glycol; that is, Fe\(^{2+}\) species formed in the reaction system seem to contribute to the formation of \( h\)-REFeO\(_3\). On the other hand, because the incorporation of amine into the solvothermal reaction suppresses the reduction from Fe\(^{3+}\) to Fe\(^{2+}\) ions owing to the chelating ability of hexamethylenediamine, \( o\)-YbFeO\(_3\) must be obtained. In addition, the reducibility of Fe\(^{3+}\) species is unsurprisingly also considered to depend on whether the ligand of the starting material is acetate or chloride.

This non-aqueous solvothermal method enables the crystallization of REFeO\(_3\) nanoparticles below 100 nm without calcination. Therefore, it is promising to control the crystal structure, shape, and particle size by adjusting the additives and solvent in the solvothermal system.

**COPRECIPITATION AND SOL-GEL METHOD**

General synthetic routes such as the coprecipitation method inevitably involve a calcination process for the synthesis of metal oxide materials, and it is difficult to synthesize the metastable phase. Therefore, \( h\)-REFeO\(_3\) is often synthesized by optimizing the crystallization process. For example, \( h\)-REFeO\(_3\) is synthesized by introducing solutions containing metal salts into a high-temperature inductively coupled plasma (ICP) (Mizoguchi et al., 1996). An instant crystallization under the ICP atmosphere yields \( h\)-REFeO\(_3\) nanoparticles sized 20–50 nm. Kumar et al. reported that the hexagonal phase is synthesized by rapidly cooling a melt of the composition REFeO\(_3\) under controlled oxygen pressure (Vijaya Kumar et al., 2008). This method requires special equipment in which the precursor is suspended on a nozzle fitted to an oxygen gas jet, thereby preventing heterogeneous

![Flow chart showing crystal structure control utilizing the solvothermal method (Left) and coprecipitation method (Right).](#)
nucleation that occurs on the walls of the container. As a result, \( h\text{-LuFeO}_3 \) with high crystallinity is obtained under an oxygen partial pressure of \( 1 \times 10^5 \) Pa.

On the other hand, in the case of \( h\text{-REFeO}_3 \) synthesis from an amorphous precursor obtained by coprecipitation method in which ammonia water is added immediately to an aqueous solution containing RE and Fe ions (Nishimura et al., 2013), \( h\text{-REFeO}_3 \) for RE ions with a smaller ionic radius than Er can be easily obtained under precisely controlled calcination conditions. For an amorphous precursor with the composition of \( Yb\text{FeO}_3 \), an exothermic peak without weight change is observed in the temperature range slightly below 800°C, by thermal gravimetric-differential thermal analysis. Therefore, the sample calcined in air at 700°C for 30 min is amorphous, and the formation of pure-phase \( h\text{-YbFeO}_3 \) is confirmed by calcining the amorphous product at 800°C for 30 min (Figure 2). Note that, when the retention time at 800°C is extended to 12 h, \( h\text{-YbFeO}_3 \) is obtained as the main product. These results strongly suggest that the exothermic peak is attributed not only to crystallization from an amorphous to hexagonal structure but also a phase transition from a hexagonal structure to orthorhombic structure. In other words, the hexagonal and orthorhombic phase can be kinetically classified by adjusting the heat retention time in the calcination process. In this manner, because a subtle change in calcination conditions leads to the formation of \( h\text{-REFeO}_3 \) from an amorphous precursor, the synthesis of \( h\text{-REFeO}_3 \) is much more difficult than that of \( o\text{-REFeO}_3 \).

Similar crystallization behavior is also observed for a precursor containing organic species synthesized by a citric acid-assisted sol-gel process (Zhang et al., 2012). For an amorphous precursor with the composition of \( Y\text{FeO}_3 \), the crystallization temperature of \( h\text{-YFeO}_3 \) is 700°C. This is lower than that of \( h\text{-YbFeO}_3 \) (800°C); therefore, the crystallization temperature depends on the ionic radius of RE ions. Interestingly, doping Pd on \( h\text{-YFeO}_3 \) via the sol-gel method stabilizes the hexagonal phase, and the phase transformation to the orthorhombic phase hardly proceeds even by calcination at 1,000°C (Li et al., 2008).

\( h\text{-REFeO}_3 \), which is obtained by the calcination of a precursor synthesized by the solution method, often comprises fine particles with a crystallite diameter below 50 nm. On the other hand, \( o\text{-REFeO}_3 \), which is obtained by phase transition from \( h\text{-REFeO}_3 \), has a much larger particle size than \( h\text{-REFeO}_3 \). For example, the particle size of \( h\text{-YbFeO}_3 \) synthesized by the coprecipitation method is approximately 20 nm, whereas that of \( o\text{-YbFeO}_3 \) is above 150 nm. A nucleation and growth mechanism has been reported to proceed in a phase transition from \( \gamma\text{-Al}_2\text{O}_3 \) or \( \theta\text{-Al}_2\text{O}_3 \) to \( \alpha\text{-Al}_2\text{O}_3 \) (Dynys and Halloran, 1982; Bagwell et al., 2001); that is, rapid crystal growth of \( \alpha\text{-Al}_2\text{O}_3 \) simultaneously progresses with the formation of crystal nuclei of \( \alpha\text{-Al}_2\text{O}_3 \), resulting in the formation of \( \alpha\text{-Al}_2\text{O}_3 \) with a very large particle size. Similar to the phenomena for \( \alpha\text{-Al}_2\text{O}_3 \), crystal nucleation and rapid crystal growth of \( o\text{-REFeO}_3 \) must proceed during the phase transition from \( h\text{-REFeO}_3 \) to \( o\text{-REFeO}_3 \). These results imply that \( h\text{-REFeO}_3 \) nanoparticles can be synthesized by the coprecipitation or sol-gel method, but \( o\text{-REFeO}_3 \) with a particle size below 100 nm is difficult to synthesize for RE ions with a smaller ionic radius than Er.

### CATALYTIC PERFORMANCE OF \( h\text{-REFeO}_3 \)

\( o\text{-REFeO}_3 \) has been applied as a catalyst material in various fields including the purification of volatile organic compound etc. (Ciambelli et al., 2001; Barbero et al., 2006). Applications of \( h\text{-REFeO}_3 \) have been rare, except for in magnetic or electronic fields, until about 15 years ago. However, recent applications have emerged in the field of catalysts (Kurzman et al., 2011; Ismail et al., 2017). For example, \( h\text{-YFeO}_3 \) has been reported to show a higher catalytic activity than \( o\text{-YFeO}_3 \) for the photodecomposition of methyl orange under visible light irradiation (>420 nm) (Zhang et al., 2012). As \( h\text{-YFeO}_3 \) (1.94 eV) has a narrower band gap than \( o\text{-YFeO}_3 \) (2.43 eV), the band structure of \( h\text{-YFeO}_3 \) may be contributed to the high catalytic activity. \( h\text{-YFeO}_3 \) with the unique band structure is also demonstrated to be suitable as a photoanode for solar water splitting (Guo et al., 2017).

The catalytic performance of \( h\text{-REFeO}_3 \) as an oxidation catalyst has actively been investigated. When \( \text{CH}_4 \) oxidations over \( h\text{-YbFeO}_3 \) and \( o\text{-YbFeO}_3 \) obtained by the solvothermal reaction are evaluated (Hosokawa et al., 2011), the \( h\text{-YbFeO}_3 \) catalysts shows extremely high combustion activity compared with \( o\text{-YbFeO}_3 \). The \( T_{50} \) value, at which the catalyst exhibits 50% \( \text{CH}_4 \) conversion, is 475°C for \( h\text{-YbFeO}_3 \), while that for \( o\text{-YbFeO}_3 \) 550°C. The surface area of the \( o\text{-YbFeO}_3 \) catalyst significantly decreases during calcination at 800°C in catalyst preparation; that is, the surface area of \( o\text{-YbFeO}_3 \) synthesized by the solvothermal method is 26 m²g⁻¹ and that of \( o\text{-YbFeO}_3 \) after calcination is 6 m²g⁻¹. Interestingly, the surface area of the \( h\text{-YbFeO}_3 \) catalyst (approximately 30 m²g⁻¹) does not change significantly during the calcination, and the well-formed hexagonal plate shape is maintained. This result suggests that the surface energy of \( o\text{-YbFeO}_3 \) is higher than that of \( h\text{-YbFeO}_3 \). In other words, because \( h\text{-YbFeO}_3 \) synthesized by the solvothermal method has high thermal stability, high catalytic activity must be achieved.

The \( h\text{YFe}_{1-x}\text{Pd}_x\text{O}_3\) catalyst synthesized by the sol-gel method has been reported to show high catalytic activity (\( T_{50} = 100°C \)) for \( \text{CO} \) oxidation under excess \( \text{O}_2 \) concentration (1,000 ppm \( \text{CO} \) and 10% \( \text{O}_2 \)), comparable to that of a \( \text{Pd}/\text{Al}_2\text{O}_3 \) catalyst with high surface area (Li et al., 2008). The ionic \( \text{Pd} \) species in the hexagonal lattice contributes to the catalytic activity. Lu et al. also reported that a \( \text{Pd} \) catalyst supported on \( h\text{-YFeO}_3 \) is more effective for \( \text{CH}_4 \) oxidation than \( \text{Pd}/\text{h-YMnO}_3 \) or \( \text{Pd}/\text{o-LaFeO}_3 \), and that the \( \text{Pd}/\text{YFeO}_3 \) catalyst maintains a high catalytic activity for \( \text{CH}_4 \) oxidation even after aging treatment at 900°C despite the phase transformation to \( o\text{-YFeO}_3 \) (Lu et al., 2014a,b, 2015). In these cases, as the \( \text{Pd} \) species is adequately anchored with the \( h\text{-YFeO}_3 \) support, the catalyst seems to have high catalytic activity.

Furthermore, to develop a noble-metal free \( h\text{-YbFeO}_3 \)-based catalyst with high catalytic activity, transition metal-modified \( h\text{-YbFeO}_3 \) catalysts are synthesized by solvothermal methods (Hosokawa et al., 2016). Mn modification by the solvothermal method dramatically improves the catalytic activity of \( h\text{-YbFeO}_3 \) itself for \( \text{CO} \) oxidation in which a reaction gas composed of 5,000 ppm \( \text{CO} \) and 5,000 ppm \( \text{O}_2 \) is introduced on catalyst bed.
The catalytic activity ($T_{50} = 120^\circ$C) of Mn-modified $h$-YbFeO$_3$ (Mn-$h$-YbFeO$_3$) with the composition of YbFe$_{0.6}$Mn$_{0.4}$O$_3$ exceeds that ($T_{50} = 134^\circ$C) of the noble metal Pd/Al$_2$O$_3$ catalyst.

**CONCLUSION**

Conventionally, a special method has been required for the synthesis of $h$-REFeO$_3$ due to its metastable nature; however, $h$-REFeO$_3$ can now be easily synthesized by precisely controlling the calcination process even when employing the coprecipitation or sol-gel methods. $h$-REFeO$_3$-based materials have been demonstrated to be applicable for catalytic materials, as well as magnetic or electronic materials. I believe that excellent catalyst materials will evolve from catalyst designs focusing on the unique crystal structure of $h$-REFeO$_3$ or hexagonal-related materials (RE$_2$Fe$_{1+1}$(3n+1)$_2$O$_{3n+5}$).

**AUTHOR CONTRIBUTIONS**

The author confirms being the sole contributor of this work and has approved it for publication.

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Conflict of Interest Statement: The author declares that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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