Ferromagnetism and optical properties of \( \text{La}_{1-x}\text{Al}_x\text{FeO}_3 \) nanopowders

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**Abstract**

\( \text{La}_{1-x}\text{Al}_x\text{FeO}_3 \) \((x = 0.0, 0.05, 0.1, 0.2, 0.3, 0.4, \text{and} \ 0.5) \) nanopowders were prepared by polymerization complex method. All prepared samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FT-IR), and UV-vis spectrophotometry (UV-vis). The magnetic properties were investigated using a vibrating sample magnetometer (VSM). The X-ray results of all samples show the formation of an orthorhombic phase with the second phase of \( \alpha-\text{Fe}_2\text{O}_3 \) in doped samples. The crystallite sizes of nanoparticles decreased with increasing Al content, and they are found to be in the range of 58.45 ± 5.90 to 15.58 ± 4.64 nm. SEM and TEM images show the agglomeration of nanoparticles with average particle size in the range of 60 to 75 nm. The FT-IR spectra confirm the presence of metal oxygen bonds of O-Fe-O and Fe-O in the FeO\(_6\) octahedra. The UV-vis spectra show strong absorption peaks at approximately 285 nm, and the calculated optical band gaps are found to be in the range of 2.05 to 2.09 eV with increasing Al content. The M-H loop of the pure sample is antiferromagnetic, whereas those of the doped samples tend to be ferromagnetic with increasing Al content. The magnetization, remanent magnetization, and coercive field of the Al-doped sample with \( x = 0.5 \) are enhanced to 1.665 emu/g, 0.623 emu/g, and 4,087.0 Oe, respectively.

**Keywords:** Ferromagnetism; Optical properties; Polymerization complex method; \( \text{La}_{1-x}\text{Al}_x\text{FeO}_3 \); Nanopowders

**Background**

\( \text{LaFeO}_3 \) with an orthorhombic phase of the ABO\(_3\)-type perovskite structure has become a currently attractive research topic because it is proposed for various applications in several advanced technologies such as catalysts [1-3], various kinds of chemical and gas sensors [4-9], and electrode materials in solid oxide fuel cells [10]. In general, LaFeO\(_3\) consists of FeO\(_6\) octahedral units with La\(^{3+}\) ions at the corners [11,12]. The advantage of this structure is the replaceability of metallic ions at both A and B sites by various transition metals. Pure and doped LaFeO\(_3\) (Pd, Al, Zn, Ag, Sr, Ir, Ca, Co, etc.) were studied for various purposes and aspects with reports of optical, electrical, and magnetic properties [13-25].

Research on pure and doped LaFeO\(_3\) nanostructures reveal that the property and quality of the materials are strongly influenced by the synthesis method. The synthesis method is usually related to the specific preparation conditions which can result in various properties of the end products. Various techniques were employed for the synthesis of pure and doped LaFeO\(_3\) such as sol-gel/combustion method [26-40], microwave-assisted method [41-43], solid-state reaction method [14,44-46], thermal decomposition [47,48], microemulsion method [49], hydrothermal method [50-52], hot soap method [53], spray drying [54], electrospinning [55], dip pyrolysis [19], and polymerization complex method [56-59]. However, polymerization complex method based on polystyrene between citric acid (CA) and ethylene glycol (EG) is the most attractive because it is simple, cost effective, time saving, and environmentally benign.

Thus, we propose in this research the synthesis of \( \text{La}_{1-x}\text{Al}_x\text{FeO}_3 \) \((x = 0, 0.05, 0.1, 0.2, 0.3, 0.4, \text{and} \ 0.5) \) nanopowders using a simple polymerization complex method. The magnetic and optical properties of the products were studied. The magnetization, coercive field, and remanent magnetization are measured, and they are expected to be enhanced due to the substitution of small-radius ions of Al on the La site.
Methods

La$_{1-x}$Al$_x$FeO$_3$ ($x = 0$, 0.05, 0.1, 0.2, 0.3, 0.4, and 0.5) were synthesized by polymerization complex method. Stoichiometric amounts of iron nitrate (Fe(NO$_3$)$_3$·9H$_2$O, Kanto Chemical Co., Chuo-ku, Japan, 99.9%), lanthanum nitrate (La(NO$_3$)$_3$·6H$_2$O, Fluka, Seelze, Germany, 99.0%), and aluminum nitrate (Al(NO$_3$)$_3$·9H$_2$O, Carlo Erba Reagenti, Milan, Italy, 99.0%) in the ratio of 1−$x$: $x$:1 (La:Al:Fe) with 1 g of citric acid (C$_6$H$_8$O$_7$·H$_2$O, VWR International Ltd., Radnor, PA, USA, 99.7%) were dissolved in 40 mL ethylene glycol and 20 mL deionized (DI) water. The mixture was magnetically stirred for 1 h in order to obtain stable metal-citric acid complexes. The obtained solution was continuously stirred at 70°C for 1 h. This solution was dried at 120°C on a hot plate. The obtained powders were pre-calcined at 400°C for 3 h to burn out the polymer. The pre-calcined powders were ground and further calcined at 900°C for 3 h in air.

The calcined powders were characterized using an X-ray diffractometer (XRD; XRD-6100, Shimadzu, Kyoto, Japan) with CuK$_\alpha$ radiation ($\lambda = 1.5405$ Å). The morphologies of the synthesized products were observed using a scanning electron microscope (SEM; 1450VP, LEO, Hurley, UK) and a transmission electron microscope (TEM; Tecnai G2 20, FEI, Hillsboro, OR, USA). The components of the powders were analyzed by energy-dispersive X-ray spectroscopy (EDX; Tecnai G2 20, FEI). Fourier transform infrared spectroscopy (FT-IR; Spectrum One FT-IR, Perkin Elmer Instrument, Waltham, MA, USA) was employed to investigate functional groups in all samples. The optical properties were studied by ultraviolet-visible spectroscopy (UV-vis; UV-3101PC, Shimadzu). The magnetizations of all samples were measured using a vibrating sample magnetometer (VSM; VersaLab™ Cryogen-free, Quantum Design, San Diego, CA, USA).

Results and discussion

XRD analysis

The XRD patterns of La$_{1-x}$Al$_x$FeO$_3$ ($x = 0$, 0.05, 0.1, 0.2, 0.3, 0.4, and 0.5) nanopowders are shown in Figure 1. The results indicate that the products are a perovskite oxide of an orthorhombic structure with the second phase of α-Fe$_2$O$_3$ in the doped samples of $x = 0.2$ to 0.5. The XRD results are in good agreement with the standard data of LaFeO$_3$ (JCPDS card no: 37-1493) and α-Fe$_2$O$_3$ (JCPDS card no: 89-0595). The average crystallite size is determined from the X-ray line broadening of the (101), (121), (220), (202), (240), (242), and (204) diffraction peaks using the Scherrer equation, and it is found to be decreased with increasing Al content, as summarized in Table 1.

SEM analysis

The SEM micrographs of La$_{1-x}$Al$_x$FeO$_3$ ($x = 0.0$, 0.1, 0.3, and 0.5) nanopowders are shown in Figure 2. In Figure 2a, the powders are almost irregularly nano-agglomerated with a mean size of approximately 60 to 75 nm. In Figure 2b,c,d, agglomeration of nanoparticles with a size larger than 100 nm and grain growth can be observed in doped samples. Moreover, the SEM images reveal a uniform grain size distribution and homogeneous nanostructure.

Table 1 Lattice parameter and crystallite size of La$_{1-x}$Al$_x$FeO$_3$ nanopowders

| $x$  | a (Å)  | b (Å)  | c (Å)  | Average crystallite size (Å) |
|------|--------|--------|--------|-----------------------------|
| 0.0  | 5.559  | 7.862  | 5.560  | 58.45 ± 5.90                |
| 0.05 | 5.544  | 7.848  | 5.549  | 39.00 ± 1.03                |
| 0.1  | 5.536  | 7.834  | 5.539  | 29.83 ± 1.784               |
| 0.2  | 5.503  | 7.812  | 5.522  | 24.30 ± 3.76                |
| 0.3  | 5.506  | 7.790  | 5.506  | 23.23 ± 5.22                |
| 0.4  | 5.443  | 7.762  | 5.502  | 22.35 ± 4.77                |
| 0.5  | 5.443  | 7.762  | 5.502  | 15.58 ± 4.64                |
TEM analysis

Figure 3a,b,c,d shows bright-field TEM images with the corresponding selected area electron diffraction (SAED) patterns and EDX spectra of La$_{1-x}$Al$_x$FeO$_3$ ($x = 0.0, 0.1, 0.3$, and $0.5$) nanopowders. It is obvious in Figure 3a1, b1,c1,d1 that the particulates consist of the agglomeration of numerous nanocrystallite particles of irregular shape, corresponding to the SEM observation in Figure 2. The average particle size is estimated and found to be approximately 60 to 75 nm. The SAED patterns in Figure 3a2,b2,c2,d2 show ring patterns, indicating that all doped samples are polycrystalline. Each SAED pattern can be indexed to a certain crystalline plane which is found to be consistent with that of the XRD results in Figure 1. The EDX spectra of these samples are shown in Figure 3a3,b3,c3,d3. The EDX results clearly show that all samples contain La, Fe, Al, and O with higher intensity peaks of Al in samples of high Al content. The Cu peaks that appeared come from the copper grid.

Figure 2 SEM micrographs of La$_{1-x}$Al$_x$FeO$_3$ nanopowders. (a) x = 0.0. (b) x = 0.1. (c) x = 0.3. (d) x = 0.5.

Figure 3 Bright-field TEM images (a1-d1) with the corresponding SAED patterns (a2-d2) and EDX spectra (a3-d3) of La$_{1-x}$Al$_x$FeO$_3$ nanopowders. (a) x = 0.0. (b) x = 0.1. (c) x = 0.3. (d) x = 0.5.
FT-IR analysis
Figure 4 shows the FT-IR spectra of La$_{1-x}$Al$_x$FeO$_3$ ($x = 0, 0.05, 0.1, 0.2, 0.3, 0.4, \text{ and } 0.5$) nanopowders. All spectra show broad absorption peaks at approximately 3,449.13 cm$^{-1}$, corresponding to the symmetric and asymmetric stretching modes of water molecules. The observed broad band at approximately 1,600 cm$^{-1}$ corresponds to the bending mode of O-H bond. The strong absorption peaks in the range of 500 to 600 cm$^{-1}$ reveal the presence of metal oxygen bonds which can be assigned to the vibrations of Fe-O and O-Fe-O bonding in the octahedral structure of La$_{1-x}$Al$_x$FeO$_3$. These results are in good agreement with the FT-IR spectra of pure and doped LaFeO$_3$ reported in the literature [14,41,43,47,50].

UV-vis analysis
The UV-vis spectra of La$_{1-x}$Al$_x$FeO$_3$ ($x = 0, 0.05, 0.1, 0.2, 0.3, 0.4, \text{ and } 0.5$) nanopowders are shown in Figure 5. In Figure 5, broad absorption peaks are observed in all samples at approximately 285 nm with the infinitesimal redshifted to approximately 290 nm. From the plot of $(\alpha h \nu)^2$ vs. $h \nu$ in Figure 6a,b,c,d, the optical band gaps ($E_g$) of the samples can be determined by extrapolating the slope to the zero value of $(\alpha h \nu)^2$, and the obtained values are summarized in Table 2. It is found that the optical band gaps do not significantly vary with increasing Al content.

VSM analysis
Figure 7a,b,c,d,e,f,g shows the magnetization curves of La$_{1-x}$Al$_x$FeO$_3$ ($x = 0, 0.05, 0.1, 0.2, 0.3, 0.4, \text{ and } 0.5$) nanopowders measured at room temperature by VSM. As can be seen in Figure 7a, the magnetization curve of the pure sample is very narrow, indicating the antiferromagnetic behavior of the sample, while those of the doped samples show larger loops of ferromagnetic behavior with higher magnetization according to higher Al content (Figure 7b,c,d,e,f,g). In addition, the values of coercive field ($H_c$), magnetization ($M$), and remanent magnetization ($M_r$) are enhanced with increasing Al content, as summarized in Table 2. In general, it is well known that pure LaFeO$_3$ exhibits antiferromagnetic behavior. This behavior is due to the anti-alignment of the magnetic moments of the Fe$^{3+}$ ions. However, LaFeO$_3$ can behave ferromagnetically due to the small crystallite size. The decrease of crystallite size can increase the uncompensated spins at the surface [60,61]. In our work, it is evident in Table 1 that the crystallite size of La$_{1-x}$Al$_x$FeO$_3$ decreases for higher Al content, resulting in the enhancement of ferromagnetism with higher $M$ value. In addition, the second phase of $\alpha$-Fe$_2$O$_3$ detected in the
XRD measurements may also be attributed to the ferromagnetism in La$_{1-x}$Al$_x$FeO$_3$. Figure 8 shows the temperature-dependent magnetization of La$_{0.5}$Al$_{0.5}$FeO$_3$ nanopowder investigated by field-cooled (FC) measurement in the temperature range of 50 to 390 K. The $M$ decreases as the temperature increases because of the thermal fluctuations causing the randomization of polarization direction. It is clearly seen in Figure 8 that the zero value of magnetization cannot be observed in the temperature range of measurement, implying that the Curie temperature ($T_c$) is above 400 K.

**Conclusions**

In summary, La$_{1-x}$Al$_x$FeO$_3$ ($x$ = 0, 0.05, 0.1, 0.2, 0.3, 0.4, and 0.5) nanopowders were successfully synthesized by polymeric complex method at a temperature of 900°C for 3 h in air. XRD analysis reveals an orthorhombic phase of the nanopowders with average crystallite size in the range of 15.58 ± 4.64 to 58.54 ± 5.90 nm. The impurity phase of $\alpha$-Fe$_2$O$_3$ is found in doped samples of $x \geq 0.2$. SEM and TEM images show agglomerated nanoparticles of irregular shape with estimated particle sizes in the range of 60 to 75 nm. The lattice parameters are found to decrease with increasing Al content. The EDX results clearly show only the main peaks of La, Fe, Al, and O in all samples. The UV-vis spectra show the infinitesimal shift from 285 to 290 nm as the Al content is increased. The increase of Al content does not significantly affect the optical band gaps which are found to be in the range of 2.05 to 2.09 eV. Al$^{3+}$ substitution in LaFeO$_3$ crystals can enhance the magnetization ($M$), coercive field ($H_c$), and remanent magnetization ($M_r$) of Al-doped samples by a factor of 8, 11, and 89, respectively. The ferromagnetism in La$_{1-x}$Al$_x$FeO$_3$ is due to the size effect and impurity.

**Competing interests**

The authors declare that they have no competing interests.

**Authors’ contributions**

YJ designed and carried out all the experiments and data analysis and participated in preparing the draft of the manuscript. SH co-supervised the research and gave discussion. ES, the project coordinator, supervised the research and gave discussion.
research, designed the experiment, participated in preparing the draft of the manuscript, and revised the manuscript. All authors read and approved the final manuscript.

Acknowledgements
The authors would like to thank the Department of Physics of the Faculty of Science, Ubon Ratchathani University for providing the XRD facility and Khon Kaen University for providing the SEM, TEM, FT-IR, UV-vis, and VSM facilities. This work is partially supported by the Nanotec-KLU Center of Excellence on Advanced Nanomaterials for Energy Production and Storage and the Integrated Nanotechnology Research Center and Department of Physics, Faculty of Science, Khon Kaen University.

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Received: 16 July 2014 Accepted: 21 August 2014

Published: 15 September 2014

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