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Magnetic and Ferroelectric Properties of Sol–Gel Synthesized Rhombohedral Phase Alfeo3 Nanoparticles

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Abstract:
The preparation of a rhombohedral phase (space group *R*3*c*) $AlFeO_3$ nanoparticles (NPs) and its magnetic and ferroelectric properties. The high purity rhombohedral phase AFO NPs of an average size 50 nm were prepared by sol – gel route followed by annealing at 700 ºC. The NPs show antiferromagnetic nature at room temperature and near room temperature, weak ferroelectric properties. The coexistence of magnetic and ferroelectric features indicate that AFO NPs can be used as a prospective lead free multiferroic material for the spintronics applications.

Keywords: Rhombohedral, $AlFeO_3$, Nanoparticles, Antiferromagnetic, Multiferroic.

1. Introduction

Recently, the perovskite type oxide ABO_3 materials exhibiting ferro or anti – ferromagnetic and ferroelectric ordering, known as multiferroics have gained significant scientific and technological attention [1-4]. In the multiferroic materials, the electric and magnetic properties are mutually controlled, which enable its use in potential device applications such as sensors, data storage devices, etc.[3-6] . In this context, the search for single-phase magnetoelectric materials, with appropriate properties for practical applications is a significant challenge for physicists and material scientists. Furthermore, most of the single-phase magnetoelectric materials are produced from heavy metal such as lead (Pb) [7, 8]. Therefore, for environmental and public health reasons, the researchers and manufacturers of devices that usage ferroelectric and/or magnetoelectric materials are increasingly interested in reducing or even, in extreme cases, completely eliminating the heavy metals from these materials i.e., in producing lead – free materials [7].$AlFeO_3$ (AFO) is a lead – free ABO_3 type perovskite material, which exists in two different phases, orthorhombic and rhmbohedral [9]. The orthorhombic AFO (O – AFO) retains collinear ferrimagnetic structure with Nèel temperature (T_N) in the range 210 – 250 K [9-11]. The magnetic ordering in O – AFO is due to the metal – oxygen – metal antiferromagnetic super exchange interactions [11]. In O – AFO, the Al and Fe atoms, respectively occupy the A and B positions of the standard ABO_3 perovskite. Thus, Fe atom is having six-fold coordination inside the oxygen octahedra of perovskite[9,12]. The preparation and multiferroic properties of O - AFObulk particles and thin films have been reported by several researchers [9-11, 13]. However, there are no experimental reports on the preparation and physicochemical properties of the rhombohedral AFO (R – AFO) particles. Here in, we report the preparation of high purity R – AFO nanoparticles and its structural, magnetic and ferroelectric properties.

2. Experimental

Preparation of $AlFeO_3$ nanoparticles

AFO nanoparticles were prepared by the chemical route followed by the annealing. Briefly, the reaction steps are as follows. All the precursors were of analytical grade and used without further purifications. The initial precursor preparation was carried out at room temperature. The precursors, $Al(NO_3)_3.9H_2O$ and $Fe(NO_3)_3.9H_2O$ in equilimolar ratio were dissolved in 20 ml Milli-Q water. The mixture was kept under constant stirring condition and 10 ml NH_4OH (25 wt % concentration) was added drop wise to above mixture. The addition of NH_4OH, turns the mixture dark red in color. The reaction was further kept under constant stirring conditions for 1 hour. The small amount of acetone was added to above reaction to precipitate the precursor required for $AlFeO_3$ nanoparticles preparation. The obtained precursor was further washed with Milli–Qwateranddriedat80ºC.The obtained powder was further annealed at 700ºC for 1 hour.   Characterizations

The as prepared nanoparticles were characterized by several characterization techniques. The X – ray diffraction (XRD) of the sample was obtained using PANALYTICAL X'Pert Pro (Cu – Kα radiation source with λ ≈1.5406 Å). The Rietveld refinement of XRD pattern was carried out using Full prof (Version July 2016). The transmission electron microscopy (TEM) of the nanoparticles was carried out using JEOL JEM – ARM200F microscope. The magnetic measurements (M – H and dc magnetization) on the nanoparticles were performed using a magnetic property measurement system (MPMS) from MPMS 5, Quantum Design Inc. San Diego, CA equipped with a 7 T superconducting magnet. The ferroelectric characteristic of the nanoparticles was studied at room temperature. For the measurement, sample in the pellet form was prepared using a conventional axial cold pressed technique followed by sintering at 500ºC for 30 minutes (pellet diameter: 5 mm, electrode material: silver paste). The measurements were carried out using aix ACCT TF Analyzer 2000 FE at a 1 kHz ac frequency.

3. Results and discussion

The phase purity of the sample was determined by XRD (seefigure1(a)). The measurement confirm the$R3c$phaseofnanoparticles[10].The latticep arameterswereobservedtobe$a$= 5.030Åand c=13.350Å,which are nearly close to the reported values for the rhombohedral phase of AFOparticles[9].

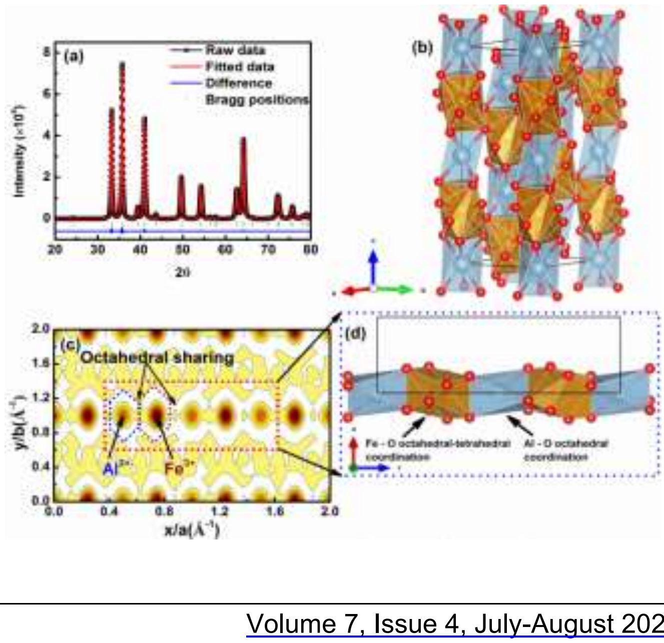

Figure 1. (a) Rietveld refined XRD pattern of AFO nanoparticles. (b) Unit cell of $AlFeO_3$ nanoparticles representing FeO_6 polyhedral and AlO_6 octahedral coordination. (c) and (d) shows 2D electron density plotofunitcell in the (104) direction and 3D representation of polyhydra (Fe –O) –octahedral (Al–O) sharing with reference to electrondensity map with in $AlFeO_3$ unitcell respectively.The refinement also shows that Fe – O coordination forms distorted octahedra and appears to be polyhedra, while Al – O coordination observed to be octahedra (see figure 1(b) and (c)). The polyhedra – octahedra coordination was observed to be either face sharing or edge sharing with this the unit cell (see figure 1(d)). The particle size was determined by TEM.The nanoparticles were observed to be an early spherical in shape with an average size ≈50 nm (see figure 2(a) and (b)).

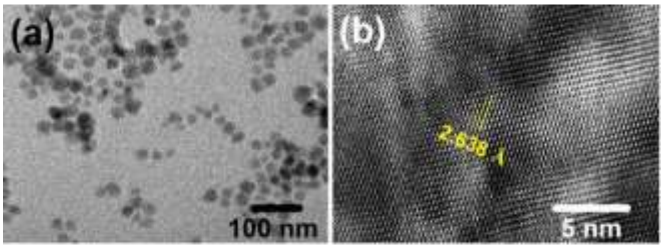

Figure2.(a)and(b)showsTEMandHRTEMmicrographsof$AlFeO_3$nanoparticles respectively.

Figure 3(a) shows magnetic measurements on AFO nanoparticles. The magnetic measurements indicate that at room temperature (300 K) AFO nanoparticles exhibit linear hysteresis loop indicating antiferromagnetic behavior of the nanoparticles.

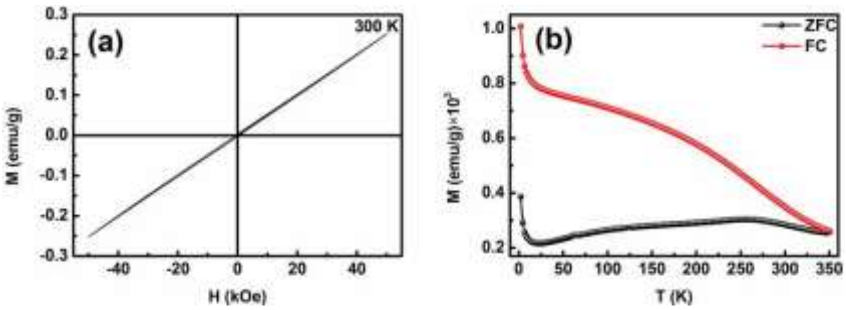

Figure3.(a)Antiferromagnetic behavior of as prepared $AlFeO_3$nanoparticles at room temperature,(b)ZFC–Fc measurements on the nanoparticles at applied field500Oe.Figure3(b) showstheZFC– FCmeasurement indicates that nanoparticles exhibit Nèeltemperature≈290K,which is nearly consistent with the reported results[9].

We observed that the nanoparticles exhibit weak and leaky ferroelectric nature proximity to Nèel temperature (see figure 4).The nanoparticles show saturation polarization≈5.3 µC/cm^2.

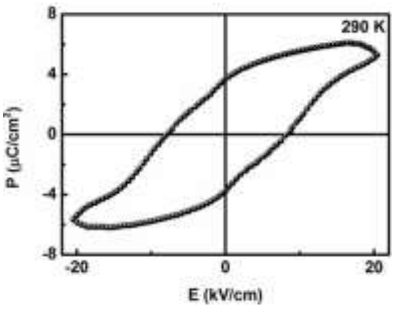

Figure4.Ferroelectrichysteres is loop acquired on the as prepared $AlFeO_3$ nanoparticles.

4. Conclusions

In summary, the perovskite rhombohedral phase $AlFeO_3$ nanoparticles of an average size 50 nm were prepared by chemical route. The magnetic and ferroelectric properties were explored on these as prepared nanoparticles. The results presented here shed some light on multiferroic behavior of AFO nanoparticles, which can be a prospective candidate for fabrication of future device applications.

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