

Structure-property relationship in ABO₃-type Rare-Earth Indate System

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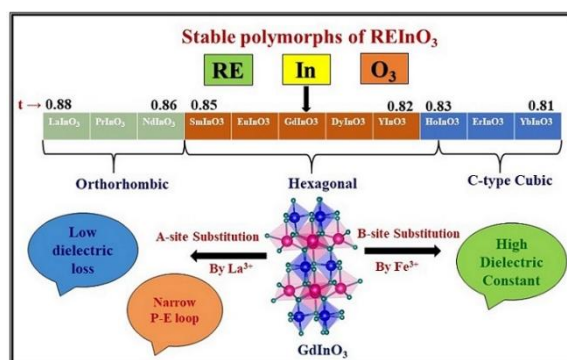
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Abstract



Rare-earth indates (REInO₃) are special class of ABO₃ type compounds which exhibit significant polymorphism and thus have drawn increasing attention due to their diverse structural behavior and interesting dielectric properties. This work discusses a comprehensive overview of the structure-properties relationship in REInO₃ compounds with an aim to understand various factors that influence their phase formation, structure, and electrical behavior. Experiments were performed to stabilize different polymorphs of the REInO₃ series by controlled syntheses under varying conditions. It was observed that temperature and composition play very important roles in the stabilization of several stable and metastable phases. Fine optimization of synthesis conditions can selectively stabilize specific polymorphs of rare-earth indates, which is crucial for tailoring their properties for potential applications. A-site and B-site substitutions have also been methodically explored to assess their influence on the structural and dielectric properties of REInO₃ compounds. The substitutions have been found to provide an effective method for tuning the dielectric behavior of the materials. By replacing either the rare-earth element (A-site) or indium (B-site) changes has been observed in phase stability and electrical performance, which are vital for optimizing their use in electronic and dielectric applications. The key findings reveal (a) temperature and composition are critical factors influencing the polymorphism of REInO₃ compounds. (b) Substitution at the A-site and B-site allows for tuning the structure and dielectric properties, offering a way to optimize these materials for practical applications.

Keywords: Rare-earth indates, Polymorph, Metastable, Lead free Relaxor.

1. Introduction

The nominal formula ABO₃ is often linked with perovskite structure. However, the ABO₃ composition can adopt varieties of structures such as corundum, bixbyite, ilmenite, perovskites and several interesting hexagonal phases, etc. [1-3]. The hexagonal perovskite-related structure exists in a narrow tolerance factor range of 0.83-0.85 and exhibits a layered arrangement of BO₅ trigonal bipyramids (TBP) linked together by AO₇ polyhedra. Recently, the observation of improper ferroelectricity in such hexagonal compounds has spurred research interest. Rare earth indates, REInO₃ (RE: La to Lu; Y), are scarcely investigated and interesting class of compounds where varieties of structures are formed depending on the ratio of the radius of RE³⁺ and In³⁺ ions. These hexagonal indates are known to exist in both paraelectric (space group: *P6₃mmc*) and ferroelectric forms (space group: *P6₃cm*), and the transition driven between these two forms is displacive in nature. Ferroelectricity in these compounds have

been found in the interplay of the bending of InO₅ trigonal bipyramid and the different RE-O bond lengths along the c-axis [2, 3]. This work elaborates on the synthesis of REInO₃ (RE = La, Pr, Nd, Sm, Eu, Gd, Y, Tb, Dy, Ho, Er, Yb), with several metastable compounds being isolated and discussions on their structure-properties relationships. It is interesting to understand the compositionally induced structural distortion and its manifestation in electrical behaviour. Tailoring of electrical properties of REInO₃ was carried out by investigating the effect of A-site and B-site substitution.

2. Experimental

REInO₃ was synthesized through a fuel-deficient gel-combustion method using glycine as fuel and a conventional solid-state method using a three-step heating protocol. Phase stabilization studies were carried out based on composition, temperature, and pressure. Extensive characterizations of samples were carried out using host of techniques. Powder XRD

(Proto AXRD-LPD) was recorded in 2θ range 10° - 90° . HT-XRD was carried out in the temperature range from RT to 1000°C through Anton Parr HTK-16N attached to Proto AXRD-LPD. Sample characterization was also carried out by Raman spectroscopy (QEPro Raman Spectrometer), and impedance spectroscopy (Novocontrol Alpha-AN impedance analyzer). High-pressure XRD was carried out at (EDXRD) beamline (BL-11) of Indus-2 (synchrotron radiation source, India).

3. Result and discussion:

Synthesis of REInO_3 (RE = La, Nd, Pr, Sm, Eu, Gd, Y, Tb, Dy, Ho, Er, Yb) was carried out via gel-combustion (GC) method using glycine as fuel in fuel-deficient ratio and solid-state route [4]. A rich phase relation has been obtained as a function of rare-earth ions, and they are depicted in Fig.1. as revealed in Fig 1(a). The lighter REInO_3 (i.e., La-Sm) get stabilized in an orthorhombic perovskite structure, the mid REInO_3 specifically (Sm-Tb) form hexagonal perovskite-related structure while the heavier REInO_3 compounds show either mixed phase (Dy, Ho) or single phasic C-type cubic (Er, Yb) structures.

	LaInO ₃	PrInO ₃	NdInO ₃	SmInO ₃	EuInO ₃	GdInO ₃	DyInO ₃	YInO ₃	HoInO ₃	ErInO ₃	YbInO ₃
GC-600°C	Orthorhombic			Hexagonal			C-type Cubic				
GC-850°C	Orthorhombic			Hexagonal			C-type Cubic				
GC-1250°C	Orthorhombic			Hexagonal						C-type Cubic	
SS	Orthorhombic				Hexagonal					C-type Cubic	

Role of synthesis route & temperature on the phase evolution in REInO₃

Role of synthesis route & temperature on the phase evolution in REInO_3

Fig. 1(a). Schematic representation of phases observed in REInO_3 system

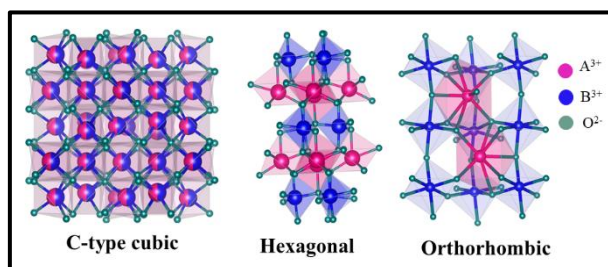


Fig.1(b). Schematic depiction of C-type, hexagonal, and orthorhombic phases observed in REInO_3 system

Fig. 1(b) shows the schematics of C-type, hexagonal and orthorhombic structures and their typical Rietveld refinement plot is shown in Fig. 1(c). The hexagonal perovskite-related structure of REInO_3 belongs to the non-centrosymmetric space group $P6_3cm$, and that has the potential to show ferroelectricity. The solid-state synthesis route yielded a pure monophasic orthorhombic modification of SmInO_3 , whereas gel-combustion synthesized SmInO_3 crystallized in a hexagonal modification.

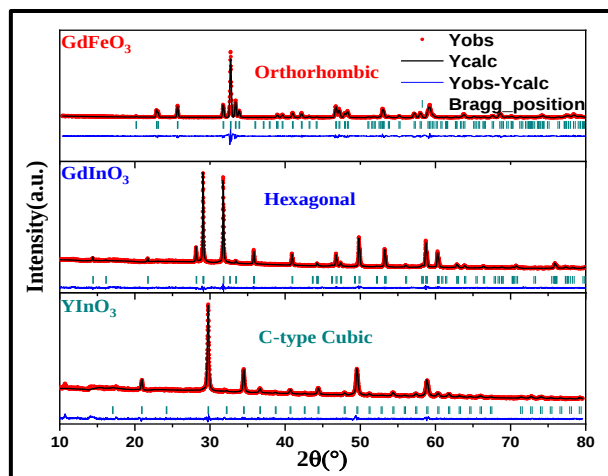


Fig.1(c). Typical fitted pattern of C-type cubic, Hexagonal and orthorhombic

These hexagonal REInO_3 compounds were further investigated by tailoring the A- and B-site cations. To explore the effect of A-site substitution, structural and electrical investigations were carried out on hexagonal $\text{Y}_{1-x}\text{Gd}_x\text{InO}_3$ ($0.0 \leq x \leq 1.0$) series synthesized by the gel-combustion method [5]. The phase relations exhibit profound temperature dependence, as shown in Fig. 2. The metastable C-type modification can be stabilized for all the compositions, which subsequently converts to stable hexagonal polymorphs upon further heating. The conversion temperature (C-type to hexagonal) increased with increased Y^{3+} content. The system was observed to be a monophasic hexagonal throughout the composition range at 1250°C .

Composition	600°C	800°C	850°C	900°C	1000°C	1250°C
GdInO ₃	Cubic	Hexa	Hexa	Hexa	Hexa	Hexa
Y _{0.1} Gd _{0.9} InO ₃	Cubic	Hexa	Hexa	Hexa	Hexa	Hexa
Y _{0.3} Gd _{0.7} InO ₃	Cubic	Cubic	Hexa	Hexa	Hexa	Hexa
Y _{0.5} Gd _{0.5} InO ₃	Cubic	Cubic	Hexa	Hexa	Hexa	Hexa
Y _{0.7} Gd _{0.3} InO ₃	Cubic	Cubic	Cubic + Hexa	Hexa	Hexa	Hexa
Y _{0.9} Gd _{0.1} InO ₃	Cubic	Cubic	Cubic	Cubic	Cubic+ Hexa	Hexa
YInO ₃	Cubic	Cubic	Cubic	Cubic	Cubic	Hexa

Fig. 2. Schematic representation of phases observed in $\text{Y}_{1-x}\text{Gd}_x\text{InO}_3$ system (C: C-type cubic; Hex: hexagonal)

Raman spectroscopic analysis highlighted a clear yet subtle structural change above $x = 0.7$. Electric field-dependent polarization measurements demonstrated the ferroelectric hysteresis loop for pure YInO_3 . The $\text{Y}_{1-x}\text{Gd}_x\text{InO}_3$ system transforms from ferroelectric behavior in YInO_3 to paraelectric in GdInO_3 . XRD, Raman, and electrical characterizations revealed that the electrical properties must be carefully tuned by controlling the tilting of InO_5 polyhedra.

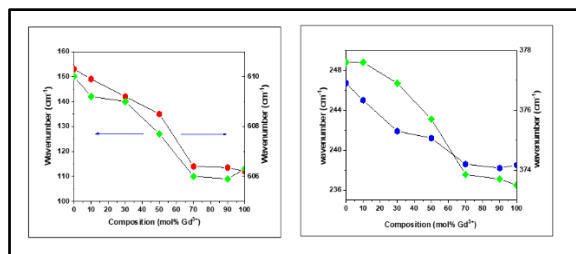


Fig. 3. Variation of frequencies of various modes in Raman spectra with composition in $Y_{1-x}Gd_xInO_3$ ($0.0 \leq x \leq 1$).

However, this tunability could not be achieved by A-site substitution, and leading to the investigation of B-site substitution. The B-site modified series $YIn_{1-x}Fe_xO_3$ ($0.0 \leq x \leq 1.0$) was synthesized and analyzed [6]. The observed phase relation in the $YIn_{1-x}Fe_xO_3$ system is shown in Fig. 4. The temperature is found to have a significant influence on the phase evolution in this system. The complete system was stabilized with C-type metastable modification in the as-synthesized form. The temperature and the synthesis route could be tuned to stabilize the nominal composition $YIn_{0.1}Fe_{0.9}O_3$ in all the three polymorphs viz—C-type cubic, hexagonal, and orthorhombic modifications.

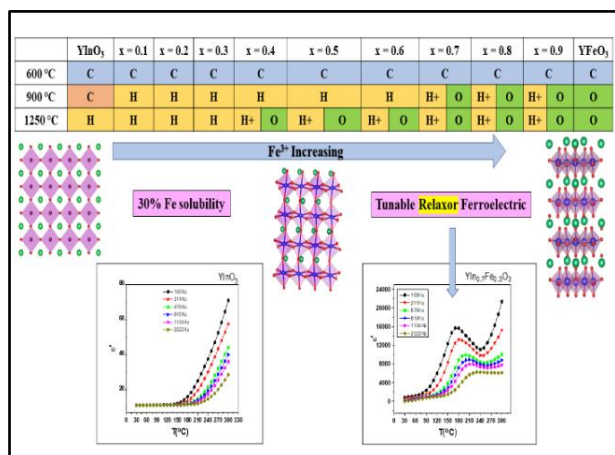


Fig. 4. Phase relations observed in $YIn_{1-x}Fe_xO_3$ series with dielectric behavior of $YInO_3$ and $YIn_{0.7}Fe_{0.3}O_3$

Raman spectroscopic investigations in the $YIn_{1-x}Fe_xO_3$ system revealed that while there is shrinkage of the lattice due to the substitution of a smaller Fe^{3+} ion at the In^{3+} -site, there is a dilation of the Y-O bond [7]. This anomaly is reflected in the electrical behavior exhibited by the system. Dielectric measurements were also carried out for the monophasic hexagonal nominal compositions, $YIn_{1-x}Fe_xO_3$ ($0.0 \leq x \leq 0.3$). The radical increase in dielectric constant from 10 for $YInO_3$ to 1000 for $YIn_{0.7}Fe_{0.3}O_3$ at room temperature (Fig. 4). This suggests the role of B-site tailoring on electrical behavior is essential. Thus, the substitution of smaller Fe^{3+} ions into $YInO_3$ to tune the electrical behavior from a dielectric to relaxor ferroelectric over the studied temperature range. $YIn_{0.7}Fe_{0.3}O_3$ compositions illustrated a relaxor ferroelectric-like behavior which is an important observation in the context of the search for new lead-free relaxor materials [8]. The hexagonal $YInO_3$ structure consists of InO_5 (trigonal bipyramids

TBP) and YO_7 (capped trigonal antiprisms). The ferroelectricity is induced due to unequal Y-O bond lengths along the c-axis, which are primarily governed by the buckling of InO_5 -TBPs with respect to the c-axis or the vertical axis of YO_7 antiprisms. From the above studies, it is apparent that substitution at B-site (here Fe^{3+} for In^{3+}) distorts BO_5 polyhedra, and this, in turn, subtly alters YO_7 antiprism. It is obvious that any distortion in BO_5 polyhedra will affect AO_7 bond lengths, thereby disturbing the original ferroelectric arrangement and introducing relaxor behavior, as shown in Fig. 5. It is evident that increasing the amount of Fe^{3+} is progressively increasing distortion in BO_5 polyhedra, which apparently leads to variations in Y-O bond lengths. This is instrumental in controlling the electrical behavior of hexagonal indates. The study is also supported by the red shift in the Raman band observed at frequency 150 cm^{-1} , which pertains to ionic motion in Y-O-Y linkages. The study inferred that substitution at the A-site in $YInO_3$ [5, 7] simply randomizes the A-site without much effect on the relative arrangement of atoms, which controls geometric ferroelectricity, while substitution at the B-site creates distortion and thereby introduces relaxor behavior in the structure.

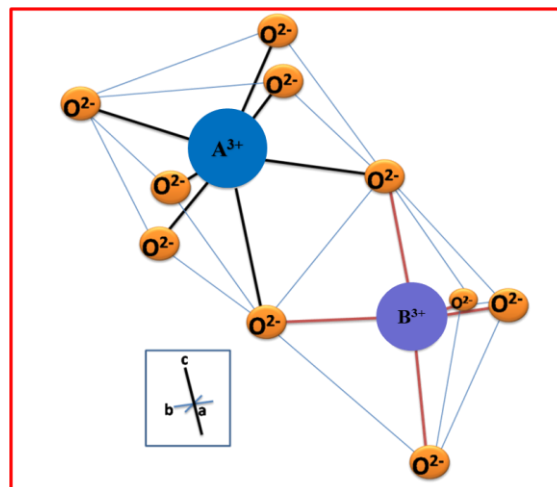


Fig. 5. Polyhedral connection of AO_7 & BO_5 polyhedra through edge in $YIn_{1-x}Fe_xO_3$

With the kind of inference from our previous work discussed above, it was envisaged that it may be because Y^{3+} is smaller than Gd^{3+} ; hence, this kind of dielectric behavior is obtained; how about substituting an ion that is bigger than Gd^{3+} for, e.g., La^{3+} at A-site? Also, as encouraging results have been obtained from Fe^{3+} substitution at the B-site, the same substitution was selected with $GdInO_3$ as the host matrix.

With this information in cognizance, A- and B-site tailored $GdInO_3$ were synthesized by gel combustion technique and annealed at four different temperatures to explore their extensive structural and electrical behaviour. Phase relations were strikingly different from the $Y_{1-x}Gd_xInO_3$ system despite having similar tolerance factors. The temperature was found to have a tremendous bearing on the phase relations. Metastable C-type modifications hexagonal, orthorhombic, and biphasic modifications in the substituted $GdInO_3$ system were observed, as shown in Fig. 6. A-site substituted ($Gd_{1-x}La_xInO_3$) system depicted

a wide orthorhombic phase up to 80 mol % Gd^{3+} . This could be attributed to the preferential stability of La^{3+} -rich phases in orthorhombic perovskite form. On the other hand, $\text{GdIn}_{1-x}\text{Fe}_x\text{O}_3$ showed wide biphasicity in orthorhombic/hexagonal phases.

La _x Gd _{1-x} InO ₃ (0.0 ≤ x ≤ 1.0)											
x	GdInO ₃	x = 0.1	x = 0.2	x = 0.3	x = 0.4	x = 0.5	x = 0.6	x = 0.7	x = 0.8	x = 0.9	LaInO ₃
600 °C	H	H	H	H	H	C	C	C+UIP	C+UIP	C+UIP	C+UIP
1150 °C	H	H	H+O	O+H	O	O	O	O	O	O	O

GdFe _x In _{1-x} O ₃ (0.0 ≤ x ≤ 1.0)											
x	GdInO ₃	x = 0.1	x = 0.2	x = 0.3	x = 0.4	x = 0.5	x = 0.6	x = 0.7	x = 0.8	x = 0.9	GdFeO ₃
600 °C	C	C	C	C	C	C	C	C	C	C	C
1150 °C	H	H	H+O	H+O	H+O	H+O	O+H	O+H	O	O	O

Fig. 6. Schematic representation of phases observed in A & B-site substituted GdInO_3 system

(C: C-type cubic; Hex: hexagonal; O: Orthorhombic; UIP: unidentified phase)

Raman spectroscopic investigations were employed to analyze the structural changes at a microstructural level to augment the XRD data e.g., in B-site substituted $\text{GdIn}_{1-x}\text{Fe}_x\text{O}_3$ ($0.0 \leq x \leq 0.1$), a general shrinkage of the hexagonal lattice due to substitution of a smaller ion at In^{3+} -site was observed. Still, an apparent dilation of the Gd-O bond was exhibited by Raman spectroscopy [9]. Electrical studies show that in $\text{Gd}_{1-x}\text{La}_x\text{InO}_3$, remanent polarisation decreases with Gd^{3+} -content, and very low & field-independent leakage currents observed for Gd^{3+} -rich compositions ($4 \times 10^{-9} \text{ A/cm}^2$) [10]. While $\text{GdIn}_{1-x}\text{Fe}_x\text{O}_3$ showed a systematic increase in dielectric constant with Fe^{3+} -content. Dielectric constant and $\tan \delta$ show a steep increase with T for the Fe-rich system. This study emphasizes the role of synthesis conditions, compositions, and coordination preference of competing ions in rare earth indates (REInO_3) systems and provides a substantial structural database that could be potential ferroelectric material.

High pressure studies on hexagonal YInO_3 and cubic solid solution of YbInO_3 [11, 12]

The structural behavior of the hexagonal phase of YInO_3 under high pressure was studied and revealed an onset of a first-order phase transition around pressure 12 GPa [9]. The ambient pressure phase of YInO_3 has more compression in the ab plane compared to the c-axis. The bulk modulus of the hexagonal $P6_3\text{cm}$ phase is determined to be $194 \pm 10 \text{ GPa}$. The high-pressure phase of YInO_3 was found to be orthorhombic perovskite (Sp. Gr. $Pnma$), confirmed through experimental and theoretical studies. The ambient hexagonal $P6_3\text{cm}$ phase was observed to coexist with high-pressure orthorhombic phase up to 29 GPa. Under pressure, the structural evolution of C-type solid solution YbInO_3 (space group $Ia3$) was also investigated. A first-order irreversible structural phase transition was observed at $\sim 15 \text{ GPa}$. The coexistence of the ambient cubic phase with the high-pressure phases up to the highest pressure achieved in the experiment, i.e., 42 GPa. Based on theoretical and experimental investigations, the high-pressure phase of c-YbInO_3 is

proposed to form an orthorhombic YbInO_3 perovskite with space group $Pnma$.

4. Conclusions

From an extensive investigation of REInO_3 compounds, it could be revealed that the rare earth ion plays a crucial role in stabilizing different polymorphs. The polymorphs stabilized via careful control of synthesis protocol, substitution, temperature, and pressure pave the way to tune the electrical properties of the hexagonal rare-earth indates. The variation of electrical properties from dielectric to ferroelectric to relaxor in REInO_3 could be demonstrated using these facts. Thus, it can be concluded that rare earth indates can have tremendous potential applications as lead-free dielectric/ferroelectrics [9].

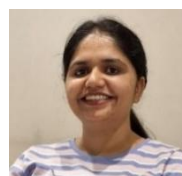
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