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CATION COORDINATION AND Fe³⁺ LUMINESCENCE IN LIAIO₂ POLYMORPHS PREPARED BY A HYDROTHERMAL METHOD

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ABSTRACT

The polymorphs α -, β -, and γ - LiAlO₂ were synthesized by a hydrothermal method. The as-prepared product obtained at 240°C was β-LiAlO₂, which converted completely to γ -LiAlO₂ above 1000°C. α -LiAlO₂ was obtained by the decomposition of LiAl(OH)₄·H₂O prepared by imbibition of LiOH into LiAl₂(OH)₇·2H₂O hydrothermally at 140°C. Solid state MAS NMR (magicangle spinning nuclear magnetic resonance) studies indicate that Li⁺ uniquely occupies octahedral sites in all the polymorphs. This observation indicates that the results of XRD and crystal structure studies on β - and γ -LiAlO₂ reported in the literature that indicate the presence of Li^+ in the tetrahedral site are apparently in error with respect to Li^+ coordination. The other cation, Al^{3+} , occupied octahedral sites in α -LiAlO₂ and tetrahedral sites in the β - and γ -LiAlO₂. The Fe³⁺ doped in the various polymorphic forms of this compound was found to uniquely occupy the octahedral Li⁺ site. EPR spectrum of the Fe³⁺ doped in these polymorphs indicates that during the transformation this site is distorted. The Fe³⁺ photoluminescent emission maximum was different for each polymorph. The difference in the luminescence characteristics among the polymorphic forms is due to the change in the site symmetry because of the distortion of the octahedra occupied by Fe³⁺ across the phase transition. The infrared spectrum indicates that site symmetry is lowered during the phase transition. © 1999 Elsevier Science Ltd

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INTRODUCTION

The compound LiAlO₂ exists in three different allotropes, namely, α -LiAlO₂, the lowtemperature (<400°C) form; β -LiAlO₂, the intermediate temperature (400–800°C) form; and γ -LiAlO₂, the most stable high temperature (>1000°C) form. The latter has received considerable attention because of its possible industrial applications, which include tritiumbreeding material in fusion reactors [1,2] and electrolyte matrix for the molten carbonate fuel cells [3,4] wherein γ -LiAlO₂ is used as the nonconducting inert matrix to contain carbonate electrolyte between the anode and the cathode. Apart from this, when doped with Fe³⁺, γ -LiAlO₂ emits in the deep red region, rendering it suitable for artificial plant illumination phosphor blends. It has been proven experimentally [5–7] that light peaking at about 730 nm is essential for optimum plant growth and flowering. The low- temperature form, α -LiAlO₂, is used as a catalyst support [8] and for the preparation of delithiated alumina compounds [9].

Synthesis and structure of α -LiAlO₂ has been reported by Poeppelmeier et al. [8]. They proposed that the structure is based upon a NaCl-like structure wherein all the metal cations are in the octahedral sites with sheets of alternating LiO₆ and AlO₆ octahedra elongated on the *c* axis, forming a hexagonal lattice. β -LiAlO₂ is isostructural with β -LiGaO₂ and has an orthorhombic cell in which all the atoms are said to be tetrahedrally coordinated by oxygen [10].

Bertaut et al. [11] determined the crystal structure of γ -LiAlO₂ by neutron and X-ray diffraction on powder samples and indicated that the structure is based on a tetragonal unit cell. Marezio [12], based on X-ray diffraction results, confirmed that γ -LiAlO₂ is tetragonal, with the space group $P4_12_12$ or its enantiomorph $P4_32_12_1$. He concluded that all the cations are tetrahedrally coordinated by oxygen.

The present investigation aims to determine the coordination of the metal cations in the allotropes through solid-state MAS NMR. The use of isotropic chemical shifts obtained from MAS NMR spectra to characterize the coordination sphere of Li⁺ and Al³⁺ is well known from the literature [13–17]. Müller et al. [13], based on their studies on aluminates and aluminum oxides, showed that the chemical shifts (δ) of ²⁷Al resonance vary with the local coordination of aluminum. The ⁷Li resonance absorption in LiO₆ group is observed at $\delta = 0-1$ ppm (with respect to LiClO₄) [15,17].

The present paper also describes the site preference of Fe^{3+} when doped in these polymorphs, as determined by electron paramagnetic resonance (EPR) technique, which is highly sensitive to change in site symmetry. The tetrahedral Fe^{3+} always shows a resonance signal of g-value of about 4 and the octahedral Fe^{3+} shows an EPR signal of g-value of about 2 [18,19]. The resonance absorption lines may show multiplicities depending upon the distortion of the sites, e.g., a rhombic distortion will yield three absorption peaks (g_x , g_y , and g_z) and an axial distortion will show two components (g_{\parallel} and g_{\perp}). The luminescent property of Fe^{3+} in LiAlO₂ polymorphs is also presented in this article.

EXPERIMENTAL

Hydrothermal preparation was carried out in a Teflon (PTFE)-lined Morey-type autoclave made of stainless steel, type SS318 (the major constituents were Fe 68.5%, Cr 21%, Mn 2%, Ni 4.5%, and Mo 2.5%). The autoclave was charged with the reactants, viz., hydrated alumina gel mixed with LiOH in the desired molar ratio. Deionized water was added to the

The Products Formed for Two Different Compositions of the Reaction Mixture		
Temperature (°C)	$Li_2O/Al_2O_3 = 1$	$\mathrm{Li}_{2}\mathrm{O}/\mathrm{Al}_{2}\mathrm{O}_{3}=1.5$
<140	LDH^{a}	LDH
160	$LDH + \beta - LiAlO_2$	$LDH + \beta - LiAlO_2$
180	β -LiAlO ₂ + γ -AlOOH	β -LiAlO ₂ + γ -AlOOH
200	β -LiAlO ₂ + γ -AlOOH	β -LiAlO ₂ + γ -AlOOH
240	β-LiAlO ₂	β-LiAlO ₂

TABLE 1

^aLDH = $LiAl_2(OH)_7 \cdot 2H_2O$.

required percentage fill so that the autogenerated pressure was in the range of 5 to 40 MPa when heated in the temperature range 140–250°C for 8–12 h. The Fe³⁺ (0.1 mol%) doped samples were prepared by coprecipitating ferric hydroxide along with alumina gel from mixed ferric chloride and aluminum sulfate solution, using 30% NH_4OH . The preparation was carried out as explained above. The lithium content in the washings was monitored to measure the extent of the reaction and to compare the composition of the solid obtained, through the wet-chemical route. Imbibition of LiOH into LiAl₂(OH)₇·2H₂O was done by charging the autoclave with the previously prepared LiAl₂(OH)₇·2H₂O and LiOH in the required molar ratio and heating below 140°C for 12 h.

Phase identification of the powders was carried out by powder X-ray diffraction (XRD), using a Scintag diffractometer. Infrared absorption spectra were recorded on a Biorad FT/IR spectrometer in the range 4000-400 cm⁻¹. Solid state ²⁷Al and ⁷Li MAS NMR spectra were obtained at 78.2 and 116.6 MHz, respectively, using a high resolution NMR spectrometer (Bruker 300 MHz) at room temperature, fitted with a magic angle spinning probe for rotating the sample at a frequency of 7 kHz. ²⁷Al MAS NMR chemical shifts (δ) were referenced to 1 M Al(H₂O)₆Cl₃ solution having the assigned $\delta = 0$ and that of ⁷Li chemical shifts were referenced to 1 M LiClO₄. Photoluminescence spectra were obtained at room temperature, using a Shimadzu RF-540 spectrofluorophotometer fitted with a Hamamatsu R952 red sensitive photomultiplier. The electron paramagnetic resonance spectra were recorded with a Varian E109 X-band spectrometer with a TE₀₁₁ cavity. The g-values were calibrated using diphenylpicryl-hydrazil (DPPH) having $g = 2.0036 \pm 0.0003$.

RESULTS AND DISCUSSION

The products formed by the hydrothermal synthesis were highly dependent on pressuretemperature (P-T) conditions as well as composition. The products formed from two different initial (charge) compositions are shown in Table 1. Temperature of the hydrothermal reactions was varied, to study the conditions of preparation at which the phase is stable. At temperatures <140°C, the product formed was always a layered double hydroxide LiAl₂(OH)₇·2H₂O (LDH). As the temperature increased to 180°C, LDH decomposed to form a biphasic mixture of β -LiAlO₂ and γ -AlOOH. At 240°C, the phase formed was a monophasic β-LiAlO₂. An increase in Li₂O/Al₂O₃ above the stoichiometric ratio resulted in better crystallinity, and the excess Li could be washed out. Our results show that the lowtemperature form, α -LiAlO₂, cannot be formed under these conditions. At low temperatures, the stability of LDH is very high; as the temperature is increased, the conditions favor the formation of β form. The reaction sequence of the formation of β and γ can be represented as follows:

Al(OH)₃·xH₂O + LiOH
$$\xrightarrow{240^{\circ}\text{C}} \beta$$
-LiAlO₂ + (x + 2)H₂O (70 < x < 105)
(hydrated alumina gel) \sim 40MPa

$$\begin{array}{ccc} \beta\text{-LiAlO}_2 & \xrightarrow{800^{\circ}\text{C}} \beta\text{-LiAlO}_2 + \gamma\text{-LiAlO}_2 \xrightarrow{>1000^{\circ}\text{C}} \gamma\text{LiAlO}_2 \\ (\text{as-prepared}) & (\beta + \gamma \text{ phases}) \end{array}$$

The α form was synthesized by decomposing the precursor having Li₂O/Al₂O₃ = 1. The precursor is a LDH with the composition LiAl(OH)4·H₂O prepared by imbibing LiOH into LiAl₂(OH)₇·2H₂O. Figure 1 shows the XRD pattern of the imbibed sample in relation to LiAl₂(OH)₇·2H₂O. The major difference is that some of the basal reflections, (004) and (006), are split. The splitting of the XRD peaks is due to the insertion of LiOH or [Li(OH)₂]⁻ ions into the intermediate layer. On further increase of LiOH, the phases stabilized are LiAl₂(OH)₇·2H₂O and β -LiAlO₂.

Infrared absorption spectra (Fig. 2) of the LiOH imbibed sample (LiAl(OH)₄·H₂O) show differences from those of the starting composition (LiAl₂(OH)₇·2H₂O) by way of intensity and sharpness of the absorption bands. However, the pattern is the same, indicating that the basic structure remained undisturbed. The imbibed sample shows absorption due to hydrogen bonded or bridged hydroxyl groups similar to that of the starting composition. The LiOH-imbibed sample shows a very strong and sharp peak at 1380 cm⁻¹ and the shoulder peaks at 1618 and 1491 cm⁻¹ are almost the same as those of the starting composition. Gain in intensity of the peak at 1380 cm⁻¹ is due to the intercalation of Li(OH)₂⁻ in the intermediate layer. The increase in sharpness as well as the intensity of absorption band below 1000 cm⁻¹ (characteristics of the AlO₆ group) indicates cation ordering in the octahedral sites.

Figure 3 shows the XRD patterns of different polymorphs obtained from decomposing the precursor LiAl(OH)₄·H₂O. The XRD patterns were indexed using the reported powder X-ray diffraction data on these polymorphs [8,10,12]. The low-temperature form, α -LiAlO₂, was stable only up to 400°C, above which the compound converted into the intermediate β form. Both the phases coexisted up to 500°C. The β form was stable up to 800°C. The intermediate phase, β -LiAlO₂, coexists with γ -LiAlO₂ up to 1000°C and was completely converted into γ -LiAlO₂ at higher temperatures. α -LiAlO₂ is highly sensitive to moisture and converts into a hydrate (LiAlO₂·H₂O) on long time exposure to humid atmosphere free of carbon dioxide.

Solid-State MAS NMR. Knowledge of Al^{3+} and Li^+ coordination is useful in those cases where complete X-ray crystal structure analyses have been not carried out because of the nonavailability of single crystals. The ⁷Li MAS NMR spectra of different polymorphs of LiAlO₂ are shown in Figure 4. All the allotropes showed a single resonance signal with the chemical shift value of 0.6 ppm with respect to LiClO₄ wherein Li⁺ are in the octahedral sites. The periodic repetitions of the satellite peaks on both sides of the 0.6 ppm peak are spinning side bands. This was verified by recording the spectrum at two different spinning speeds, whereby the peaks showed shift in the maxima. The nominal chemical shift value of ⁷Li with respect to LiClO₄ indicates that the chemical environment of ⁷Li in both compounds is the same. This shows that Li⁺ ions uniquely occupy octahedral sites in all the polymorphs. These results indicate that the conclusion drawn on the basis of X-ray diffraction on powder



FIG. 1

XRD tracings of (a) $LiAl_2(OH)7\cdot 2H_2O$, (b) $LiAl(OH)4\cdot H_2O$, and (c) the multiphase obtained on imbibing with excess LiOH.

samples by Poeppelmeir et al. [8] regarding the Li^+ coordination in α -LiAlO₂ is correct, whereas Marezio's [10,12] conclusion on the Li^+ coordination in β - and γ -LiAlO₂ is doubtful. Accurate deduction of the coordination number of a lighter element such as Li^+ is difficult by powder X-ray diffraction techniques. Nuclear magnetic resonance is a versatile technique for determining the local environment of such ions by referencing to a standard substance wherein the coordination is known.

Figure 5 shows the ²⁷Al MAS NMR spectra obtained by referencing $[Al(H_2O)_6]Cl_3$ ($\delta = 0$). The chemical shift values differed among the polymorphs. The low-temperature (<400°C) form, α -LiAlO₂, showed a chemical shift of 9.5 ppm corresponding to the resonance behavior of ²⁷Al in the octahedral site. The NMR signal of β -LiAlO₂ is observed at $\delta = 78.6$, indicating the resonance behavior of ²⁷Al in tetrahedral sites [14]. The γ -form



Infrared absorption spectra of (a) LiAl₂(OH)7·2H₂O and (b) LiAl(OH)4·H₂O.

showed a splitting in the resonance absorption peak with a chemical shift of 70 and 66 ppm, respectively. The appearance of two resonance peaks is due to the presence of two types of tetrahedral Al, perhaps differing from one another by their distortion accompanied by a variation in the nearest as well as the next-nearest environment around the aluminum nuclei. The line broadening indicates that γ -LiAlO₂ is more disordered than the lower temperature polymorphs.

The above results indicate that the α -to- β transformation involves a change in coordination of Al^{3+} accompanying the structural conversion from hexagonal to an orthorhombic unit cell; whereas, the β -to- γ transformation does not involve any change in the coordination of Al^{3+} . The difference in the chemical shift and the observed splitting in the resonance peaks indicate multiplicity in the local site symmetry for Al^{3+} , accompanying the orthorhombic-to-tetragonal transformation.

Infrared Spectra. Figure 6 shows the infrared spectra of α -, β -, and γ -LiAlO₂ in the range 400–1200 cm⁻¹. All the polymorphs show multiple absorption bands in the region below 1200 cm⁻¹. α -LiAlO₂ shows a spectrum different from that of either β - or γ -LiAlO₂. The absorption peaks observed at 790, 737, 650, 636, and 477 cm⁻¹ are due to the presence of two types of structural groups, viz., AlO₆ and LiO₆ group. The two absorption peaks at 790 and 737 cm⁻¹ are due to the Al–O antisymmetric stretching (ν 3) vibrations, and the shoulder



FIG. 3 XRD pattern of (a) α -LiAlO₂, (b) β -LiAlO₂, and (c) γ -LiAlO₂.

at 650 cm⁻¹ and peak at 636 cm⁻¹ are due to the antisymmetric bending (ν 4). The absorption peak at about 477 cm⁻¹ is due to antisymmetric stretching vibrations of LiO₆ group.

The IR absorption spectra of β - and γ -LiAlO₂ are distinctly different from the spectrum of α -LiAlO₂. The spectrum of β -LiAlO₂ shows a broad absorption band centered at 844 cm⁻¹; a triplet at 670, 640, and 610 cm⁻¹; and three sharp peaks at 513, 457, and 422 cm⁻¹. By comparing the present spectrum to that of a compound wherein only AlO₄ polyhedra are present, e.g., BaAl₂O₄ [20], the absorptions due to AlO₄ groups can be identified. Accordingly, the broad absorption band centered at 844 cm⁻¹ can be assigned to Al–O antisymmetric stretching (ν 3), the triplet thereafter is due to the antisymmetric bending (ν 4), and the 422 cm⁻¹ absorption peak is due to symmetric bending (ν 2). The sharp peaks at 513 and 457 cm⁻¹ are due to the LiO₆ antisymmetric stretching and antisymmetric bending, respectively. γ -LiAlO₂ showed a similar spectrum, hence the assignment of the bands remained the same.



However, the absorption bands show modifications: The 844 cm⁻¹ peak corresponding to the antisymmetric stretching of AlO₄ is broader. The band corresponding to antisymmetric bending of AlO₄ shows a doublet instead of triplet as observed in β -LiAlO₂. The antisymmetric stretching band of LiO₆ has broadened, which may be due to the merging of the third absorption band of AlO₄ and β and β

absorption band of AlO_4 antisymmetric bending. The antisymmetric bending of LiO_6 shows a doublet. The intensity of the absorption band due to symmetric bending of AlO_4 has been reduced. The assignment of absorption bands to lithium polyhedra in γ -LiAlO₂ to LiO_4 groups by Tarte [21] appears to be incorrect, since solid-state ⁷Li MAS NMR shows that lithium is in 6-coordination in all the polymorphs.



 ^{27}Al MAS NMR spectra of (a) $\alpha\text{-LiAlO}_2$, (b) $\beta\text{-LiAlO}_2$, and (c) $\gamma\text{-LiAlO}_2$.

The modification of the IR spectrum from one polymorph to another indicates the change in site symmetry. The presence of multiple IR absorption bands indicates the lowering of the site symmetry. The LiO₆ absorption in the α -LiAlO₂ shows a broad single band that has split into two sharp bands in β -LiAlO₂ and into a triplet in γ -LiAlO₂, which indicates the Li⁺ site is more symmetric in the α -LiAlO₂, is lowered in the β -LiAlO₂, and is more asymmetric in γ -LiAlO₂. The site symmetry of Li⁺ in α -LiAlO₂ is D_{3d}, which is lowered to C_{2v} in β -LiAlO₂ and is further reduced to C_s in γ -LiAlO₂. The asymmetry in this site may be



IR spectra of (a) α -LiAlO₂, (b) β -LiAlO₂, and (c) γ -LiAlO₂.

affected by the distortion of octahedra in different directions during the phase transition. The difference in the Al–O stretching frequency region between the polymorphs, α -, β -, and γ -LiAlO₂, is due to the change in the coordination viz., Al³⁺ is in octahedral coordination in α -LiAlO₂ and in tetrahedral coordination in the other two polymorphs. Furthermore, modifications in the IR absorption bands of γ -LiAlO₂ are due to the distortion of the AlO₄ tetrahedra. Also, broadening of the infrared bands usually indicates the distortion in the coordination polyhedra. The effect of change in the site symmetry is reflected in the optical properties, such as luminescence. The change in local environment around the optically active ion due to the polyhedral distortion results in altering of the crystal field, which causes the difference in the splitting of energy states of the optically active ion from one polymorph to another.



EPR spectra of Fe³⁺(0.1 mol%) doped (a) α -LiAlO₂, (b) β -LiAlO₂, and (c) γ -LiAlO₂.

EPR Spectra of Fe³⁺ Ions. Figure 7 shows the EPR spectrum of Fe³⁺ (0.1 mol%) doped in different polymorphs. All the polymorphs show a single resonance absorption peak corresponding to the g-value of ~ 2.00. Ferric ion with a d⁵ configuration, with S = 5/2, should show a 5-line spectrum corresponding to the five S-state transitions. Because of large initial splitting, only the signal corresponding to a $+1/2 \leftrightarrow -1/2$ transition is observed in the spectrum recorded using an X-band spectrometer. It is well known from the literature [18,19] that the octahedral Fe³⁺ shows an EPR signal at g ~ 2.00 and the tetrahedral Fe³⁺ shows an EPR signal at g ~ 4.2. Thus, the Fe³⁺ ions preferentially occupies the octahedral Li⁺ sites, rather than Al³⁺ sites, in LiAlO₂, irrespective of the polymorphic form. Table 2 shows the linewidth of the EPR signal in the different polymorphs. The linewidth of EPR signal in

Linewidth of the Fe ³⁺ EPR Signal in Three Polymorphs at 25°C			
Polymorphic form	Linewidth (Gauss)		
α-LiAlO ₂	350		
β -LiAlO ₂	400		
γ-LiAlO ₂	700		

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Photoluminescence excitation and emission spectra of Fe³⁺ (0.1 mol%) doped in different polymorphs of LiAlO₂ at 300 K. (a), (b), and (c) are the excitation spectra of α -, β -, and γ -LiAlO₂ for $\lambda_{emi} = 712$, 724, and 732 nm, respectively. (a'), (b'), and (c') are the emission spectra of α -, β -, and γ -LiAlO₂ when excited at 294 nm in the case of α -LiAlO₂ and 264 nm in the case of β - and γ -LiAlO₂. (d), (e), and (f) are low temperature (200 K) emission spectra of α -, β -, and γ -LiAlO₂, respectively. Φ is the spectral radiant output power and q_r is the quantum output per unit wavelength interval.

 γ -LiAlO₂ is two times that of α -LiAlO₂. The EPR of Fe³⁺ shows line broadening because of the increased disorder in the lattice.

Luminescence Spectrum. Figure 8 shows photoluminescence–excitation and emission–spectra of Fe³⁺ doped (0.1 mol%) LiAlO₂ in the various polymorphic forms. The excitation spectra of α -LiAlO₂ have a strong band at 294 nm followed by a weak band at 404 nm and a broad band of medium intensity at 612 nm. Other polymorphs of LiAlO₂:Fe³⁺ exhibit similar spectrum with the difference being that the excitation bands, except for the peak at 404 nm, have shifted to shorter wavelengths. The 404 nm peak remained at the same position. The excitation spectrum of β -LiAlO₂ shows a strong band at 264 nm followed by a weak band at 404 nm and a medium strong band at 512 nm. The half bandwidth of the 264 nm band has reduced considerably from that of the 294 nm band in α -LiAlO₂. The excitation spectrum of γ -LiAlO₂ is similar to that of β -LiAlO₂ except that the intensities of all the bands have increased. Emission spectrum of all the polymorphs show a single broad band with different emission maximum. The emission of α -LiAlO₂:Fe³⁺ peaks around 712 nm and that of β - and γ -LiAlO₂ at 724 and 732 nm, respectively. The emission spectra (Fig. 8d–f) recorded at low-temperature (200 K) show a sharp band followed by a broad band with superimposed fine structures. For α -LiAlO₂, the sharp band is observed at 670 nm; whereas, in the case of β - and γ -LiAlO₂, it is observed at 710 nm.

Ferric ion (Fe³⁺) has d⁵ electronic configuration and involves the intraconfigurational d-d transitions. The electric dipole transitions are both spin and parity forbidden. However, mixing of the opposite parity states by odd components of the crystal field violates the selection rules. The ion situated at a site that lacks inversion symmetry exhibits stronger optical transitions than those at centrosymmetric sites. In all the polymorphs, Fe^{3+} is in octahedral sites, as indicated by the EPR results. Even though, in α -LiAlO₂ both Al³⁺ and Li⁺ are in octahedral sites, Fe³⁺ occupies the Li^+ site (octahedral) as in the other polymorphs, as indicated by the similarity of excitation and emission spectra. For the reasons given above, a strong excitation band is not expected from this type of transition. Hence the strong band in the short wavelength region of the excitation spectra (264 nm in the case of β - and γ -LiAlO₂; 294 nm for α -LiAlO₂) can be assigned to the $Fe^{3+} \leftarrow O^{2-}$ charge transfer band. The shift in the charge transfer band to shorter wavelengths in β and γ forms and the increase in intensity are due to the change in site symmetry, as indicated by the IR results. Prevalence of this charge transfer band is essential for the observation of luminescence as the energy absorbed is transferred on to the emitting levels. This is further substantiated by recording the emission spectrum with 404 nm fixed as the excitation maximum, which shows a very weak emission spectrum. Irrespective of the emission maximum, the charge transfer band is the strongest among all the excitation bands, indicating that the energy is derived from the charge transfer band. This type of band is also observed in $LiAl_5O_8$: Fe³⁺[17] at 294 nm. The weaker bands thereafter are due to the internal transitions of Fe³⁺ center, which are indicated in Figure 6 by spectroscopic notations. The 404 nm peak position did not change in the different polymorphs. This can be explained using the Tanabe-Sugano diagram [22], which shows the crystal field dependence of the energy levels of the Fe³⁺. The excited ${}^{4}E_{g}$, ${}^{4}A_{1g}({}^{4}G)$ state is parallel to the ground state, i.e., no shift is observed with change in the crystal field; hence, in all the three polymorphs, the position of this band remained the same. Assignment of the other bands was done by fixing the 404 nm peak as the highest energy transition.

The sharp band observed in the emission spectrum recorded at low-temperature (200 K) is the zero phonon line (ZPL) and is assigned to ${}^{4}T_{1g}({}^{4}G) \rightarrow {}^{6}A_{1g}({}^{6}S)$ transition. The assignment is further supported by the overlap of this band in the excitation and emission spectrum at the same position. The associated broad band is a vibronic band, and the superimposed fine structure is due to the vibronic transitions. The shift in the emission band can be explained based on the change in site symmetry. IR results indicate a lowering of site symmetry across the phase transition. The effect of this reduced symmetry is to modify the crystal field, which, in turn, modifies the splitting of energy states of the optically active ion, which is reflected in the luminescence spectrum. Lowering of the site symmetry is due to the distortion in the octahedral sites as a result of the rearrangement of coordination polyhedra during the transformation from α to β or γ . The distortion is also indicated by the broadening of the EPR signal of Fe³⁺, as shown in Figure 6. As the electric dipole transition is forbidden for Fe³⁺ ion occupying a totally symmetric site, the intensity of emission is very low as this type of transition lacks strong excitation bands. As the site symmetry deviates, the probability of transition increases and hence the intensity of the emission increases.

CONCLUSIONS

The hydrothermal route is a convenient synthetic method for the preparation of $LiAlO_2$ in different polymorphic forms. The γ -LiAlO₂ prepared through this route is phase-pure and highly stable. The structural transitions do not involve any change in the Li⁺ coordination

that occupies the octahedral sites in the three polymorphs. Whereas across the α -to- β transformation, Al³⁺ changes its coordination from octahedral to tetrahedral. The β -to- γ transformation does not involve the change in Al³⁺ coordination, although the distortion due to the rearrangement of polyhedra is obvious. The MAS NMR results clearly rule out the presence of Li⁺ in the tetrahedral sites in β - and γ -LiAlO₂, in contrast to the conclusions of Marezio [10,12] from XRD studies. The ferric ion occupies the octahedral site in the lattice and can be an excellent structural probe since its spectroscopic properties vary with the site symmetry.

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