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Intercalation studies of several layered lanthanide oxychlorides with pyridine

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Abstract

A series of new intercalation compounds of the layered lanthanide oxychlorides, LnOCl (Ln = Ho, Er, Tm and Yb), with pyridine has been successfully obtained at both room and high temperature (85 °C). The intercalated pyridine stoichiometries (x) in the $(py)_x$LnOCl compounds, determined by thermal gravimetric analysis, are independent of the reaction temperature and time after 2 weeks with the $(py)_x$ErOCl and $(py)_x$YbOCl, but are affected by the reaction temperature and time with the $(py)_x$HoOCl and $(py)_x$TmOCl. An average interlayer expansion of ~5 Å between the LnOCl layers upon pyridine intercalation suggests that the pyridine ring is oriented perpendicular to the host layers. The pyridine species inserted between the host layers are neutral pyridine molecules. The presence of water in pyridine leads to the pyridinium ion that also intercalates and has been identified by IR spectroscopy.

1. Introduction

The lanthanide oxychlorides LnOCl (Ln = Ho, Er, Tm and Yb) are known to crystallize in a $R\bar{3}m$ layered structure-type in which adjacent layers are held together primarily by van der Waals forces [1]. Although the intercalation chemistry of layered materials containing transition metals has been extensively studied [2–6], very little is known about the intercalation chemistry of layered lanthanide materials. The interest in studying the lanthanide intercalation compounds is due to their potential optical, magnetic and catalytic properties [7]. We have previously reported the synthesis and characterization of YbOCl intercalated by sodium and pyridine [8,9]. For $Na_x(NH_3)_y$YbOCl, intercalation occurs with reduction of the host. For $(py)_x$YbOCl, however, we have proposed that intercalation occurs without reduction of the host and is best considered to be an acid-base reaction [9]. An acid-base reaction mechanism has also been postulated for the intercalation of Lewis bases into transition metal oxide host lattices [10,11], although intercalation of pyridine into NbS_2 and TaS_2 is postulated to occur with reduction of the host [12,13]. We have now extended the work on pyridine intercalation to TmOCl, ErOCl and HoOCl. This paper presents the effect of a variety of reaction conditions on the formation of $(py)_x$LnOCl compounds.

2. Experimental details

2.1. Synthesis

Synthetic methods utilized in the preparation of LnOCl (Ln = Ho, Er, Tm and Yb) by the reactions of Ln_2O_3 with a 20% molar excess of NH_4Cl have been described elsewhere [1,8,9,14]. The products, containing a composite phase of SmSI and YOF structure-types, were converted into a more crystalline phase (the diffraction peaks are less broad) by LiCl/KCl flux at 450 °C (LnOCl:LiCl/KCl = 1:20) as shown in Fig. 1.

Pyridine was obtained from Aldrich, dried over KOH pellets and then distilled from CaH_2. Anhydrous pyridine was stored over 4-Å molecular sieves and degassed before use. Pyridine intercalation compounds were prepared by immersing weighed solids of LnOCl in pyridine solutions. Since all the intercalates formed are moisture sensitive, the compounds were handled in a drybox and manipulated under a N_2 atmosphere in order to perform the property measurements. In each preparative reaction, the excess solvent after intercalation was removed by a syringe. The product was dried under vacuum for several hours to remove any pyridine possibly adsorbed on the surface of the product, and then transferred into a drybox.

2.2. X-Ray diffraction

A Siemens X-ray powder diffractometer using Cu Kα radiation was used to obtain the data for the powder patterns and for the calculation of the lattice parameters of all the compounds prepared in this work.

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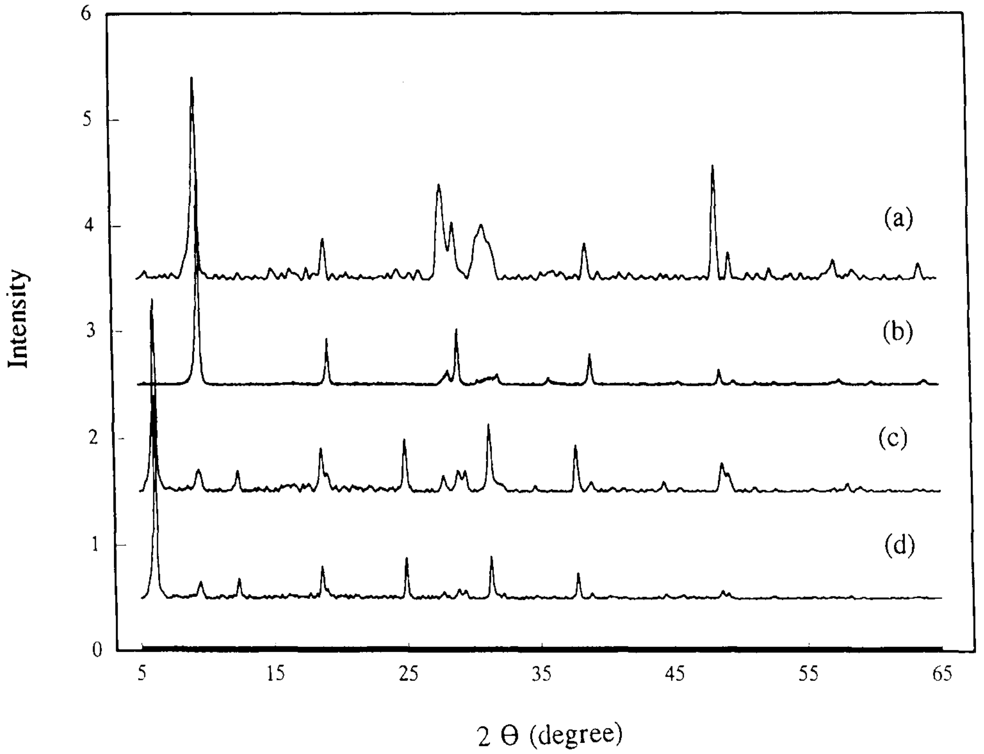

Fig. 1. X-Ray powder diffraction patterns for ErOCl (a) from the reaction of Er_2O_3 with NH_4Cl (disordered) and (b) after the flux reaction (crystalline), and for $(py)_xErOCl$ prepared at (c) 85 °C (3 weeks) and (d) room temperature (4 weeks).

2.3. *TGA*

Thermal gravimetric analysis was performed on a DuPont Model 951 Thermogravimetric Analyzer. Experimental details are similar to those published previously [9]. The composition of the deintercalated compounds after TG analyses were identified immediately by X-ray powder diffraction (Guinier, Cu $K\alpha_1$).

2.4. *IR spectroscopy*

Infrared spectra were recorded in a range of 400–4000 cm^{-1} with a resolution of 2 cm^{-1} on an IR/32 IBM 9000 FTIR system. The sample was ground together with KBr and the mixture was pressed into a pellet. An equal mass of KBr was used as the reference. All the measurements were carried out under flowing N_2 gas.

3. Results and discussion

3.1. *LnOCl*

The layered structure of LnOCl can be described as consisting of two layers of hexagonally packed lanthanide atoms with oxygens filling the tetrahedral holes, sandwiched between layers of hexagonally packed chlorine atoms [15,16]. The interplanar Cl–Cl distance of ~3.7 Å is approximately twice the Cl radius, indicating that the layers are held together by van der Waals forces. The layered structure of LnOCl includes the SmSI and YOF structure-types in which the only difference is in the stacking sequence of the layers [1,15,16].

Although it has been reported that the LiCl/KCl flux converts the products obtained from the reactions of Ln_2O_3 (with the exception of Ln = Ho) with NH_4Cl to a single structure-type [1,8,9], products obtained in this work were determined by X-ray powder diffraction to still be a mixture of SmSI and YOF structure-types ($R\bar{3}m$-type). The only effect that the flux appears to have is to provide a product with a higher degree of crystallinity, as shown in the example of ErOCl in Fig. 1(a),(b). The major distinctions between the powder diffraction patterns of the two structure types are the reflections corresponding to (1 0 4) which have calculated intensities (*e.g.*, YbOCl) of 9% and 87%, and (0 1 5) which should have an intensity of 57% and 20%, for the YOF and SmSI structure-types, respectively [1, 15]. The composite phase ($R\bar{3}m$-type) obtained in the present work (indicated by the presence of both the (1 0 4) and (0 1 5) reflections in the powder diffraction pattern) may be attributed to a larger quantity of material involved in the flux. The products obtained before the flux reaction will be referred to as LnOCl (disordered), to indicate that it is a mixture of two phases that are not very crystalline, and after the flux, as LnOCl (crystalline).

3.2. $(py)_x$LnOCl

A series of new intercalation compounds of LnOCl with pyridine has been prepared. In order to better understand the intercalation process, various reaction conditions were investigated. LnOCl (crystalline) were reacted with pyridine at room temperature or at 85 °C over different periods of time: 1, 2, 3 and 4 weeks, in order to obtain the maximum stoichiometry of the pyridine content (x) for the $(py)_x$LnOCl compounds and to determine the effect of temperature on intercalation. LnOCl (disordered) were reacted with pyridine at room temperature for 4 weeks, in order to elucidate the effect of the crystallinity of host materials on pyridine intercalation by comparing with the similar reactions carried out above with LnOCl (crystalline). LnOCl (crystalline, Ln = Er and Yb) were also reacted with pyridine in the presence of water or with a mixture of pyridine and cyclohexane at room temperature for 2 weeks, in order to find out if the presence of water or cyclohexane could change the stoichiometry and type of pyridine species that is intercalated.

Table 1 shows the stoichiometries (x), lattice parameters, and changes in interlayer spacing (Δd) of LnOCl and $(py)_x$LnOCl compounds, prepared under a variety of conditions. All the intercalates show a Δd of approximately 5 Å, indicating that the pyridine ring is perpendicular with respect to the LnOCl planes. In the case of $(py)_x$ErOCl and $(py)_x$YbOCl, the content of intercalated pyridine (x) increases in the first 2 weeks and then shows little change up to 4 weeks. Higher temperature (85 °C) employed in the intercalation process has no effect on the amount of pyridine that can be intercalated. In the case of $(py)_x$HoOCl and $(py)_x$TmOCl, however, the content of intercalated pyridine (x) continues to increase with time and is negatively affected by higher temperature. The X-ray powder diffraction patterns of typical $(py)_x$ErOCl compounds, prepared at both room and high temperatures, are shown in Fig. 1(c),(d). They are essentially identical regardless of reaction temperature. Similar results are observed for all the intercalates. There are at least two possible explanations which would account for the lower stoichiometries of pyridine and the absence of new reflection peaks of a decomposition product in the X-ray powder diffraction patterns for $(py)_{0.06}$HoOCl and $(py)_{0.09}$TmOCl prepared at 85 °C. We speculate that this could be attributed to either a reversible diffusion effect or thermal decomposition to an amorphous or soluble product.

TGA results shown in Fig. 2 provide the pyridine stoichiometries given in Table 1 for all the $(py)_x$LnOCl compounds. HoOCl and its pyridine intercalates start to decompose after heating to 300 °C whereas the other LnOCl and intercalates do not decompose until 600 °C as shown in Fig. 2. The products of the decomposition for HoOCl are Ho_2O_3, identified by the X-ray powder diffraction, with the evolution of HCl gas [14]. The instability of layered HoOCl lattice may be attributed to the larger size lanthanum cation which prefers higher coordination [1] and may account for the negative effect of temperature on the amount of intercalated pyridine.

TABLE 1. Stoichiometries of pyridine (x), lattice parameters and interlayer spacing changes (Δd) for LnOCl and $(py)_x$LnOCl compounds

Compound	x	Reaction[a]	a (Å)	c (Å)	Δd (Å)
$(py)_x$HoOCl	0.00		3.7697(7)	27.766(6)	
	0.08	RT, 2 weeks	3.764(2)	42.78(1)	5.00
	0.10	RT, 4 weeks	3.767(3)	42.90(2)	5.04
	0.06	85 °C, 3 weeks	3.758(5)	42.82(3)	5.02
$(py)_x$ErOCl	0.00		3.745(1)	27.719(8)	
	0.17	RT, 2 weeks	3.740(2)	42.72(4)	5.00
	0.17	RT, 4 weeks	3.739(2)	42.76(3)	5.01
	0.18	85 °C, 3 weeks	3.730(1)	42.86(4)	5.05
$(py)_{0.18-x}(pyH^+)_x$ErOCl		RT, 2 weeks[b]	3.741(2)	42.91(4)	5.06
$(py)_x$TmOCl	0.00		3.708(2)	27.72(1)	
	0.11	RT, 2 weeks	3.722(4)	42.60(6)	4.96
	0.15	RT, 4 weeks	3.718(2)	42.68(6)	4.99
	0.09	85 °C, 3 weeks	3.727(4)	42.72(7)	5.00
$(py)_x$YbOCl	0.00		3.704(2)	27.68(2)	
	0.15	RT, 2 weeks	3.697(1)	42.68(2)	5.00
	0.14	RT, 4 weeks	3.699(2)	42.70(4)	5.01
	0.14	85 °C, 3 weeks	3.700(2)	42.85(4)	5.06
$(py)_{0.16-x}(pyH^+)_x$YbOCl		RT, 2 weeks[b]	3.700(2)	42.77(5)	5.03

[a] RT, room temperature. [b] Intercalation reaction with pyridine in the presence of water.

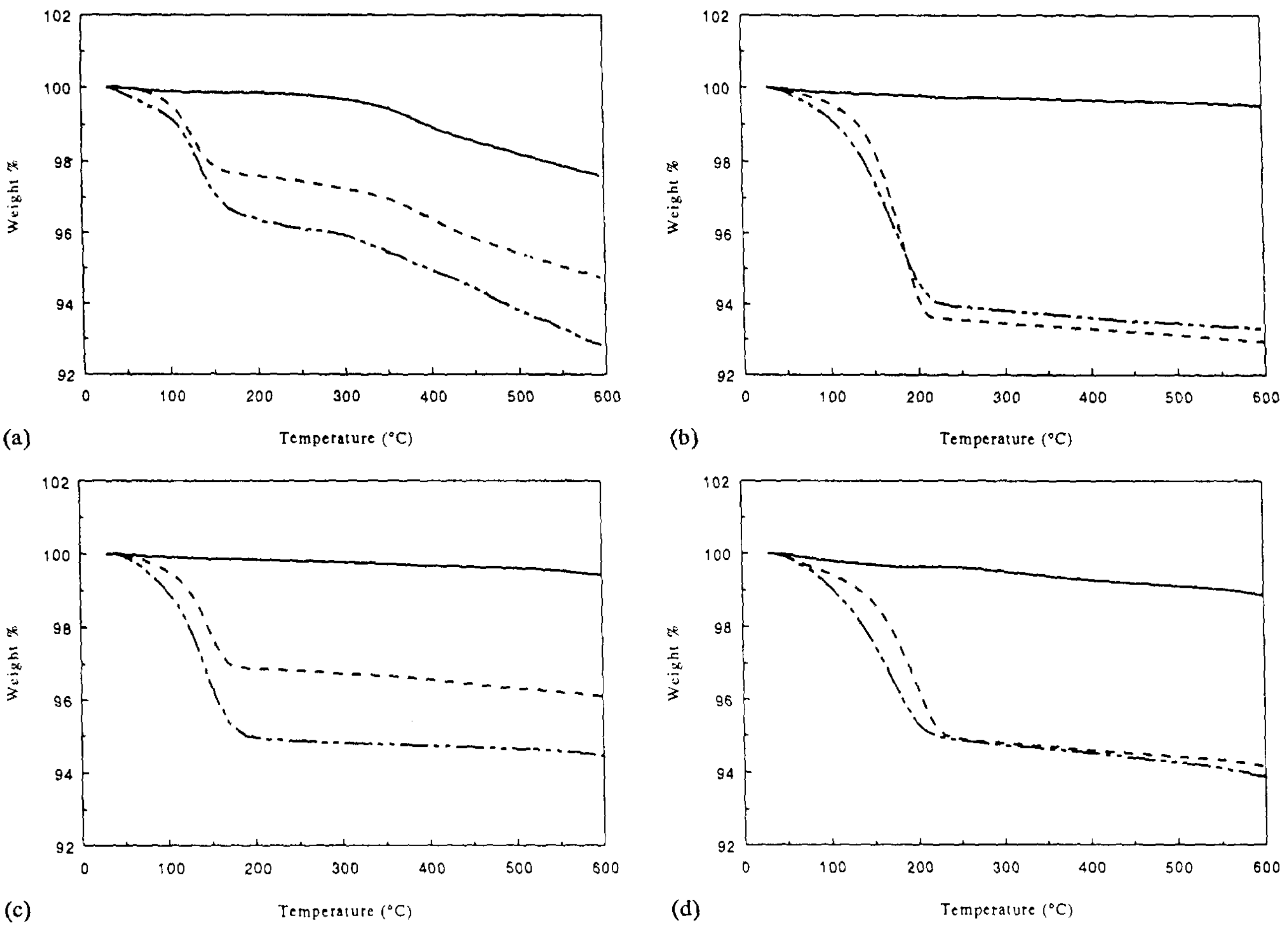

Fig. 2. Thermal gravimetric analysis (TGA) curves for (a) HoOCl and (py)$_x$HoOCl, (b) ErOCl and (py)$_x$ErOCl, (c) TmOCl and (py)$_x$TmOCl, and (d) YbOCl and (py)$_x$YbOCl. —— LnOCl, - - - (py)$_x$LnOCl prepared at 85°C (3 weeks), and -·-·- (py)$_x$LnOCl prepared at room temperature (4 weeks).

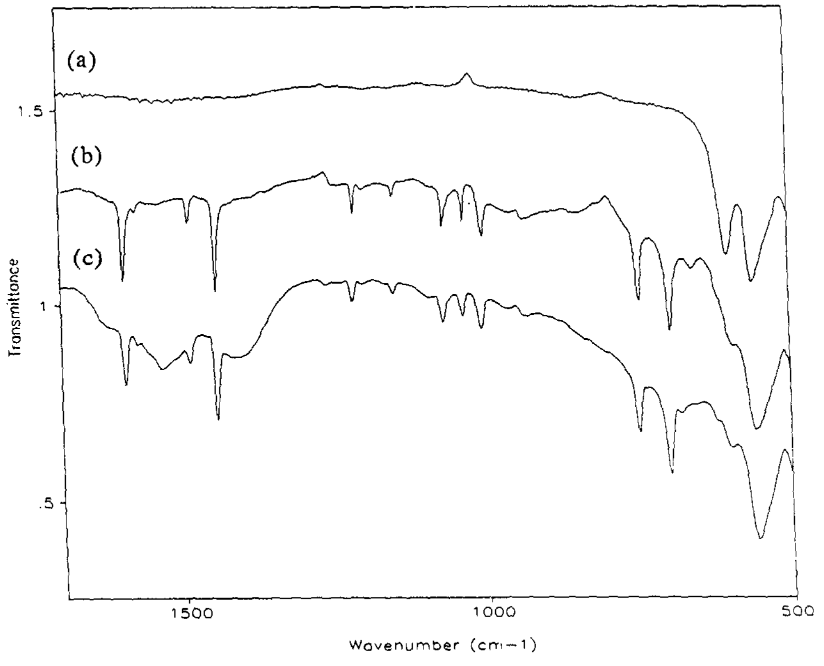

Fig. 3. IR spectra for (a) ErOCl, (b) (py)$_{0.17}$ErOCl, prepared at room temperature for 2 weeks in the absence of water, and (c) (py)$_{0.18-x}$(pyH$^+$)$_x$ErOCl, prepared at room temperature for 2 weeks in the presence of water.

However, a similar argument cannot be applied to TmOCl, which does not decompose until 600 °C.

TGA results obtained from the intercalation reactions of pyridine into the LnOCl (disordered) and LnOCl (crystalline) at room temperature in the same period of 4 weeks show that greater amounts of pyridine can be intercalated into the disordered hosts than the crystalline ones. Intercalation compounds of $(py)_{0.14}HoOCl$, $(py)_{0.20}ErOCl$ and $(py)_{0.18}YbOCl$ are formed by the reactions of pyridine with LnOCl (disordered), while $(py)_{0.10}HoOCl$, $(py)_{0.17}ErOCl$ and $(py)_{0.14}YbOCl$ are prepared with LnOCl (crystalline) (see Table 1).

The participation of cyclohexane in the intercalation of pyridine into both the ErOCl and YbOCl (crystalline) hosts at room temperature for a period of 2 weeks has no effect on the content of intercalated pyridine, determined by TGA data. The presence of water in the intercalation of pyridine into the two hosts also shows little effect on the stoichiometry of intercalated pyridine, but produces the pyridinium ion that also intercalates. The resulting compounds, $(py)_{0.18-x}(pyH^+)_xErOCl$ and $(py)_{0.16-x}(pyH^+)_xYbOCl$, are formed, in comparison with $(py)_{0.17}ErOCl$ and $(py)_{0.15}YbOCl$ which are prepared in the absence of water. IR spectra of ErOCl, $(py)_{0.17}ErOCl$ and $(py)_{0.18-x}(pyH^+)_xErOCl$ are shown in Fig. 3. All the new peaks observed in the $(py)_{0.17}ErOCl$ spectrum, in comparison to ErOCl, can be assigned to pyridine [11,17]. A characteristic peak at 1534 cm^{-1} for pyridinium species [11,18] is clearly shown in the $(py)_{0.18-x}(pyH^+)_xErOCl$ spectrum.

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