Scandium-Containing Layered Hydroxides

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Abstract—A scandium analogue of hydtotalcite and a mixed sample containing both scandium and aluminum have been synthesized and characterized. It is known that both samples have a layered structure; the unit cell parameters of the scandium-containing samples are slightly higher than the respective values of an ordinary aluminum-containing sample. The mixed-metal scandium–aluminum sample easily regains its layered structure after a dehydration/rehydration cycle, while the scandium analogue after this treatment is restored only partially.

THEORETICAL ANALYSIS

Layered double hydroxides (LDHs) mean compounds that are, strictly speaking, hydroxo salts. Inasmuch as hydrotalcite (magnesium aluminum hydroxocarbonate) is the best known natural LDH, term "hydrotalcite-like compounds" is sometimes used. This class of materials has been in the focus of research in the last few decades because of their high potential for use as adsorbents [1], anion exchangers [2], catalysts, and their precursors [2–5]. The ability of LDHs to regain their layered structure after dehydration/rehydration cycles (the memory effect) is also being studied.

The idealized formula of layered hydroxide is $M^{2+}_{1-x}M^{3+}_{x}(OH)_2[(A^{n-})_{x/n} \cdot mH_2O]$, where M^{2+} and M^{3+} are metal cations and A^{n-} is virtually any anion. The unit cell of an LDH is described by an octahedron centered by a cation with six oxygen atoms in the vertices [2, 6–8]. Octahedra are linked into a network and form layers. The isomorphic substitutions of triply charged for doubly charged cations generate an excess positive charge, which is balanced by interlayer anions.

A wide range of natural and synthetic LDHs with various doubly charged cations (zinc, nickel, copper, magnesium, and others) is known [2, 6, 9]; the synthesis of LDHs with a singly charged (lithium) cation has been described [10]. Triply charged (chromium, iron) cations can also substitute for aluminum [2, 11].

This work intended to synthesize and characterize scandium-containing layered hydroxides. Hydrotalcite-like scandium-containing compounds have not been documented.

EXPERIMENTAL

Magnesium scandium (Mg/Sc) and magnesium scandium aluminum (Mg/AlSc) layered hydroxides were synthesized through precipitation from aqueous salt solutions, followed by thermostating, ion exchange for carbonate ions, washing, and drying. For reference, magnesium aluminum (Mg/Al) layered hydroxide was prepared by the same method. The formulas of the compounds were derived from chemical analysis for scandium, aluminum, and magnesium. Crystal water was estimated from DTA–TG analysis.

Layered hydroxides were identified and some their properties were studied using powder X-ray diffraction (a DRON-3 X-ray diffractometer; 2θ scan steps, 0.5°; CuK_α radiation).

RESULTS AND DISCUSSION

The samples synthesized have X-ray diffraction patterns typical of well-crystallized layered hydroxides (Fig. 1). Their unit cell parameters a and c and grain sizes were calculated from X-ray diffraction data (Table 1).

Most literature sources use the parameter c as the main characteristic of layered hydroxides. This parameter characterizes the interlayer spacing and is calculated as the tripled d/n value for the first peak corresponding to plane 003 on the X-ray diffraction pattern [2]. The parameter a shows the distance between the nearest-neighboring cations in a brucite-like layer; this parameter is equal to the doubled interplanar spacing for reflection (110) [2].

Table 1 makes it clear that in the Mg/Sc sample the distance between metal-hydroxide layers is greater than in magnesium aluminum hydrotalcite, in agreement with the ionic radii of the relevant cations [12]: the crystal-chemical radius of the scandium cation (0.82 Å) is far greater than the aluminum cation radius (0.57 Å). Interestingly, the greatest interlayer spacing is in the sample in which scandium partially substitutes for alu-

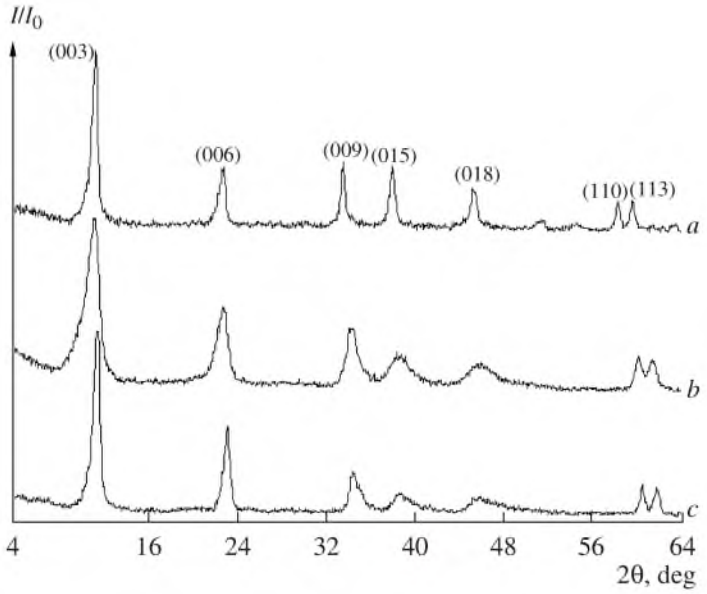

Fig. 1. X-ray diffraction patterns for LDH samples: (a) Mg/Sc, (b) Mg/AlSc, and (c) Mg/Al.

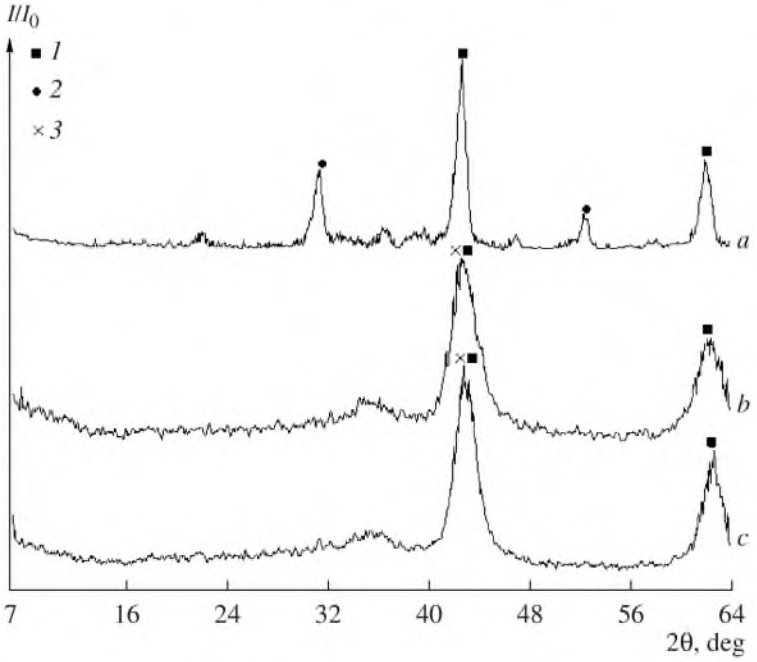

Fig. 2. X-ray diffraction patterns for LDH samples calcined at 823 K: (a) Mg/Sc, (b) Mg/AlSc, and (c) Mg/Al. Notations: (*1*) scandium oxide Sc_2O_3, (*2*) magnesium oxide MgO, and (*3*) aluminum oxide Al_2O_3.

minum in hydrotalcite; probably, this is due to the structure distortion induced by a combination of triply charged cations with different radii in a layer. The grain size and the unit cell parameter *a* rise systematically with increasing scandium proportion in the sample, signifying an increase in the unit cell.

To study the memory effect, we calcined samples at 823 K for 2 h, then rehydrating them for 2 days in deionized water with stirring at room temperature and drying at 372 K. As expected, the samples dehydrated during calcination, losing their layered structure. The X-ray diffraction patterns of the calcined samples display reflections that can be unambiguously assigned to metal oxides (Fig. 2).

The Mg/Al and Mg/Sc samples easily regain their layered structure during rehydration, which is demon-

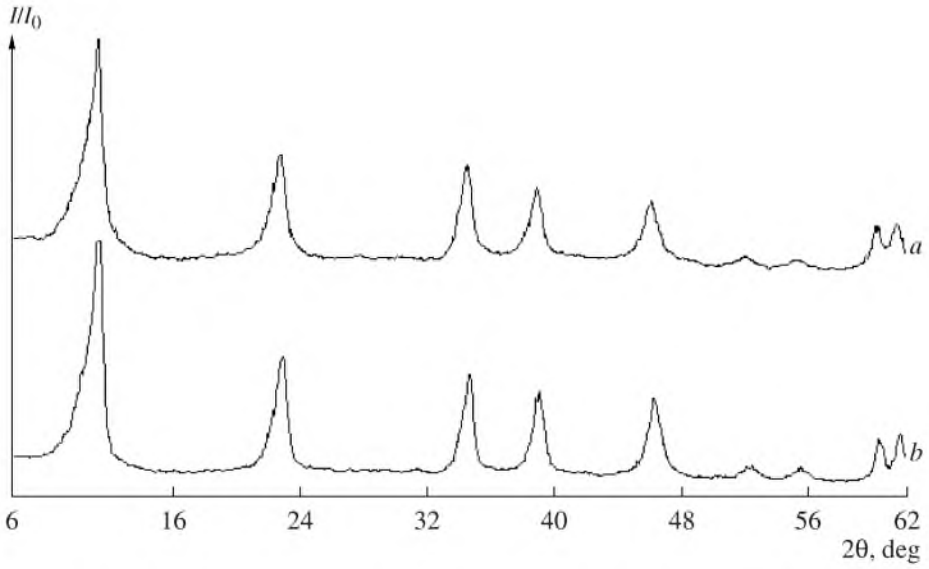

Fig. 3. X-ray diffraction patterns for restored samples: (a) Mg/AlSc and (b) Mg/Al.

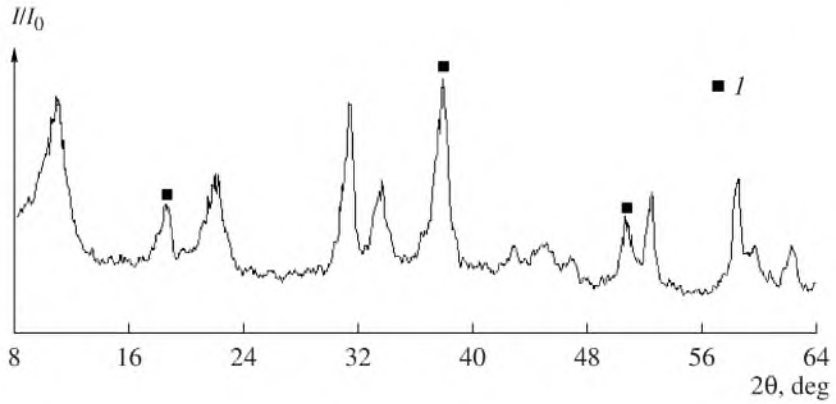

Fig. 4. X-ray diffraction pattern for a rehydrated Mg/Sc sample. Notation: (*1*) magnesium oxide.

strated by single-crystal X-ray diffraction data: the restored samples have the set of basal reflections that are intrinsic to the hydrotalcite structure (Fig. 3). The unit cell parameters and grain sizes for the restored samples are listed in Table 2. The restored samples far less differ in their unit cell parameters than the starting samples; this is likely because the layered hydroxide formed during dehydration–hydration cycling in the scandium-containing system is close in its composition to hydrotalcite.

Magnesium scandium layered hydroxide after dehydration–rehydration cycling only partially regains its layered structure: reflections from magnesium hydroxide in the X-ray diffraction pattern of the rehydrated samples are rather strong (Fig. 4).

Table 1. Unit cell parameters for LDH samples synthesized

Sample	Formula unit	c, Å	a, Å	V, Å^3
Mg/Sc	$Mg_{0.677}Sc_{0.323}(OH)_2(CO_3)_{0.162} \cdot 0.805H_2O$	23.61	3.16	204.2
Mg/AlSc	$Mg_{0.819}Al_{0.167}Sc_{0.014}(OH)_2(CO_3)_{0.091} \cdot 0.783H_2O$	23.91	3.08	196.4
Mg/Al	$Mg_{0.780}Al_{0.220}(OH)_2(CO_3)_{0.110} \cdot 0.947H_2O$	23.28	3.06	188.8

Table 2. Unit cell parameters for restored samples

Sample	c, Å	a, Å	V, Å^3
Mg/AlSc	23.49	3.08	193.0
Mg/Al	23.49	3.07	191.7

CONCLUSIONS

Our studies show that, in spite of the significant difference between the aluminum and scandium cation radii, a scandium analogue of hydrotalcite can be synthesized, as well as scandium/aluminum mixed-metal hydrotalcite-like material. The latter can fully regain its layered structure after dehydration–rehydration cycling, while magnesium scandium layered hydroxide after this treatment is restored only partially.

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