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**XRD ANALYSIS OF THE STRUCTURAL PROPERTIES OF
LAYERED DOUBLE HYDROXIDES COMPRISING Zn AND Al
PARTIALLY SUBSTITUTED WITH Cu AND Ce
AND THEIR DERIVED MIXED OXIDES**

BY

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Abstract. The structural changes of layered double hydroxides (LDHs), when zinc was partially substituted by copper and aluminum was partially substituted by cerium in the layer of the LDHs matrix was monitored by X-ray diffraction (XRD), while the bulk composition of the studied samples was confirmed by X-ray fluorescence (XRF). The substituted samples preserved the layered structure, but the constrictions of the network appeared as a result of the substitution. After calcination at 850°C for 7 h, well crystallized mixed oxides containing copper and cerium were formed. The results point out that the calcination temperature is important to establish the structural features of the resulting mixtures of mixed oxides.

Keywords: layered double hydroxides; XRD; mixed oxides; copper; cerium.

1. Introduction

Layered double hydroxides (LDHs) are a class of cheap, human health friendly anionic clays with varied applications as catalysts or catalyst

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precursors, adsorbents, sensors, fillers, drug supports, drug carriers, etc (Carja *et al.*, 2001). They can be represented by the formula $\text{Me}^{2+}\text{Me}^{3+}(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$. It presents a positively charged brucite-like layers ($\text{Mg}(\text{OH})_2$) in which some of Me^{2+} are replaced by Me^{3+} in the octahedral sites of the hydroxide sheets. Interstitial layers formed by CO_3^{2-} anions and water molecules compensate the excess of the positive charge resulting from this substitution. The layers are stacked one on top of the other and are held together by weak interactions of hydrogen bonds. A high diversity of divalent or trivalent cations so a wide range of compositions containing various combinations of Me^{2+} and Me^{3+} and different anions A^n can be synthesized (Carja *et al.*, 2005). Thermal decomposition of hydrotalcite-like materials around 550°C gives rise to stable, high surface area, homogeneous and highly dispersed mixed metal oxides owing active acid-base sites. Moreover, the incorporation of cations with redox properties in the LDHs network offers the perspective to design new bifunctional mixed oxides with a unique combination of acid-base and redox properties. Therefore, these materials are good candidates as precursors for production of highly dispersed mixed oxides (Cavani *et al.*, 1991; Carja *et al.*, 2003). Considering this information this work presents the structural characterisation of ZnAILDHs in which part of Zn (Me^{2+}) was partially substituted by Cu^{2+} while part of Al (Me^{3+}) was partially substituted by Ce^{3+} in the layers of the ZnAILDH matrix. The structural characterization of the clay matrix was done by using X-ray diffraction analysis while the bulk composition of the studied layered materials was analyzed by using X-ray fluorescence technique. Moreover, the structural properties of the mixed oxides evolved after calcination at 850°C are also reported.

2. Experimental

2.1. Materials Preparation

The hydrotalcite-like materials were synthesized following a coprecipitation method similar to that described by Reichle (1986) at a constant pH, under constant flow of nitrogen in the reaction medium and vigorous stirring in an inert atmosphere. Zinc, aluminum, copper and cerium nitrates, in the desired molar ratio, were used as precursors and $\text{NaOH} / \text{Na}_2\text{CO}_3$ as precipitants. The obtained precipitates were separated by centrifugation, washed extensively with warm deionized water until sodium and chloride free and dried under vacuum at 338 K. For instance, the LDH1 sample was prepared as following: an aqueous solution (250 mL) of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.03 mol) / $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ((0.01 mol-x)) / $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (0.03-x mol, $0.003 \leq x < 0.01$), CeNO_3 , x mol, and an aqueous solution of $\text{NaOH} / \text{Na}_2\text{CO}_3$ (1M), were added dropwise together, over a period of 2 h, at a constant pH value. The samples were denoted as LDH1 for ZnAILDH, LDH2 and LDH3 for the substituted samples and presented in Table 1.

2.2. Materials Characterization

XRF: the chemical compositions of synthesized samples were determined by X-ray fluorescence spectroscopy (Shimadzu XRF-1700 sequential X-ray fluorescence spectrometer).

XRD: X-ray powder diffraction patterns were recorded on a Philips PW 1840 diffractometer using monochromatic $\text{CuK}\alpha$ radiation ($\lambda = 0.154$ nm), operating at 40 kV and 30 mA over a 2θ range from 4 to 70 degree. The interlayer space of the synthesized LDHs was determined from the diffraction peak positions with structural analysis software.

3. Results and Discussions

Chemical compositions as Zn / Cu / Ce / Al atomic ratios and the structural properties of the samples are presented in Table 1. The Zn / Cu / Ce / Al atomic ratios determined by XRF are coincident, within the experimental errors, with those of the starting mixed aqueous solutions. The DRX patterns of the samples exhibit sharp and symmetric reflections for the (003), (006), (110) and (113) planes and broad asymmetric reflections for the (102), (105) and (108) planes, which are characteristics of these materials (Carja *et al.*, 2001; Cavani *et al.*, 1991).

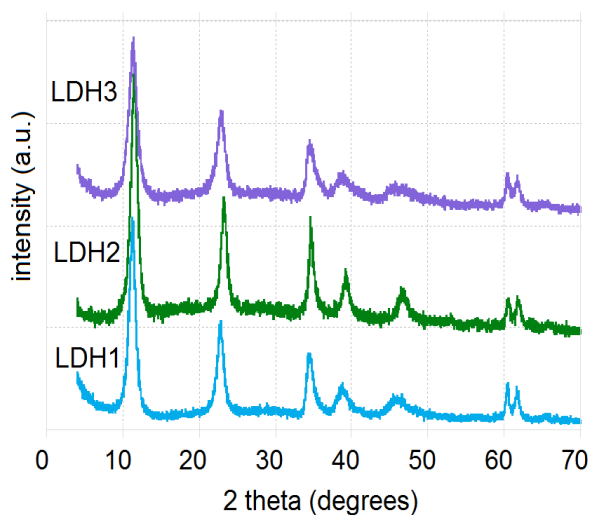


Fig. 1 – The X-ray diffraction pattern of the LDH –as synthesized sample.

In Fig. 1 we present the XRD pattern of the LDH1-LDH3. The lattice parameters were calculated by indexing the peaks under a hexagonal crystal system. The parameter “ a ” increases from 3.057 Å for LDH1 sample to 3.064 Å

for the LDH3. While a correspondence exists between the ionic radius of Cu^{2+} hexacoordinate (0.73 Å, -Shanon ionic radius) (Shannon, 1976) and the ionic radius of Zn^{2+} hexacoordinate (0.57 Å, -Shanon ionic radius) the ionic radius of Ce^{3+} (1.01 -Shanon ionic radius) is larger than the ionic radius of Al^{3+} (0.53 Å - Shanon ionic radius). This explains the altered values of the “a” parameter.

Regarding the “c” parameter the values decrease when copper and cerium are substituted Zn and respectively Al in the layered structure of the LDHs. The decrease can be attributed to emphasized electrostatic interactions between the layer and the interlayer network when another metal is introduced in the LDH layer. The interlayer free spacing (IFS) values calculated by subtracting the thickness of the LDH layer from the calculated d_{003} spacing (DRX, Bragg’s law) is decreasing from 2.99 Å for LDH1 to 2.79 Å for LDH2 pointing out that the interlayer space decreases when copper and cerium are introduced in the anionic clay structure. Calcination of these materials at 550°C for 5 h leads to the destruction of the HT-like network and gives rise to an amorphous pattern characteristic to the mixed oxides with poor crystallinity. In Fig. 2 we present the XRD pattern of the LDH3 sample after the calcination process.

Table 1
Chemical Composition and the Lattice Parameters of the Studied Samples

Samples	Lattice parameters [Å]		Cu / Ce atomic ratio in the sample (*)	S_{BET} [m ² /g]
	a	c		
LDH1	3.057	23.37	–	90.5
LDH2	3.061	22.81	3.81	79.3
LDH3	3.064	22.85	3.85	67.0

After calcined at 850°C for 7 h of LDH3 the obtain patterns is shown in Fig. 3. The diffraction peaks corresponding to mixtures of mixed oxides type CuO, CeO and ZnAl_2O_4 can be identified in the corresponding XRD pattern. Segregation of ZnO, with most intense (200) and (220) reflections (shifted towards higher angles on comparison to pure ZnO (Kannan and Swamy, 1999), is also observed after calcination at this temperature. We also noticed that the decrease of copper and cerium content gives rise to a lower intensity of the characteristic reflections corresponding to well crystallize mixed oxides.

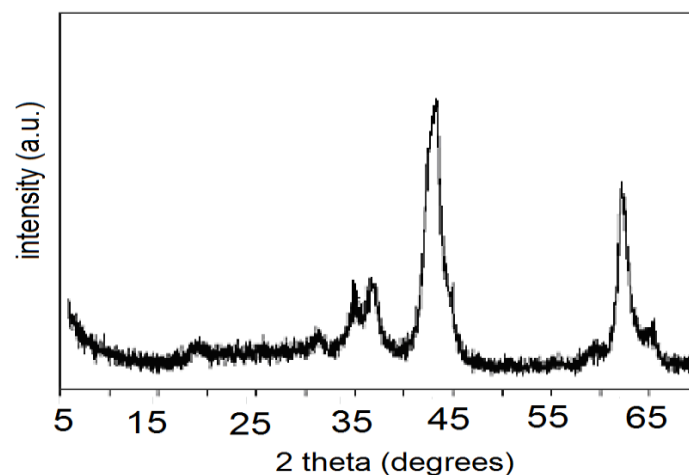


Fig. 2 – The X-ray diffraction pattern of LDH3 calcined at 550°C for 5 h.

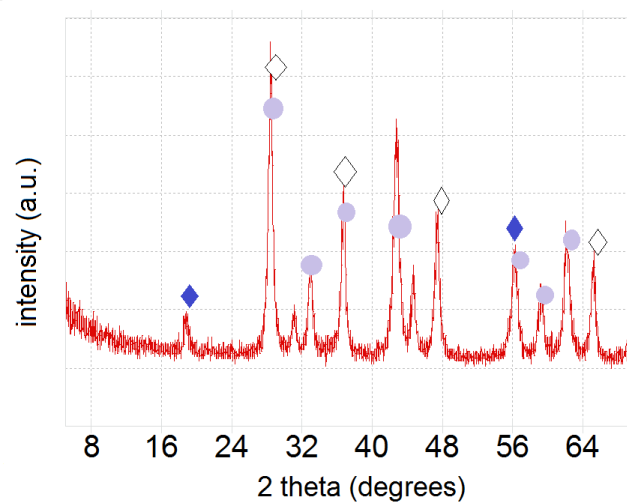


Fig. 3 – The X-ray diffraction pattern of LDH3 calcined at 850°C for 7 h.

(◆) CeO, (●) ZnO (◇) CuO.

The XRD peaks, shown in Fig. 3, are well defined and have high intensity. Therefore, the obtained mixed oxides are well crystallized pointing out that the calcination process of the partially substituted layered double hydroxides is a successful method to obtain mixtures of mixed oxides containing metals with redox properties. Moreover, the mixtures of mixed oxides obtained by this method are characterized by a high degree of dispersity.

4. Conclusions

Copper and cerium partially substituted ZnAlLDHs were successfully synthesized and their structural transformation during the thermal treatment was studied by using XRD analysis. The introduction of copper and cerium in the layered network of the clay alter the lattice parameters.

Upon calcination at 550°C for 5 h the layered structure of the substituted hydrotalcite is destroyed and the XRD analysis reveal the formation of mixed oxides with poor crystallinity. After calcination at 850°C copper and cerium containing well dispersed mixed oxides formed. The calcination temperature is important for establishing mixed oxides composition and their degree of crystallization. XRD analysis proves to be a useful tool for studying the structural transformations of the partially substituted as synthesized and thermally treated anionic clay – like materials.

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ANALIZA STRUCTURALĂ PRIN DIFRAȚII CU RAZE X
ALE HIDROXIZILOR DUBLU STRATIFICAȚI CONȚINÂND Zn ȘI Al PARȚIAL
SUBSTITUIȚI CU Cu ȘI Ce ȘI OXIZII LOR MICȘTI DERIVAȚI

(Rezumat)

Modificările structurale ale hidroxidurilor dublu stratificați (LDH), atunci când zincul a fost parțial substituit cu cupru și aluminiu a fost parțial substituit cu ceriu în stratul matricei LDH-ului, au fost monitorizate prin difracție cu raze X (XRD), în timp ce compoziția în masă a probelor studiate a fost confirmată folosind tehnica de fluorescență cu raze X (XRF). Probele substituite au păstrat structura stratificată, dar constricțiile rețelei au apărut ca rezultat al substituției. După calcinare la 850°C, timp de 7 ore, se formează oxizi micști bine cristalizați care conțin și cupru și ceriu. Rezultatele arată că temperatura de calcinare este importantă pentru stabilirea caracteristicilor structurale ale amestecurilor de oxizi micști.