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$LnAlO_3$ obtained by the complexation and the self-propagating combustion methods

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Two series of polynuclear coordination compounds $[AlLn(C_6O_7H_{11})_2(C_6O_7H_{10})_2]\cdot 4H_2O$ (where Ln(III) = La, Nd, Er; $C_6O_7H_{11}^-$ = gluconate anion) and $[AlLn(CH_2(NH_2)COOH)_4](NO_3)_6\cdot 4H_2O$ (where Ln(III) = Nd, Er; $CH_2(NH_2)COOH$ = glycine) have been synthesized by two soft chemical methods: complexation method and self-propagating combustion method. These compounds have been characterized by elemental chemical analysis and physico-chemical measurements (IR and UV-Vis spectra). The mixed oxides obtained by the decomposition of these compounds have been characterized by X-ray diffraction, SEM, IR and UV-Vis spectra.

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1. Introduction

The lanthanide aluminates are of great interest in catalysis. One of the promising candidates for catalytic materials, the lanthanum aluminate ($LaAlO_3$) has been used as catalyst for oxidative coupling of methane, hydrogenation and hydrogenolysis of hydrocarbons and as a support or wash coat for combustion catalysis [1-3].

The activity of catalytic materials can be strongly affect by their preparation method. Generally, the active catalyst needs to be prepared at temperature as low as possible since the lower temperature leads to a high-surface area material.

The common way to prepare $LaAlO_3$ is the solid-state reaction at high temperatures (1500-1700 °C) [4]. Although, it is very simple, this process presents several drawbacks, such as: high reaction temperature, large particle size, limited chemical homogeneity and low sinterability. From this point of view, $LaAlO_3$ conventionally produced is not suitable for its use in catalysis.

In recent years, various low temperature chemical routes have been used for the preparing fine and homogeneous powders. The coprecipitation method is a simple way for the obtaining of lanthanum aluminate [5]. Kakihama and Okubo have explored another solution route namely polymerization route [6]. Taspinar and Tas obtained pure $LaAlO_3$ powder by homogeneous precipitation and self-propagating combustion methods [7]. Some other low temperature methods have been tried for synthesizing $LaAlO_3$: EDTA route [8], combined gel synthesis [9] and evaporation route [10].

Considerable efforts have been made to develop "soft chemistry" methods, in which polynuclear coordination compounds with two or more metal ions are formed as precursors. These compounds are capable of given orthoaluminates by thermal decomposition. Among them, there are the "complexation method" and the self-propagating combustion method.

In this research work, we investigate the synthesis of lanthanide perovskite-type aluminates, $LnAlO_3$ (where Ln(III) = La, Nd, Er) obtained by these two methods. Moreover, we have tried to demonstrate that the polynuclear coordination compounds are the precursors of orthoaluminates both in the complexation method and, in the self-propagating combustion method.

2. Experimental

2.1. Synthesis of complex compound precursors

The precursors - polynuclear coordination compounds have been prepared as follows:

$[AlLn(C_6O_7H_{11})_2(C_6O_7H_{10})_2]\cdot 4H_2O$, where Ln(III) = La, Nd, Er. Aluminum and lanthanum nitrates were dissolved in the minimum amount of water and mixed with an aqueous solution of gluconic acid (1:1:6 molar ratio). A white fluffy precipitate was formed by adding methanol. A solution of $NH_4OH : CH_3OH$ (1:1) was added until the pH rose to ~5. The white precipitate was filtered, washed with methanol and dried on P_4O_{10}.

For the compound based on neodymium and aluminum, as well as the erbium and aluminum compound, was used the same procedure.

Elemental analysis was consistent with the formula:
$[AlLa(C_6H_{11}O_7)_2(C_6H_{10}O_7)_2]\cdot 4H_2O$ Calcd/Found:
Al%: 2.66/2.75; La%: 13.69/13.65; C%: 28.34/28.43;
H%: 4.92/4.90.
$[AlNd(C_6H_{11}O_7)_2(C_6H_{10}O_7)_2]\cdot 4H_2O$ Calcd/Found:
Al%: 2.65/2.70; Nd%: 14.12/13.75; C%: 28.20/28.40;
H%: 4.89/4.95.
$[AlEr(C_6H_{11}O_7)_2(C_6H_{10}O_7)_2]\cdot 4H_2O$ Calcd/Found:
Al%: 2.59/2.69; Er%: 15.93/15.22; C%: 27.57/27.82;
H%: 4.78/4.25.

$[AlLn(CH_2(NH_2)COOH)_4](NO_3)_6\cdot 4H_2O$ where
Ln(III) = Nd, Er

Aluminium(III) nitrate, neodymium(III) nitrate and glycine were mixed in an agate mortar (1:1:4 molar ratio) till a concentrate homogeneous solution was formed. The reaction solvent is the water hydration of nitrates, only. This solution is placed on P_4O_{10}. After 48 hours a light - violet compound was obtained.

For the compound based on erbium and aluminum was used the same procedure. A pink compound was formed.

Elemental analysis was consistent with the formula:
$[AlNd(CH_2(NH_2)COOH)_4](NO_3)_6{\cdot}4H_2O$ Calcd/Found:
Al%: 2.95/2.90; Nd%: 15.75/15.80; C%: 10.49/10.35;
N%: 15.30/15.41.
$[AlEr(CH_2(NH_2)COOH)_4](NO_3)_6{\cdot}4H_2O$ Calcd/Found:
Al%: 2.87/2.89; Er%: 17.82/17.92; C%: 10.23/10.30;
N%: 14.92/15.02.

2.2. Physical measurements

The polynuclear complex compounds have been characterized by *elemental chemical analysis*: the metal content was determined by atomic absorption technique; the carbon, nitrogen and hydrogen content were performed by microcombustion.

IR spectra (400-4000 cm^{-1}) were recorded with a BIO – RAD FTIR 135 type spectrophotometer, in KBr pellets.

Diffuse reflectance spectra (200-900 nm) were recorded at room temperature on a UV4 Unicam spectrophotometer, using MgO as standard.

The crystalline phases in the calcinated powders were identified by *XRD powder methods* using a Rigaku-Multiflex X-Ray diffractometer (Cu K_α radiation).

3. Results

In this work, the complexation method and the self-propagating combustion method were used for obtaining of lanthanide perovskite-type aluminates.

The selection of the anion of gluconic acid as ligand is justified by the multiple function of gluconate anion, which can act as a ligand with one, two or even three negative charges.

From this reason, the following systems were studied:
Al(III) : Ln(III) : $6C_6O_7H_{11}^-$ (Ln(III) = La, Nd, Er).

The polynuclear coordination compounds:
$[AlLn(C_6O_7H_{11})_2(C_6O_7H_{10})_2]{\cdot}4H_2O$ (Ln(III) = La, Nd, Er) were separated.

In the self-propagating combustion method, the system glycine/nitrates was used. The property of glycine to act as complexing agent for a number of metal ions is known. On the other hand, glycine can also serve as a fuel in the combustion reaction, being oxidized by nitrate ions. The following systems were investigated:
Al(III) : Ln(III) : $4CH_2(NH_2)COOH$ (Ln(III) = Nd, Er).

Elemental chemical analysis and physico-chemical measurements (IR, UV-VIS spectra) have indicated that the coordination compounds correspond to the general formulae:
$[AlLn(CH_2(NH_2)COOH)_4](NO_3)_6{\cdot}4H_2O$ (Ln(III) = Nd, Er).

The initial ratio of the mixture containing aluminium and lanthanide nitrates and glycine was derived from the total oxidizing and reducing valences of the oxidizer and fuel using the concepts of propellant chemistry. The stoichiometric composition of the redox mixture needed is:

$$(-15) + (-15) + n(+9) = 0,\ n = 30/9 = 3.33$$

Thus, the reactants were combined in the molar proportion 1:1:4.

4. Discussion

The IR spectra of $[AlLn(C_6O_7H_{11})_2(C_6O_7H_{10})_2]{\cdot}4H_2O$ compounds (where Ln(III) = La, Nd, Er) were recorded over 400-4000 cm^{-1} and compared with that of the free ligand.

The spectrum of gluconic acid shows a band at ~1720 cm^{-1}, assigned to the vibration ν(CO) of free carbonyl groups. After the formation of the coordinated compounds, this band disappears and it is replaced by two bands ($\nu_{asym}(COO^-)$ ~ 1620 $cm^{-1}$and $\nu_{sym}(COO^-)$ ~1400 cm^{-1}) assigned to coordinated COO^- groups (Fig. 1).

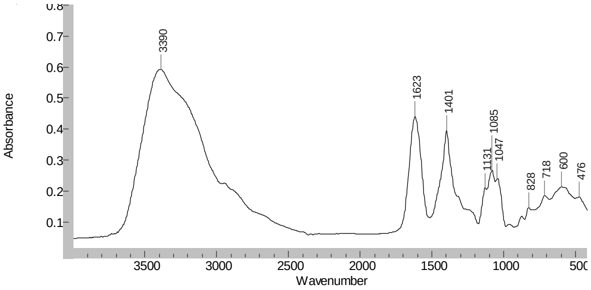


Fig. 1. The IR spectrum of $[AlNd(C_6O_7H_{11})_2(C_6O_7H_{10})_2]{\cdot}4H_2O$.

The comparation of the IR spectrum of $[AlNd(C_6O_7H_{11})_2(C_6O_7H_{10})_2]{\cdot}4H_2O$ with that of gluconic acid indicates a shift of the doublet from 1100-1120 cm^{-1} towards smaller values (~ 1090 cm^{-1}, ~1050 cm^{-1}, respectively) corresponds to the coordination at one or several OH groups. The H_2O molecules are identified due to the presence of a broad band in the range 3500-3200 cm^{-1} assigned to the formation of hydrogen bonds.

The IR spectra of $[AlLn(CH_2(NH_2)COOH)_4](NO_3)_6{\cdot}4H_2O$ compounds (where Ln(III) = Nd, Er) were recorded over 400-4000 cm^{-1}. The IR spectrum of $[AlNd(CH_2(NH_2)COOH)_4](NO_3)_6{\cdot}4H_2O$ compound (Fig. 2) shows two bands ($\nu_{asym}(COO^-)$ ~1637 cm^{-1} and $\nu_{sym}(COO^-)$ ~1380 cm^{-1}) assigned to COO^- groups. The value of $\Delta\nu$~257 cm^{-1} suggests a monodentate bonding of this group to the metal ion. The presence of NO_3^- is supported by the existence of two bands $\nu_{asym}(NO_3^-)$ ~1382 cm^{-1} (this band is completely overlapped with that due to the $\nu_{sym}(COO^-)$) and $\nu_{sym}(NO_3^-)$ ~820 cm^{-1} [11].

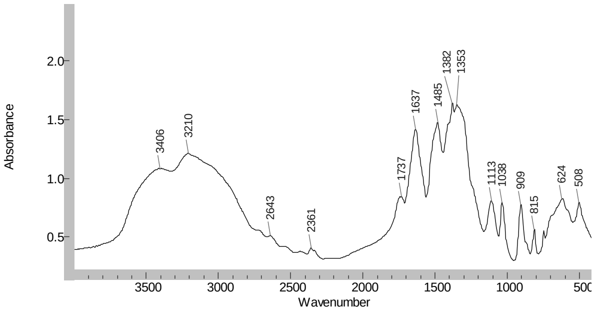
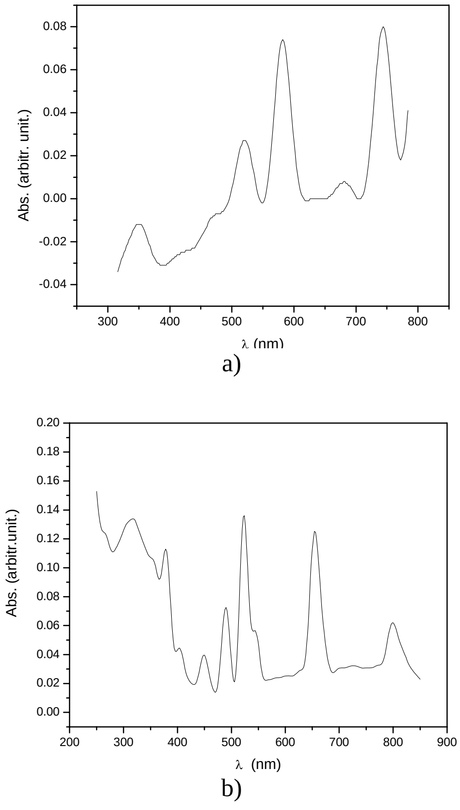


Fig. 2. The IR spectrum of $[AlNd(CH_2(NH_2)COOH)_4](NO_3)_6·4H_2O$.

The electronic spectra recorded within 200 – 900 nm for all types of compounds supplied data about the sterochemistry of metal ions. The reflectance spectra of $[AlNd(C_6O_7H_{11})_2(C_6O_7H_{10})_2]·4H_2O$ and $[AlEr(CH_2(NH_2)COOH)_4](NO_3)_6·4H_2O$ compounds are given in Fig. 3. The absorbtion bands due to the transition from the ground level ($^4I_{9/2}$) for Nd(III) and ($^4I_{15/2}$) for Er(III) respectively, to the excited levels of Nd(III) and Er(III) ions are identified [12].



a)

b)

Fig. 3. Diffuse reflectance spectra: (a) $[AlNd(C_6O_7H_{11})_2(C_6O_7H_{10})_2]·4H_2O$ and (b) $[AlEr(CH_2(NH_2)COOH)_4](NO_3)_6·4H_2O$.

The transition $^4I_{15/2} \rightarrow {}^2H_{11/2}$ at ~525 nm suggests a six-coordinated geometry of this ion in the complex $[AlEr(CH_2(NH_2)COOH)_4](NO_3)_6·4H_2O$. This fact is in accordance with the literature data [13].

In order to establish the adequate conditions of the oxides obtaining, the thermal behaviour of the coordination compounds was investigated. The $[AlLn(C_6O_7H_{11})_2(C_6O_7H_{10})_2]·4H_2O$ (Ln(III) = La, Nd, Er) compounds underwent a five stepped decompositions in the temperature ranges 40 – 890 ^oC/40-900 ^oC (neodymium/erbium).

The observed mass losses 78.81%/77.38% (neodymium/erbium compounds) are in good agreement with the calculated one, considering as end product lanthanide-aluminum perovskite (78.53%/76.80%, neodymium/erbium compounds).

The oxide products obtained from gluconate and glycinate precursors have a rather low crystallinity. The crystallinity of the oxide products was improved by a thermal treatment at 1000 °C/1hr.

The final products were characterized by X-ray diffraction, SEM, IR and UV-Vis spectra. The diffractograms confirmed the formation of orthoaluminates from gluconate and glycinate complex compounds. For example, Fig. 4 displays the formation of single-phase $NdAlO_3$ through the decomposition of $[AlNd(CH_2(NH_2)COOH)_4](NO_3)_6·4H_2O$ precursor.

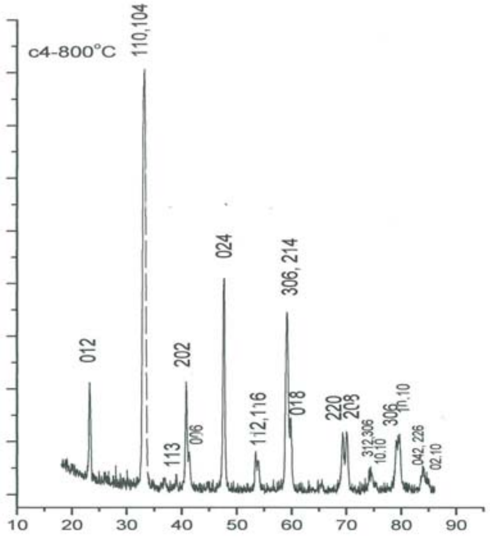


Fig. 4. XRD pattern of $NdAlO_3$ obtained byself–propagating combustion of $[AlNd(CH_2(NH_2)COOH)_4](NO_3)_6·4H_2O$ after a heating treatment of 1000 ^0C/1 hr.

The SEM image (Fig. 5) shows that $NdAlO_3$ obtained by self–propagating combustion of $[AlNd(CH_2(NH_2)COOH)_4](NO_3)_6·4H_2O$ after a heating treatment of 1000 ^0C/1 hr have an irregular powder morphology. Due to the large amount gases evolved during the decomposition, numerous voids between the crystallites formed.

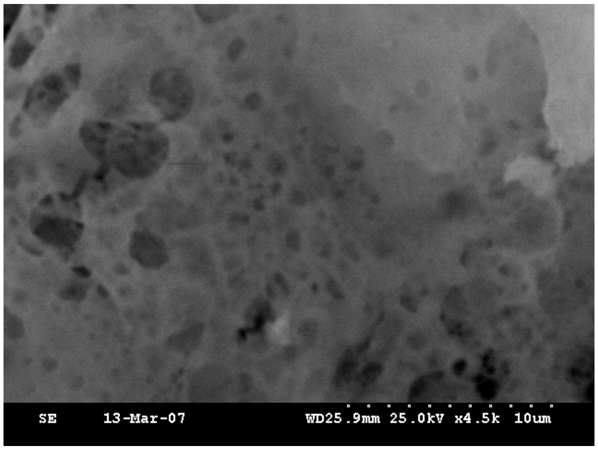


Fig. 5. SEM image of $NdAlO_3$ obtained by self–propagating combustion of $[AlNd(CH_2(NH_2)COOH)_4](NO_3)_6{\cdot}4H_2O$ after a heating treatment of 1000 ^0C/1 hr.

The IR spectra were performed on the oxide samples calcinated at 1000 ^0C/1 hr. All these spectra sustained the formation of orthoaluminates (680 and 450 cm^{-1}) from gluconate and glycinate complex compounds. In Fig. 6 is presented the IR spectrum recorded for the $NdAlO_3$ obtained by the decomposition of the $[AlNd(C_6O_7H_{11})_2(C_6O_7H_{10})_2]{\cdot}4H_2O$ compound as an example.

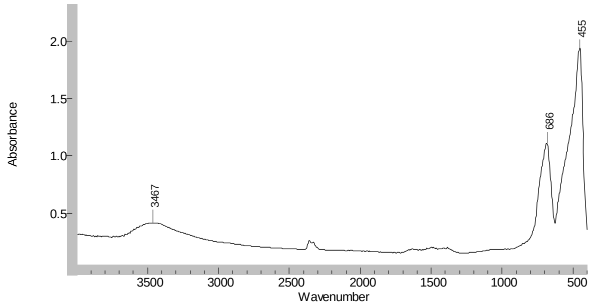
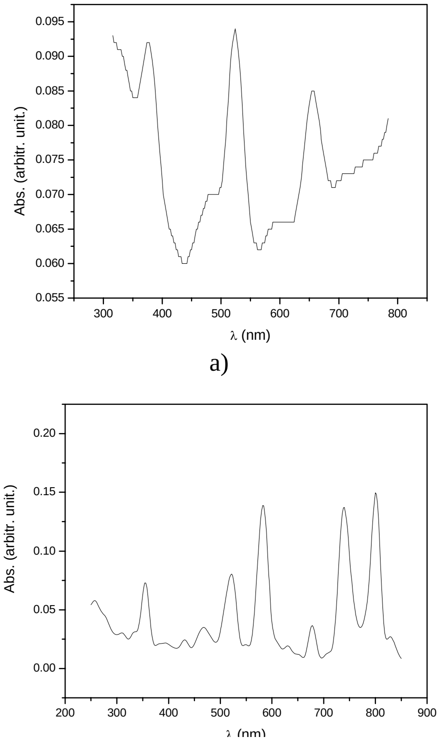


Fig. 6. The IR spectrum of $NdAlO_3$ obtained by thermal decomposition of $[AlNd(C_6O_7H_{11})_2(C_6O_7H_{10})_2]{\cdot}4H_2O$ after a heating treatment of 1000 ^0C/1 hr.

The diffuse reflectance spectra of $ErAlO_3$ and $NdAlO_3$ are shown in Fig. 7. These spectra evidence absorbtion bands which may be assigned to transitions characteristic to Er(III) and Nd(III) ions.



a)

b)

Fig. 7. Diffuse reflectance spectra: (a) $ErAlO_3$ and (b) $NdAlO_3$ obtained by self–propagating combustion of $[AlLn(CH_2(NH_2)COOH)_4](NO_3)_6{\cdot}4H_2O$ after a heating treatment of 1000 ^0C/1 hr.

5. Conclusions

$LnAlO_3$ were obtained by two different synthesis techniques: the complexation method (Ln(III) = La, Nd, Er) and the self-propagating combustion method (Ln(III) = Nd, Er). We demonstrated that in both these methods the precursors of orthoaluminates were polynuclear coordination compounds.

The precursors and orthoaluminates were characterized by IR, UV-Vis spectroscopy, thermal analysis, X-ray diffraction and SEM.

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References

[1] K. Ichimura, Y. Inoue, I. Yasumori, Properties and Application of Perovskite-Type oxides, Chem. Ind. (Dekker) **50**, New York, 235 (1993).

[2] P. E. Marti, M. Maciejwski, A. Baiker, Proceedings for the 6th Int. Symp. On Preparation of Catalysts, Louvain in Neuve, Belgium, **2**, 211 (1994).
[3] V. Matei, L. Patron, D. Matei, C. Suciu, A. Borcea, D. Petre, Prog. Catal. **11**, 51 (2002).
[4] G. Y. Sung, K. Y. Kang, S.-C. Park, J. Am. Ceram. Soc. **74**, 437 (1991).
[5] W. Li, M. W. Zhuo, J. L. Shi, Mat. Lett. **58**, 365 (2004).
[6] M. Kakihama, T. Okubo, J. Alloy. Compd. **266**, 129 (1998).
[7] E. Taspinar, A. C. Tas, J. Am. Ceram. Soc. **80**, 133 (1997).
[8] D. Zhou, G. Huang, X. Chen, J. Ku, S. Gong, Mater. Chem. Phys. **84**, 33 (2004).
[9] S. K. Behera, P. K. Sahu, S. K. Pratihar, S. Bhattacharyya, Mat. Lett. **58**, 3710 (2004).
[10] A. K. Adak, P. Pramanik, Mat. Lett**. 30**, 269 (1997).
[11] K. Nakamoto: Infrared and Raman Spectra and Coordination compounds, Elsevier Publ. Comp., Amsterdam, London, New-York (1986).
[12] A. B. P. Lever: Inorganic Electronic Spectroscopy, Elsevier Publ. Comp., Amsterdam, Oxford, New-York, Tokyo (1984).
[13] (a) D. G. Karraker, Inorg. Chem. **6**, 1863 (1967); (b) D. G. Karraker, Inorg. Chem., **7**, 473 (1967)

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