SINTEZA $YBa_2Cu_3O_{7-\delta}$ PRIN REACŢIE DE AUTOCOMBUSTIE MODIFICATĂ
SYNTHESIS OF $YBa_2Cu_3O_{7-\delta}$ BY A MODIFIED AUTOCOMBUSTION METHOD

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In this paper we describe the synthesis of $YBa_2Cu_3O_{7-\delta}$ superconductor powder by a modified autocombustion route. The purpose was to obtain $YBa_2Cu_3O_{7-\delta}$ with nanosized crystallites by a new synthetic pathway, since the literature data reported so far are limited, using stoichiometric amounts of yttrium acetate with barium and copper nitrate without the addition of organic fuel. The auto-combustion reaction transformed the precursor gel into a dark-brown ash powder, during an intense self-ignited exothermic reaction. After calcination at 900°C the obtained black powder was sintered using Spark Plasma Sintering (SPS) at 510°C. The final material was analyzed by X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS).

În această lucrare descriem sinteza materialului supraconductor $YBa_2Cu_3O_{7-\delta}$ prin reacţie de autocombustie modificată. Scopul urmărit vizează obţinerea acestuia în stare pură, cu dimensiuni ale cristalitelor de ordinul nanometrilor, printr-o nouă cale de sinteză, întrucât datele de literatură raportate până în prezent pe acest subiect sunt limitate, folosind cantităţi stoechiometrice de acetat de ytriu şi azotaţi de bariu şi cupru fără adaos de combustibil organic. Reacţia de autocombustie transformă gelul precursor într-un material pulverulent maro-închis, în timpul unei reacţii puternic exoterme. După procesul de calcinare la 900°C pulberea neagră obţinută este supusă procesului de sinterizare folosind Spark Plasma Sintering (SPS) la 510°C. Materialul final a fost analizat prin difracţie de raze X (XRD), microscopie electronică de baleiaj (SEM) şi spectrometrie de raze X cu dispersie în energie (EDS).

Keywords: *autocombustion, acetate-nitrate, supraconductors, plasma sintering*

1. Introduction

Since the discovery of high temperature superconductors (HTSs), the researchers have been trying to synthesize those compounds with fewer impurities and with optimal surface morphology and physical properties [1]. For the preparation of $YBa_2Cu_3O_{7-\delta}$ (YBCO 123) powders several techniques are used, such as solid-state synthesis [2], co-precipitation [3,4], sol-gel process [5] and combustion synthesis [6]. The most common method for preparing yttrium-based superconductor is a solid-state technique. The starting materials used are high purity oxides and carbonates. The samples obtained by this technique present a lower quality due to high annealing temperatures and longer heating duration.

For the co-precipitation technique the starting materials can be nitrates[7], chlorides[8], carbonates [9], acetates [10], oxalates [9] and combinations thereof[11].The use of these salts as starting materials has a number of disadvantages such as long precipitation time for carbonates, multiple washings of the precipitate to eliminate ion contamination for chlorides, the addition of pH adjusting agents in the case of using nitrates as starting materials.

For another technique, the trifluoracetates-metal organic deposition (TFA-MOD), the main disadvantage of the conventional process is the large amount of HF that is released during the pyrolysis step, requiring a long time of synthesis and a good evacuation of the resulting gas. The precursor films obtained after a single coating and pyrolysis step has low values of thickness [12].Critical temperature for superconducting material YBCO 123 obtained through fluorine-free sol-gel synthesis was between 90 and 94K [13,14]. Another research field is related to thin film synthesis, where PLD method yields high purity and good homogeneity materials [15].

To avoid the disadvantages of the methods presented above, in our work, we used the autocombustion process. This technique has several advantages including simple and fast fabrication process. The samples prepared by this technique are pure, homogeneous and have a

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crystalline structure with nano-sized particles [6]. The critical temperature for HTCs synthesized by autocombustion is about 90 K and particle size depends on citrate/nitrate ratio [16, 17].

The interest in YBCO based material is related to the possible applications in high temperature superconductors. In this work, we employed acetate-nitrate combustion reaction for obtaining pure $YBa_2Cu_3O_{7-\delta}$ powder with nano-sized particles. The resulted powder was calcinated followed by spark-plasma sintering (SPS) processing.

2. Experimental

All reagents used for synthesis were analytical grade, as commercial products. Barium nitrate ($Ba(NO_3)_2$) and copper nitrate ($Cu(NO_3)_2*3H_2O$) were purchased from Merk and yttrium acetate ($Y(CH_3COO)_3*4H_2O$) from Alfa Aesar.

Stoichiometric amounts of yttrium acetate and barium and copper nitrate were dissolved in pure water to obtain the starting solution. The pH was adjusted by adding ammonium hydroxide and the solution was heated using a gas burner. As the temperature of the solution increased, an exothermic self-propagating combustion reaction occurred yielding a spongy, dark-brown ash, following the expected reaction pathway:

$$\mathbf{8}Y(CH_3COO)_3+\mathbf{16}Ba(NO_3)_2+\mathbf{24}Cu(NO_3)_2 \longrightarrow \mathbf{8}YBa_2Cu_3O_7+\mathbf{50}NO_2+\mathbf{48}CO_2+\mathbf{36}H_2O+\mathbf{15}N_2 \quad (1)$$

The flow chart of the process for obtaining sintered YBCO 123 is as follows (Fig 1):

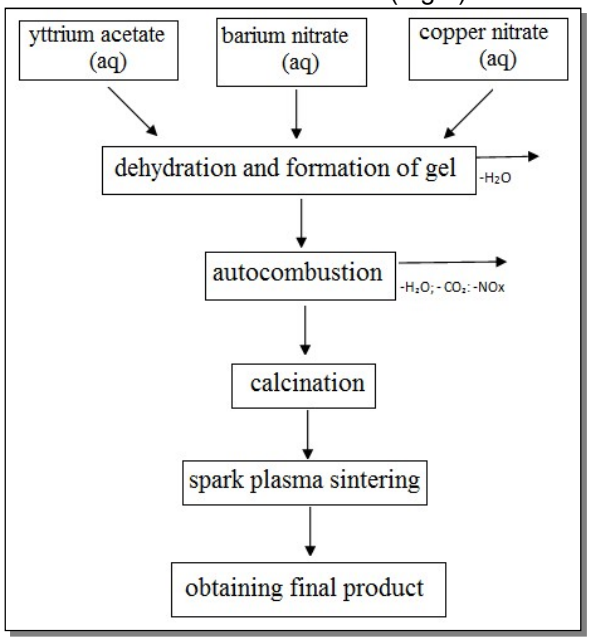

Fig. 1 - Flow chart of the process for obtaining sintered YBCO 123 / *Schema de flux pentru obţinerea YBCO prin autocombustie modificată*.

The ash obtained according to the described process was calcined at 900ºC for one hour and allowed to cool in the oven. After the calcination process the sample was sintered using SPS, in a FCT System GmbH-Spark Plasma Sintering Furnace type HP D 1.25 at 510^0C. Sintering was performed in vacuum, at a uniaxial pressure of 12MPa, with a heating rate of 100^0C/min, temperature plateau 5 minutes. The sintering process was used in order to enhance YBCO 123 phase yield and the whole ceramic material homogeneity. A 8mm diameter compact black pellet was obtained and used for further characterization.

X-ray diffraction was carried out on a PANalytical Empyrean equipment which uses CuK_α radiation (1.541874), equipped with programmable divergence slit on the incidence side and a programmable anti-scatter slit mounted on PIXcel3D detector on the diffracted side. The scan was done by using Bragg Brentanno geometry with a step size of 0.02° and a counting time per step of 100 s in the range of 2θ = 20-70.

Scanning electron microscope (SEM) QUANTA INSPECT F field emission gun resolution 1.2 nm was used to observe the sample surface morphology, and using energy dispersive X-ray (EDX) with the resolution to MnK_α 133 eV, elemental distribution in the powder was determined.

3. Results and Discussion

XRD semi-quantitative analysis performed before sintering process indicates the presence of three phases within the powder resulted after calcination: YBCO 123, YBCO 211 (Y_2BaCuO_5) and $BaCuO_2$. Specific YBCO XRD patterns before sintering are shown in Figure 2a.

XRD semi-quantitative analysis performed after sintering process indicates the presence of the two phases YBCO 123 and YBCO 211 as it is shown in the Figure 2b. X-ray diffraction performed at low speed between 2θ (45.5-48.5) showed splitting peaks of the planes (200) (020) and (006) which allowed calculation of network parameters according to the interplanar spacing of the orthorhombic system in which YBCO 123 crystallized [18].

The lattice parameters calculated from the XRD pattern (Table 1) being in very good agreement with the value mentioned in the PDF file 00-038-1433.

Rietveld refinement type was performed using the program High Score Plus, and the Agreement indices shows that a good refinement was done as it is shown in Table 1.

The average crystallite size of YBCO 123 calculated from Debye-Scherrer is 45.59 +/- 0.05 nm.

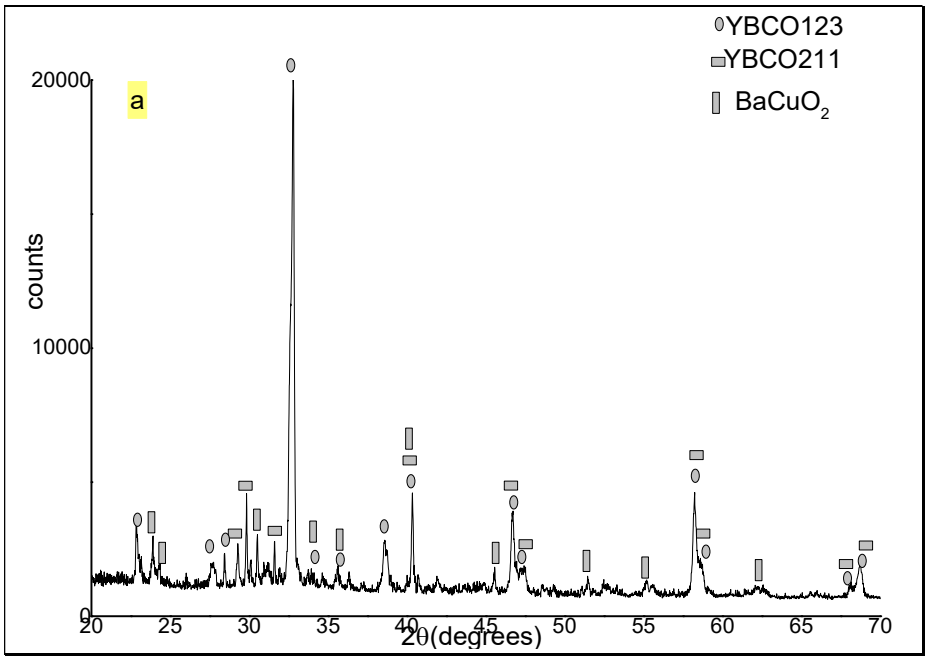

Fig. **2a -** XRD patterns of the combustion-synthesized powder YBCO before sintering / *Difractograma pentru YBCO pudră obţinută prin reacţie de autocombustie modificată acetat-nitrat înainte de sinterizare.*

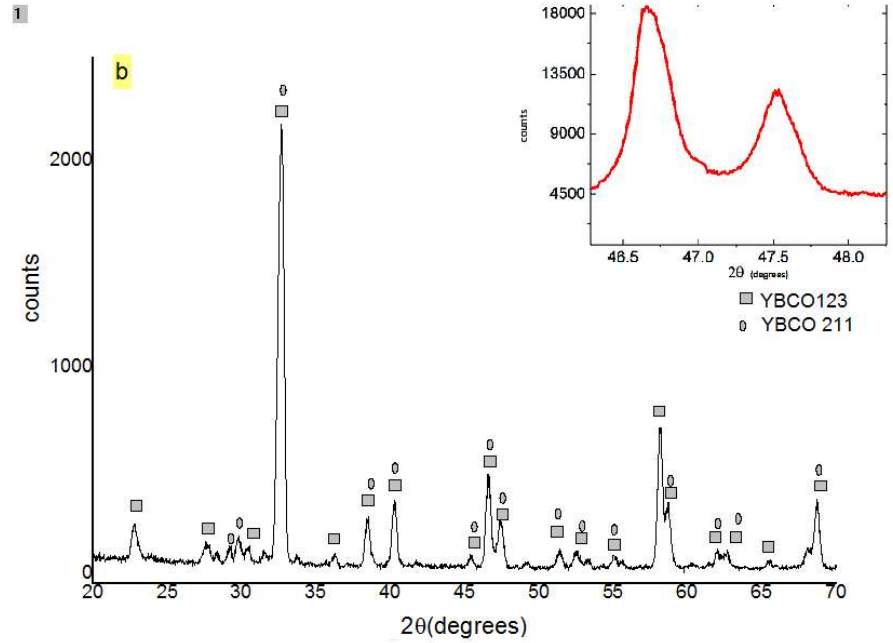

Fig. **2**b **-** XRD patterns of the combustion-synthesized powder YBCO after sintering whith detail for 2θ 45.5-47.5 / *Difracţtograma pentru YBCO pudră obţinută prin reacţie de autocombustie modificată acetat-nitrat după sinterizare cu detaliu pentru 2θ 45.5-47.5*

Table 1

Cell parameters and agreement indices for YBCO123
Parametrii celulei şi indici de concordanţă pentru YBCO 123

Cell parameters	
a (nm)	0.38243 +/- 0.00002
b (nm)	0.38843 +/- 0.00003
c (nm)	1.16759 +/- 0.00012
Agreement indices	
$R_{expected}$	10.32385
$R_{profile}$	11.27617
Weighted R profile	14.77652
Goodness of fit	2.04862

TG-DTA curve measured in the temperature range 20-1000 °C (Figure 3) shows thermal decomposition of the oxide precursors. The sample was analyzed with a Perkin Elmer derivatograph, using synthetic air (20% O_2) with a flow rate 30ml / min., in a crucible of alumina, with a heating rate of 10°C/min. The analyzed oxide precursors exhibit a highly exothermic decomposition at 250 °C (sharp peak on DTA curve) characteristic to decomposition of nitrates. A decrease in mass by 45% can also be observed. 574 peak is attributed to the decomposition of barium nitrate and 634 the decomposition of yttrium acetate [19].

The characteristic SEM images of the black powder obtained after calcination are presented in Figure 4. The agglomerates were first analyzed at low magnification (10 - 20kx) as shown in Figure 4a and 4b. Micrometric pores and large independent or interconected particles can be visualized. 50kx magnification allows the identification of the individual particles which compose the agglomerates. These nanoparticles are of 100 - 250nm (Figure 4c). At 100kx, a sponge-like network

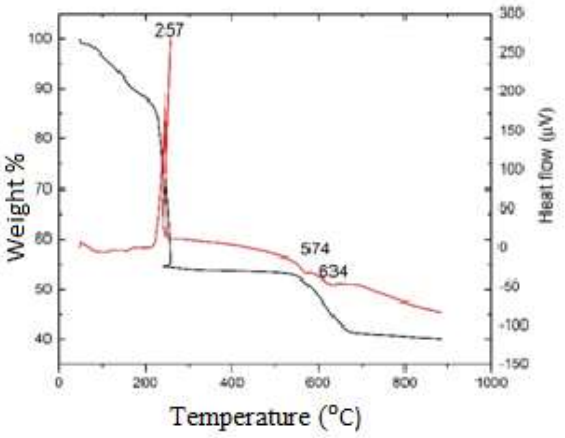

Fig. 3 - TG-DTA curve for YBCO *ICurba TG-DTA pentru YBCO.*

can be identified (Figure 4d). Based on these images, it can be concluded that autocombustion followed by calcination leads to porous materials, the particles being strongly agglomerated forming conglomerates of few micrometers.

EDX analysis (Fig.5) carried out after the combustion reaction proves the sample does not contain carbon and nitrogen.Therefore, no organic residues can be identified, this being an essential requirement for the application of these materials as superconductors.

Spliting the peak at 46 degrees in 020 plane we calculate the *b* lattice parameter, from 200 plane at 47 degrees we calculate the *a* lattice parameter and from 006 plane at 46 degrees we calculate the *c* lattice parameter. The the percentage ration (b-a)/a is calculated, which can have a value between 0 and 2. These values are introduced in a graphic on the ordinate axis,while the critical transition temperature is placed on the abscissa axis with values between 60-100 K. Experiments were carried out in order to determine values for (b-a)/a according to Tc. The value of Tc is determined by extrapolation acording to (b-a)/a [18] (Table2).

$\lambda CuK\alpha$=1,5406Å

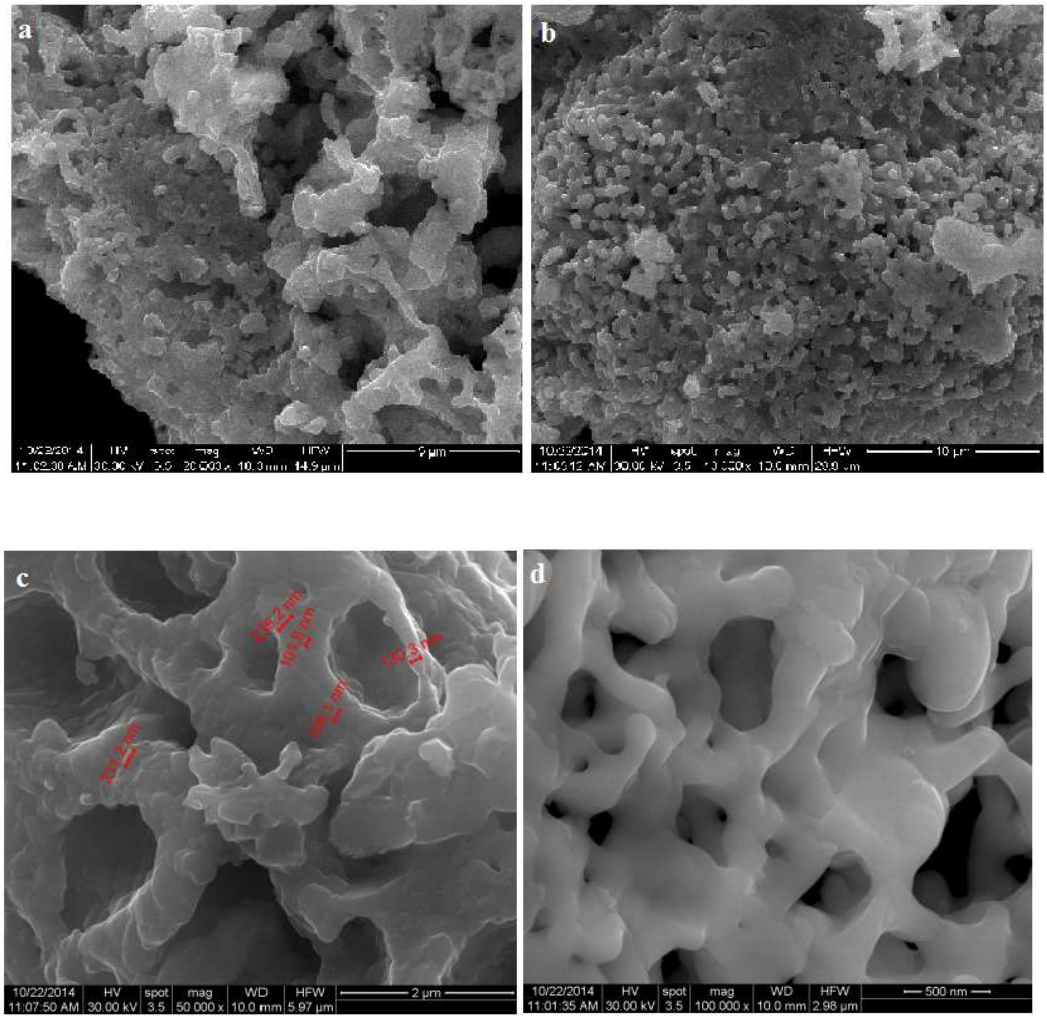

Fig. 4 - Representative SEM images of YBCO powder prepared by a modified autocombustion synthesis / *Imagini SEM caracteristice pentru pulberea YBCO123 obţinut prin reacţie de autocombustie modificată* (a – 10k, b – 20k, c – 50k, d - 100k).

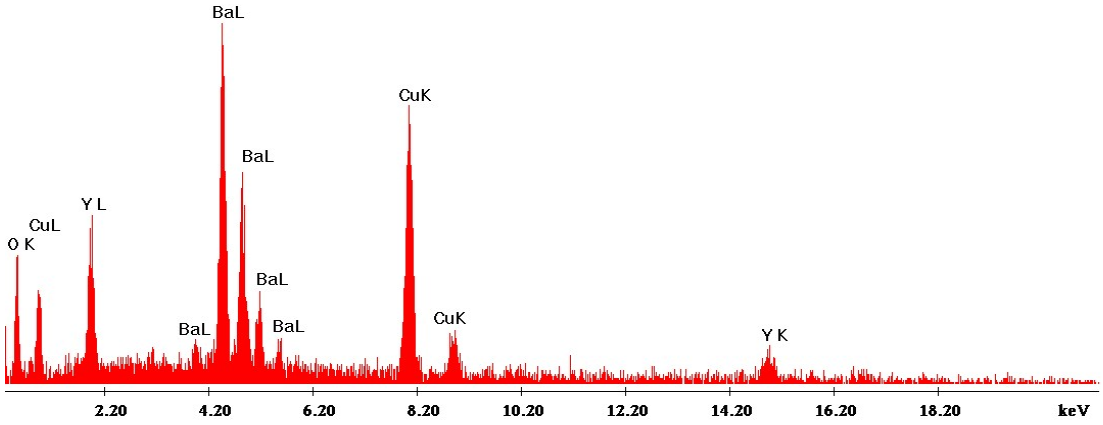

Fig. **5 -** EDS spectrum for YBCO / *Spectrul EDS pentru YBCO.*

Table 2

Tc calculation from network parameters for YBCO obtained by a modified autocombustion synthesis
Calculul Tc din parametrii de reţea pentru YBCO obţinut prin reacţie de autocombustie modificată

Y123	2θ [grad] Acording pdf JCPDS 40-0159 for $YBa_2Cu_3O_7$	2θ [grad] obtained experimental	lattice parameters [Å]	$\frac{b-a}{a}$ [%]	T_c [K]
(2 0 0)	47.502	47.53305	3.822727	1.687	~90.27
(0 2 0)	46.711	46.69712	3.887225		
(0 0 6)	46.704	46.65105	11.672549	-	

(2 0 0) $a = \frac{\lambda}{\sin\frac{2\theta_1}{2}}$;

(0 2 0) $b = \frac{\lambda}{\sin\frac{2\theta_2}{2}}$;

(0 0 6) $c = \frac{3\lambda}{\sin\frac{2\theta_3}{2}}$

The autocombustion reaction without organic fuel addition proved that the proposed goals of the experimental section are feasible, YBCO 123 was obtained and the sample was characterized through the proposed techniques. During combustion process, the precursor dark-blue gel auto-ingnites, involving an energic reaction transforming the gel into a spongy and dark-brown ash, further used without characterization in the next steps of the synthesis. The further calcination process transformed this hygroscopic and reactive ash into a dense, stable black powder of $YBa_2Cu_3O_{7-\delta}$. The obtained material was sintered by Spark Plasma Sintering at 510^0C and the final product was a compact and dense black pellet. The structure of the oxide was proved by XRD.

4. Conclusions

Ceramic material, YBCO 123, was synthesized using a modified autocombustion route, starting from a stoichiometric combination of yttrium acetate and barium and copper nitrate without adding organic fuel. The powder thus obtained was sintered at 510□C and in vacuum, at a uniaxial pressure of 12MPa, under SPS conditions. After sintering the sample contain two phases, YBCO123 and YBCO211, which was confirmed by semi-quantitative XRD analysis. X-ray diffraction also confirms obtaining YBCO 123 in orthorhombic phase, with good phase purity (low amounts of YBCO 211 phase are detectable in the final material). Further works will be done in order to characterize the electric properties of these materials, at different conditions, especially at different temperature.

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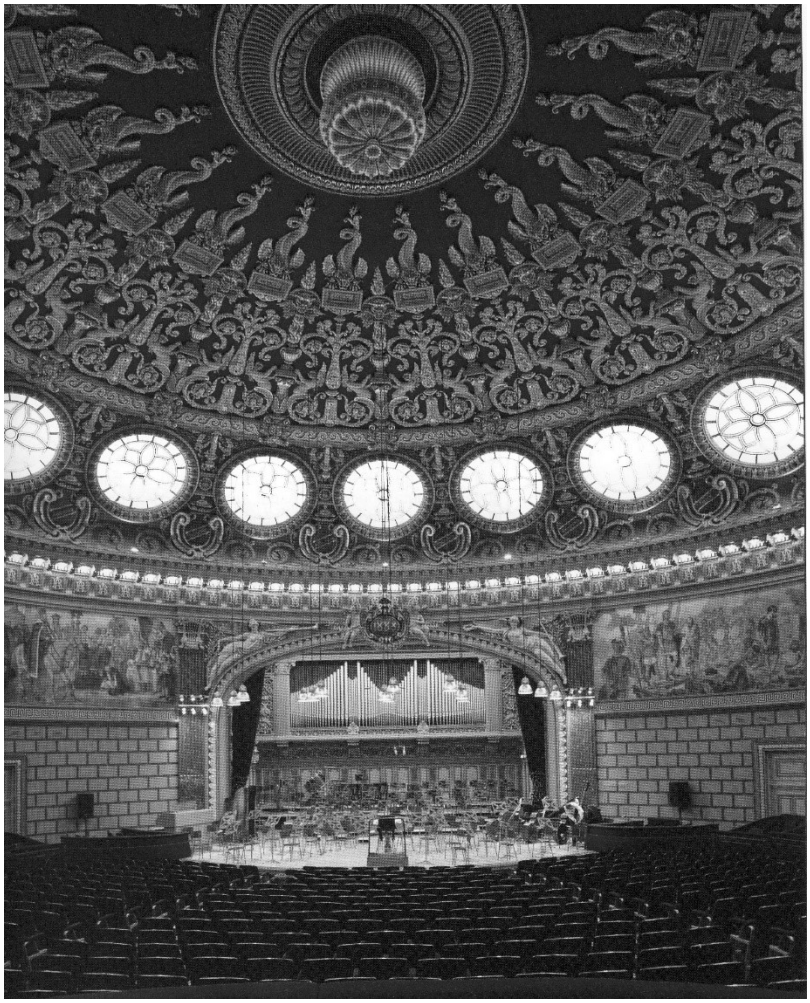

Imagine de ansamblu din sala mare de concerte (pg. 27 - Nicolae St.Noica - ATENEUL ROMÂN ŞI CONSTRUCTORII SĂI)