Synthesis and Stability of the Strontium Cobaltite Thermally Treated in Air

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This paper reports, the studies on chemical transformations at thermal treatment of a mixture of $SrCO_3$ and Co_3O_4 corresponding to stoichiometric ratio of $SrCoO_3$ compound. The mixture of raw materials was prepared by mechanical activation. Thermal analysis, X-ray diffraction and scanning electron microscopy were used for these studies. It was found that $SrCoO_3$ forms at 930°C but is not stable and turn immediately into $Sr_2Co_2O_5$ by eliminating of oxygen. This compound, $Sr_2Co_2O_5$, is unstable and by increasing of the temperature decomposes in $Sr_3Co_2O_6$ and cobalt oxide. At temperatures above the 1250°C, the samples melt and $Sr_3Co_2O_6$ crystallizes from vitreous phase by cooling.

Keywords: $SrCoO_3$, synthesis, mechanical activation, XRD, SEM

The compounds with a perovskite structure are widely studied due to their applications in technical fields such as solid electrolytes, ionic/electronic mixed conductors, electrodes, catalysts, sensors, etc.

The strontium cobaltite is characterized by a large variation of properties due to the presence of the defects and their ordering in the crystalline lattice. Also, it shows a wide domain of non-stoichiometry due to different states of valence of the cobalt (II, III and IV). Structure and properties of strontium cobaltite are influenced by the method of preparation, partial oxygen pressure, temperature and thermal treatment applied.

$Sr_2Co_2O_5$ was obtained by the thermal treatment in the air and has two types of structures, of which one is orthorhombic and is stable at high temperature and another is hexagonal and is stable at low temperature. The compound with orthorhombic structure is obtained by fast cooling from 1000°C and is metastable at room temperature. $Sr_2Co_2O_5$ with hexagonal structure was obtained by slow cooling [1].

The phase diagram of the system Sr-Co-O established by heating in air [2] confirmed the existence of two compounds at high temperature, namely, $Sr_2Co_2O_5$ and $Sr_3Co_2O_6$. The first is an incongruent compound in solid phase and can dissociate in $Sr_3Co_2O_6$ and cobalt oxide. The second, $Sr_3Co_2O_6$ is also incongruent and decomposes in SrO and a liquid.

Different methods of obtaining non-stoichiometric strontium cobaltite were developed, as solid phase reactions [3], combustion [4,5], sol-gel method [6], co-precipitation [7], etc. So, Zhang and collaborators [8] obtained $SrCoO_x$ by polymerization based on citrate method and by co-precipitation. They obtained $SrCoO_x$ by calcination at 800-900°C, but finally observed that this contains low quantities of Co_3O_4 and $SrCO_3$. Munoz and collaborators [9] using citrate method observed that after 12 hours of calcination at 900°C, followed by cooling in liquid nitrogen, a polycrystalline phase with a orthorhombic structure without any traces of hexagonal phase was obtained. The hexagonal phase usually is obtained in the case of the slow cooling. Calles and collaborators [1,10] made an extensive study on obtaining of orthorhombic $Sr_2Co_2O_5$ and on its structural transformations at heating and cooling below the temperature of 1000°C.

The mechanical activation method is currently used to intensify chemical reactions because this increases the specific surface area of the precursors and their proportion of defects causing an increased reactivity [11-20]. This fact allows reducing the temperature at compound formation [21].

The mechanical activation is used for a process in which the chemical reactivity of a system increases under the influence of mechanical energy, while the chemical composition remains the same. In this case, the temperature for carbonate dissociation gets lower and the diffusion speed gets higher. Mechanical activation leads to changes in the powder morphology and ensures better homogenization. When the grinding time is longer, the crystalline lattice of the raw materials may undergo changes, too. Chances are that the mechanical activation will lead to the formation of a relatively large ratio of an amorphous phase or to the formation of equilibrium compounds at low thermal treatment temperatures. Then again, there are papers indicating the formation of compounds in the mechanically activated raw mix only when the raw mix is thermally treated after grinding.

Knowing of the reaction mechanisms at synthesis of perovskite non-stoichiometric compounds is very important because their structure and properties are very sensitive to the conditions of preparation and heat treatment. Oxygen content of the cobaltites varies both because of the instability of the compounds formed as well due variable valence of cobalt ions. Many studies were performed regarding non-stoichiometric compounds of the strontium cobaltite but the results are often imprecise and sometimes contradictory. For this reason in our paper the formation of the strontium cobaltites and their chemical transformations at the thermal treatment in air was studied.

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Experimental part

The raw materials $SrCO_3$ and Co_3O_4 from Fluka were used for the synthesis of $SrCoO_3$. The mixture was prepared by the mechanical activation. For this purpose the planetary mill of the type Pulverisette 5 was used, the ratio balls: mixture was of 10:1 and the time of milling of 15 hours. Details about this method are given in the paper [21]. The particle size distribution of obtained powder was determined using a Brookhaven 90 Plus particle size analyzer [22]. This has a unimodal distribution of the particle sizes with a modal diameter of 429 nm and a relative width of 3.6%.

The resulted powder was thermally analyzed with simultaneous recording of the DSC, TG and DTG curves performed with apparatus STA 449 F3 Jupiter.

The pellets with 10 mm diameter were pressed uniaxial at 100 MPa. These were heated in the electrical furnace at different temperatures for two hours. The cooling of samples was performed either fast in liquid nitrogen or slowly with the furnace.

The phase composition of samples after thermal treatment of the pellets was performed by X-ray diffraction (XRD) on Shimadzu 6100 using CuKα radiation.

Samples were also analyzed with Scanning Electron Microscopy (SEM) FEG-SEM-FIB Auriga Workstation. The elementary chemical composition determined by Energy Dispersive X-Ray Analysis (EDAX) was used for grain identification and was calculated the ratio:

$$R = \frac{Co}{Co + Sr}$$

where Co and Sr are the proportions of these elements expressed in percent weight.

Results and discussion

Thermal behavior of the mixture

In order to examine the development of reactions the DSC, TG and DTG thermal analyses were simultaneously performed on the powders synthesized by mechanical activation and curves recorded are given in Figure 1.
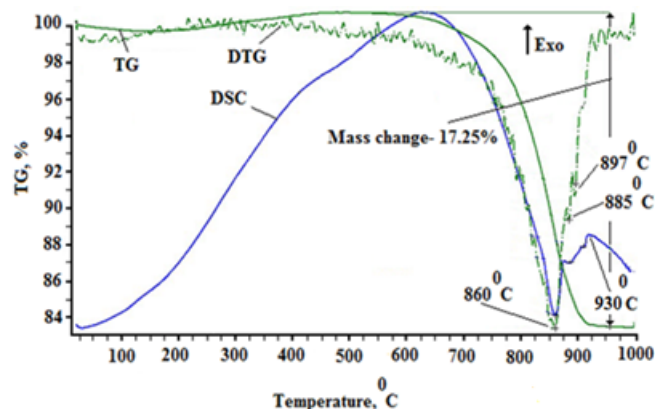

Fig. 1. Thermal analyses curves for synthesized powder

Three endothermic effects may be noticed on the DSC curve, all of them being accompanied by loss of mass. The first effect is observed at 860°C and may assigned to the oxygen loss from the Co_3O_4 structure, which turns into CoO. According to the data from literature, the dissociation temperature of Co_3O_4 depends on the obtaining method and the particle sizes, varying between 866 and 922°C [23]. The second effect, as seen on the DSC curve, is wider and duplicated, and may be assigned to the elimination of the CO_2 from the structure of the strontium carbonate. On the DTG curve may be noted that this effect takes place in two stages, namely at 885 and respectively 897°C, that is

at lower temperatures as compared to literature data. The lower dissociation temperatures in the case of the examined sample may be explained by the structural modifications that take place during the mechanical activation process leading to a decreasing of the crystallinity degree of the respective raw material. The dissociation of $SrCO_3$ in two stages, may be due to the fact that CO_2 release can partially reverse the reaction as results from the paper [24]. The exothermic effect from 930°C corresponding to the crystallization of $SrCoO_3$ may be also seen on the DSC curve.

Phase composition

The phase composition was determined on the pressed pellets, thermally treated at various temperatures. At the beginning the sample was heated at 930°C and then cooled slowly into the furnace. The XRD spectrum resulting at room temperature for this sample is shown in Figure 2.
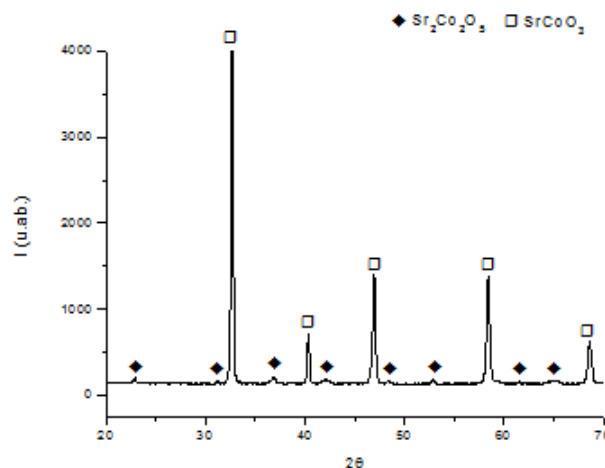

Fig. 2. XRD pattern of the sample thermally treated at 930°C and cooled slowly

It is noticed that c-$SrCoO_3$ (JCPDS 38-1148) practically is formed at 930°C, but very weak lines of $Sr_2Co_2O_5$ may also be seen, that shows that this begins to decompose as a result of oxygen loss. Previously, for the synthesis of this compound high pressure and high temperature in oxygen atmosphere were used [25,26]. The compound may also be stabilized by introducing various oxides into the structure, with which it forms solid solutions [27] or by electrochemical oxidation [28].

The sample thermally treated at 1000°C, was developed in two alternative ways: one of them with fast cooling in liquid nitrogen and the other with slow cooling. The XRD spectra as they have been obtained are shown in the Figure 3.

Thus, in Figure 3(a), which refers to fast cooling sample, the specific lines of $Sr_2Co_2O_5$ (JCPDS 34-1475) are noticed. However a few weak lines are also present corresponding to the $Sr_3Co_2O_6$ (JCPDS-83-0377) compound. This shows that $Sr_2Co_2O_5$ is not entirely stable, even if cooling has been very fast. So, it is confirmed the fact presented in paper [2], namely that $Sr_2Co_2O_5$ is incongruent and dissociates.

Through slow cooling (Fig. 3(b)) an increased proportion of $Sr_3Co_2O_6$ is noticed, which lead to increased intensity of its lines.

Figure 4 shows the spectra for the samples thermally treated at 1100 and 1200°C respectively, using slow cooling.

Figure 4 (a) confirms the existence of the two crystalline phases $Sr_2Co_2O_5$ and $Sr_3Co_2O_6$, but in figure 4(b) all lines belong to the compound $Sr_3Co_2O_6$.
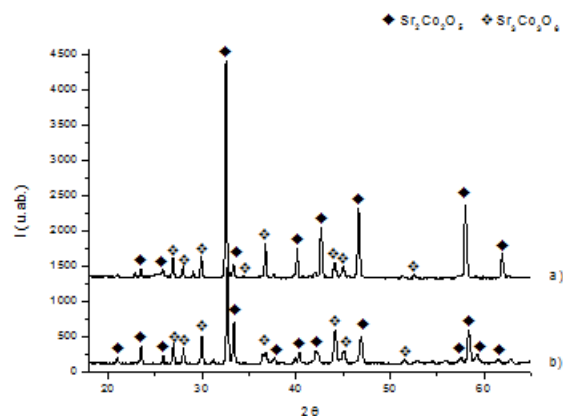
Fig. 3. XRD pattern of the sample thermally treated at 1000°C:
(a) fast cooling in liquid nitrogen ; (b) slow cooling in air

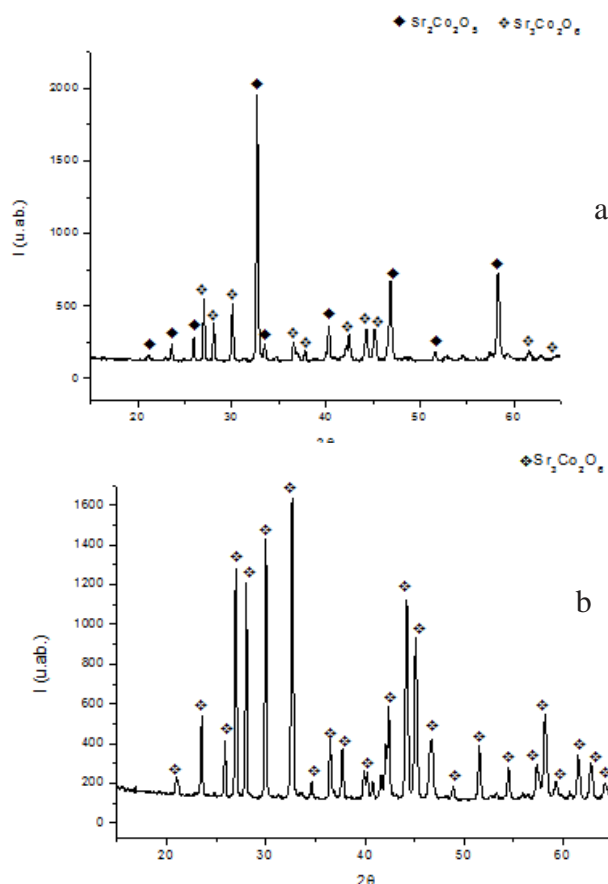Fig. 4. XRD pattern of the sample thermally treated at: a).1100°C;
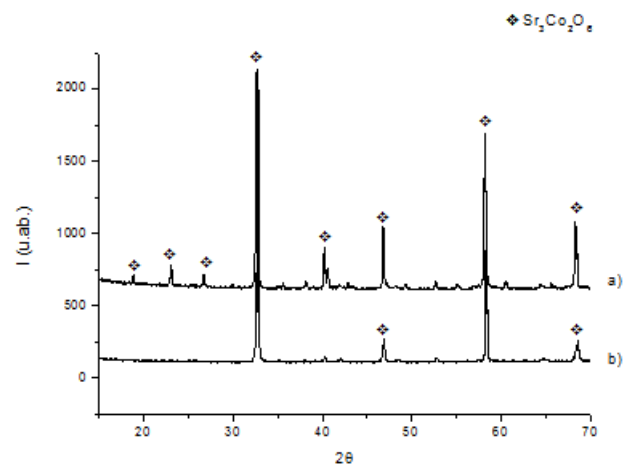b)1200°C and cooled slowly

Fig. 5. XRD pattern of the sample thermally treated: (a) 1250°C;
(b) 1300°C and slow cooled

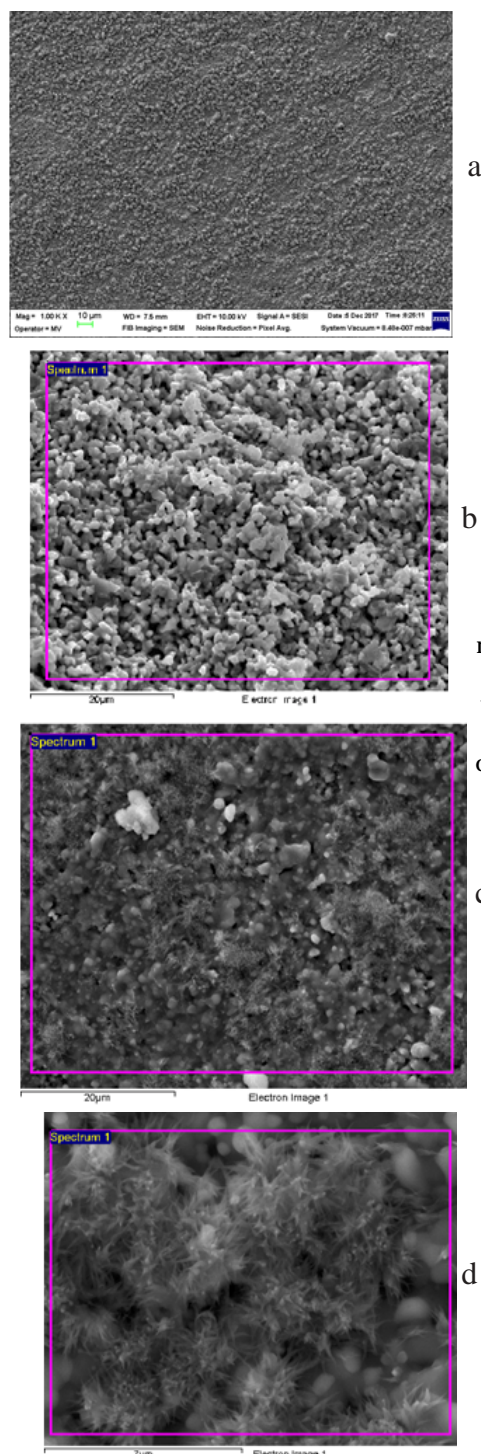Fig. 6. Electron microscopy image of sample thermally treated at 1000°C: (a); cooled fastly (b-d) details

In Figure 5, at higher temperatures (1250 and 1300°C) only some weak diffraction lines corresponding to $Sr_3Co_2O_6$ are noticed that has crystallized in the slow cooling process.

No specific lines of Co_2O_3 have been ascertained through X-ray diffraction, although upon complete dissociation of $Sr_2Co_2O_5$ the oxide quantity can be of approximately 14%. This may be explain by the fact that the cobalt oxide resulted during the dissociation process does not have the crystallinity degree required to obtain a XRD spectrum.

Electron microscopy studies

Some informations with regard to phase compositions has been obtained with the elementary chemical analysis performed by EDAX. In the figure 6 are shown the Scanning Electron Microscopy images of the sample termally treated at 1000°C which then was cooled in liquid nitrogen.

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| Figure	Temperature [°C]	Nr. grains	$R = \dfrac{Co}{Co+Sr}$	Assigning
6b		-	0.431	$Sr_2Co_2O_5$ + cobalt oxide
6c	1000	-	0.360	$Sr_3Co_2O_6$ + $Sr_2Co_2O_5$
6d		-	0.325	$Sr_3Co_2O_6$ + $Sr_2Co_2O_5$
7	1200	1	0.296	$Sr_3Co_2O_6$
		2	0.313	$Sr_3Co_2O_6$
		3	0.922	Cobalt oxide-rich grain
		4	0.300	$Sr_3Co_2O_6$
		5	0.875	Cobalt oxide-rich grain
8	1250	1	0.426	$Sr_3Co_2O_6$ + vitreous phase
		2	0.847	vitreous phase
		3	0.515	$Sr_3Co_2O_6$ + vitreous phase
		4	0.898	vitreous phase
		5	0.323	$Sr_3Co_2O_6$ + vitreous phase
Compounds				
$Sr_2Co_2O_5$	-	-	0.402*	-
$Sr_3Co_2O_6$	-	-	0.309*	-

*-theoretical values
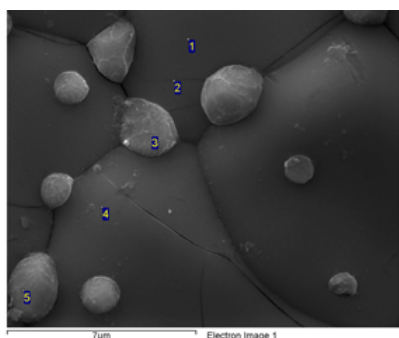
Fig. 7. Electron microscopy image of the sample thermally treated at 1200°C with a slow cooling

Grains of various shapes and sizes can be seen, as shows the details in Figure 6(b-d). For each of the three details the elementary chemical analysis was performed and the ratio $\dfrac{Co}{Co+Sr}$ was calculated, the results being given in Table 1.

In same table the theoretical values of this ratio for the two compounds identified by XRD namely $Sr_2Co_2O_5$ and $Sr_3Co_2O_6$ are presented. Thus from Figure 6(b) it is observed that the grains have this ratio near to that corresponding to the compound $Sr_2Co_2O_5$, which according to X-ray diffraction is the main component in the sample. For the details (c) and (d), this ratio is between the values corresponding to the two compounds identified by XRD.

At 1200°C (Fig. 7) only grains with a ratio corresponding to $Sr_3Co_2O_6$ are observed and grains richer in cobalt oxide formed as a result of the dissociation of $Sr_2Co_2O_5$.

The XRD spectra, show that the sample thermally treated at 1200°C mainly contains the $Sr_3Co_2O_6$.

Figure 8 shown the electron microscopy images of the sample thermally treated at 1250°C with a slow cooling.

The liquid phase which appears at 1250°C (Fig. 8) is located at the boundary between grains and may diffuse inside them. In the paper [2] it is shown that this liquid phase is rich in cobalt oxide. Nevertheless, the presence of some grains having the ratio corresponding to the $Sr_3Co_2O_6$

compound can be ascertained, which confirms the results obtained through X-ray diffraction.
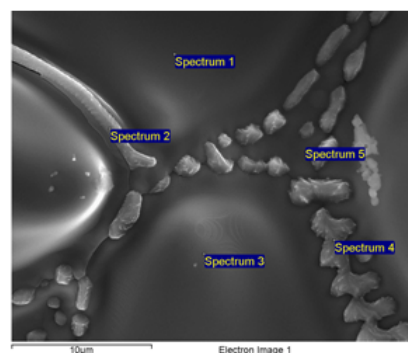

Fig. 8. Electron microscopy image of sample thermally treated at 1250°C with a slow cooling

Dissociation mechanisms of $SrCoO_3$ and $Sr_2Co_2O_5$

Based on the XRD and EDAX studies performed according to the heat treatment temperature, the dissociation mechanisms of $SrCoO_3$ were studied. $SrCoO_3$ is formed by solid-phase reactions at low temperatures, i.e. at 930°C, its crystallization being marked by an exothermic effect on the DSC curve (fig.1). The formed compound is incongruent in solid phase, and its chemical composition is gradually changes. For this reason the temperature of 930°C is not a polymorphic transformation temperature as it appears from the literature. $SrCoO_3$ undergoes a dissociation process. First, at temperatures between 930 and 1000°C, oxygen is eliminated in accordance with the reaction:

$$2SrOCoO_3 \rightarrow Sr_2Co_2O_5 + \frac{1}{2}O_2 \qquad (1)$$
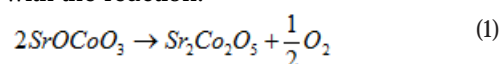
with formation of an oxygen deficient compound $Sr_2Co_2O_5$. Then, at increase of temperature above this limit $Sr_2Co_2O_5$ undergoes deeper changes by losing of a Co_2O_3 molecule in solid phase:
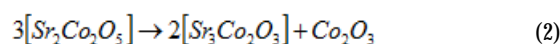
$$3[Sr_2Co_2O_5] \rightarrow 2[Sr_3Co_2O_3] + Co_2O_3 \qquad (2)$$

and it forms a compound richer in strontium oxide. Therefore, $Sr_3Co_2O_6$ is not a polymorphic variety of $Sr_2Co_2O_5$, but is a compound with chemical composition and its own properties. At 1200°C sample consist of a single crystalline phase, namely $Sr_3Co_2O_6$. By electron microscopy it was found that at this temperature began formation of the liquid phase. At higher temperatures, the 1250 and 1300°C samples are practically melted and in the cooling process only $Sr_3Co_2O_6$ crystallizes.

Conclusions

In this paper the chemical reactions that take place, when the mixture of $SrCO_3$ and Co_3O_4 is heated in air to forms $SrCoO_3$ were studied. Thus, initially $SrCoO_3$ is formed, which is unstable and begins immediately to turn into $Sr_2Co_2O_5$. This compound, unstable in its turn, dissociates in solid phase passing into a compound richer in strontium oxide $Sr_3Co_2O_6$. The dissociation of $Sr_2Co_2O_5$ is complete at 1200°C. At temperatures exceeding 1250°C the liquid phase appeared. After the slow cooling of the sample together with the furnace from 1250 and 1300°C, the compound $Sr_3Co_2O_6$ was found by XRD. This compound was crystallized from the vitreous phase at the cooling.

References

1.de la CALLE, C, ALONSO, J.A., FERNANDEZ-DIAZ, M.T, Z. Naturforsch., **63**, no. b, 2008, p. 647-654
2.JANKOVSKY, O., SEDMIDUBSKY, D., VITEK, J., SIMEK, P., SOFER, Z., J. Eur. Ceram.Soc., **35**, no.3, 2015, p.935-940
3.GANGOPADHAYAY, S., INERBAEV, T., MASUNOV, A.E., ALTILIO, D., ORLOVSKAYA, N., ACS Appl. Mater. Intefaces, **1**, no.7, 2009, p. 1512-1519
4.PERIANU, E.A., GORODEA, I.A., PRIHOR, F., MITOSERIU, L., IANCULESCU, C.A., IORDAN, A., R., PALAMARU, M.N., Rev. Chim. (Bucharest), **61**, no. 3, 2010, p.242-244
5.PERIANU, E.A., GORODEA, I.A., GHEORGHIU, F., SANDU, A.V., IANCULESCU, A.,C., SANDU, I, IORDAN, A., R., PALAMARU, M., N., Rev. Chim. (Bucharest), **62**, no. 1, 2011, p. 17-20
6.MAKHLOUFI, S., OMARI, M., AMSE Journals-AMSE IIETA, **78**, no. 2, 2017, p. 116-124
7.AGILANDESWARI, K., KUMAR, A.R., Superlattices and Microstruct., **68**, 2014, p.27–37
8.ZHANG, G., LIU, Y., XIA, Y., WEI, Y., SHIXI, O., LIU, H., Mater. Chem. Phys,.**9**, no.1, 2006, p.988–95
9.MUNOZ, A., de la CALLE, C., AlONSO, J. A., BOTTA, P.M., PARDO, V., BALDOMIR, D. , RIVAS, J., Phys. Rev. B Condens. Matter. **78**, 2008, p. 054404-1-054404-8
10.de la CALLE, C., AGUADERO, A., ALONSO, J.A., FERNANDEZ-DIAZ, M.T, Solid State SCI, **10**, no. 12, 2008, p. 1924-1935
11.ZYRYANOV, V.V., SCI Sinter., **37**, 2005, p. 77-92
12.VELCIU, G., IANCULESCU, A.C., MELINESC, A., MARINESCU, V., PREDA, M., Rev. Chim. (Bucharest), **68**, no. 9, 2017, p. 2043-2047
13.Q. ZHANG, T. NAKAGAWA, F. SAITO, J. Alloy Compd., **308**, no.1-8, 2000, p.121–125
14.STOJANOVIC, B.D., PAIVA-SANTOS, C. O., CILENSE, M., ZORICA, E. J., LAZAREVIC, Z, Mater. Resh.Bull.**43**, no.7, 2008, p.1743–1753
15.PATEL, F., PATEL, S., Res. J. Recent Sci., **11**, ISC-2011, 2012, p.52-159
16.FILIPOVIC, S., OBRADOVIC, N., PAVLOVIC, V., MARKOVIC, B., S., MITRIÆ, M., RISTIC, M.M, SCI Sinter., **42**, no.2, 2010, p.143-151
17.KARAGEDOV, G.R., LYAKHOV, N.Z., Kona, **21**, 2003, 76-86
18.WU, H., LI, Q., J. Adv. Ceram., **1**, no.2, 2012, p.130-137
19.SAHOO, S., DASH, U., PARASHAR. S.K.S,.ALI, S. M, J., Adv. Ceram., **2**, no.3, 2013, p.291–300
20.SAHOO S., J. Adv. Ceram., **7**, no.2, 2018, p.99–108
21.VELCIU, G., MELINESCU, A., MARINESCU, V., PREDA, M., Ceram. Int. **41**, no.5 Part B, 2015, p.6876-6881
22.WEINER B., Brookhaven Instruments Corporation White Paper, 2011
23.SINKO K., SZABO G., ZRINYI M., JNN, **11**, 2011, pp.1-9
24.SCHOLTEN, M.J., SCHOONMAN, J., VAN MILTENBURG, J.C., OONK, H.A.J., Solid State Ionics, **61**, no.1-3, 1993, p.83-91
25.BALAMURUGAN, S., TAKAYAMA-MUROMAKI, E., J. Solid State Chem., **179**, no.7, 2006, p. 2231-2236
26.BALAMURUGAN, S., YAMAURA, K., KARKI , A.B., YOUNG, D.P., ARAI, M., TAKAYAMA-MUROMACHI, E., Phys. Rev. B, **74**, 2006, p.172406-1-172406-4
27.BALAMURUGAN, S., XU, M., MURUMACHI, E.T., J. Solid State Chem. **178**, no.11, 2005, p. 3431-3436
28.NEMURDY, A., RUDOLF, P., Schollhorn, R., Chem. Mater. **8**, no. 9, 1996, p. 2232-2238