Mixtures with general chemical type $\text{Ba}_{3-x}\text{Pb}_x\text{Ca}_2\text{Cu}_3\text{O}_y$ (where $x = 0.2, 0.4, ..., 1.0$) were prepared by suitable proportions of $\text{BaO}$, $\text{PbO}$, $\text{CaCO}_3$, and $\text{CuO}$. Then crystalline powder samples were obtained by heating in the air, at a temperature of $870^\circ\text{C}$, for 36h and then for other 36h. The study of the phase creation and evolution, as a function of the quantity $x$, has taken place by X-ray diffraction measurements. The crystalline phases were characterized using the PDF2 database. Furthermore, the Powder Profile Analysis (Rietveld’s method) was used for the crystallographic study of the samples and the exact determination of the structures and phase percentages. Seven crystal phases were defined for all the samples, namely $\text{BaCuO}_2$, $\text{Ba}_2\text{PbO}_4$, $\text{CaO}$, $\text{BaCO}_3$, $\text{CaPbO}_3$, $\text{Ba}_2\text{PbCuO}_6$, and $\text{CuO}$, five for each sample. The first three phases are common in all the samples, while the next two are common in the first two samples and the last two are common in the last three samples. Analysis about the morphology of the samples and the concentrations of the elements took place by Scanning Electron Microscopy (SEM).

*Key words:* Superconductors, crystal structure, Rietveld analysis.

**INTRODUCTION**

The materials under study constitute a series of five samples corresponding to a general chemical formula $\text{Ba}_{3-x}\text{Pb}_x\text{Ca}_2\text{Cu}_3\text{O}_y$ (where $x = 0.2, 0.4, ..., 1.0$). They are a part of oxide-compositions, which are created from mixtures of oxides (or salts) of component elements $\text{Ba}$, $\text{Pb}$, $\text{Ca}$, $\text{Cu}$, by heating in air, at high temperatures (higher than $860^\circ\text{C}$). Materials with analogous synthesis, $\text{Pb}_2\text{YBaSrCu}_2\text{O}_8$ [1] or $\text{PbY}_{1-x}\text{Ca}_x\text{Ba}_2\text{Cu}_3\text{O}_y$F$_2$ [2], appear high temperature superconductivity, with a high critical temperature $65\text{K}$ and $50\text{K}$, respectively. The production conditions of materials, the synthesis and the structural properties of produced compounds were studied in this paper. Moreover, the percentages of crystal phases in the samples and the distribution of $\text{Pb}$ were defined.

COMPOSITION-CHARACTERIZATION

As initial materials for the preparation of five sample-mixtures the BaO, PbO, CaCO₃ and CuO were used, in proportions corresponding to the general chemical formula \( \text{Ba}_{(3-x)}\text{Pb}_x\text{Ca}_2\text{Cu}_3\text{O}_{8+d} \), where \( x=0.2, 0.4, \ldots, 1.0 \) (Table 1). The five mixtures (samples 1,2,3,4,5) were heated for 36 in air, at a temperature of 870°C and then were cooled gradually to room temperature. To homogenize the samples they were repowdered and then reheated at the same temperature (870°C) for 36h, and finally cooled gradually to room temperature. The products were black ceramics. Next, they were repowdered and the results of diffraction were measured at room temperature, by an X-Ray diffractometer, with Bragg-Brentano geometry (θ-2θ) and CuKα radiation, in a range from 5 to 90 degrees.

Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>Quantity x</th>
<th>BaO</th>
<th>PbO</th>
<th>CaCO₃</th>
<th>CuO</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.2</td>
<td>2.8</td>
<td>0.2</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>2</td>
<td>0.4</td>
<td>2.6</td>
<td>0.4</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>3</td>
<td>0.6</td>
<td>2.4</td>
<td>0.6</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>4</td>
<td>0.8</td>
<td>2.2</td>
<td>0.8</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>5</td>
<td>1.0</td>
<td>2.0</td>
<td>1.0</td>
<td>2</td>
<td>3</td>
</tr>
</tbody>
</table>

The five XRD diagrams (Fig.1) were plotted and studied by the program PLOTPOW [3]. As it is shown in Figure 1, some regions present significant

![Fig. 1 – XRD diagrams of five powder samples with CuKα radiation.](image-url)
interest. For example, the region 28°-31°, where the three strong peaks resulted almost to one peak, as the quantity x is increased from 0.2 to 1.0. Also there are some characteristic regions in which the peaks increase or decrease with the increase of quantity x. Each of the samples was characterized by the program EVAWIN [4], which uses the PDF2 [5] database. Thus the phases BaCuO$_2$ [6], Ba$_2$PbO$_4$ [7], CaO [8], BaCO$_3$ [9], CaPbO$_3$ [10] for the first two samples were defined, while the phases BaCuO$_2$, Ba$_2$PbO$_4$, CaO, Ba$_2$PbCuO$_6$ [11], CuO [12] for the next three. Detailed information about the defined phases is shown in Table 2.

STRUCTURE DETERMINATION AND REFINEMENT

Initial values of the crystal structure parameters (space group, unit cell parameters and atomic coordinates) of the seven phases defined for all the samples, were taken from the bibliography and the ICSD [13] database. The refinement of the structure parameters was carried out by the program DBWSWIN [14], which is an edition of the program DBWS9411 [15] for Windows, based on the profile analysis (Rietveld’s method) [16], improved and enhanced by a plotting program (DBWSPLT) and a bond-length bond-angle calculating program (BONDL), in order to take useful results directly.

![Fig. 2 – Results of the profile analysis with the Rietveld’s method for the sample 1 (x=0.2).](image)

Fig. 3 – Results of the profile analysis with the Rietveld’s method for the sample 2 (x=0.4).

Fig. 4 – Results of the profile analysis with the Rietveld’s method for the sample 3 (x=0.6).
Fig. 5 – Results of the profile analysis with the Rietveld’s method for the sample 4 (x=0.8).

Fig. 6 – Results of the profile analysis with the Rietveld’s method for the sample 5 (x=1.0).
At the first stage of the crystal structure refinement, for each of the samples, an overall isotropic temperature factor and unitary populations were used. In the next stages the populations of some atoms that belong to the different phases were refined, step-by-step, keeping stable all the other factors. The final values of the atomic populations have assisted to calculate the correct chemical formula of crystal phases. The chemical formula, the space group, the number $z$ of formulae units per unit cell (f.u/u.c.) and the mean unit cell parameters of the seven crystal phases (A,B,C,D,E,F,G) are given in Table 2. The final percentages of these phases in the different samples, as well as the final R-factors are given in Table 3.

The results of refinement with the powder profile analysis (Rietveld’s method) for the five samples, are plotted in Figures 2,3,4,5,6. In these Figures the diagrams $I_0$ and $I_c$ as functions of the angle $2\theta$ are shown. The degree of agreement between $I_0$ and $I_c$ is shown with the transposed differential diagram $I_0-I_c$. For better illustration and comprehension of the results, the profiles of the component phases are analytically plotted in the same figures. Moreover the phase indices are recorded as additional assistance.

**DISCUSSION**

The characterization of the five samples and their refinement resulted in total in seven phases (A,B,C,D,E,F,G), with three of these (A, B and C) common in all samples. As it is shown in Table 3, the strong phase A (BaCuO$_2$) presents a decrease of percentage from 55.45% to 9.22 % for the samples 1 to 5. The phase Ba$_2$PbO$_4$ increases lightly from 11.1% to 19.2% for the samples 1 to 2 and then decreases from 19.2% to 3.8% for the samples 2 to 5. The phase CaO decreases from 18.1% to 7.8% for the samples 1 to 5, and also the two phases BaCO$_3$ and CaPbO$_3$ decrease from 6.3% to 3.4% and 9.1% to 5.9%, respectively, for the samples 1 to 2 and is nullified for the remaining samples. The next two phases, Ba$_2$PbCuO$_4$ and CuO, appear in the last three samples with an increasing of the first from 27.6% to 73.4% and conversely decreasing of the second from 12.2% to 5.8% for the samples 3 to 5. The two phases BaCuO$_3$, Ba$_2$PbCuO$_6$ like main phases for samples 1, 2 and 4, 5, respectively and almost equilibrate for the sample 3 (31.4% and 27.6% respectively).

The existance of the unwanded phases CuO and CaO in the three last samples (3-5) and in all the phases (1-5) means these are in excess for the desirable synthesis.
The total quantity x of Pb was considered that is distributed in the respected Pb positions of phase Ba$_2$PbO$_4$ for all the samples, as well as in the Pb positions of the CaPbO$_3$ and Ba$_2$PbCuO$_6$ phases for the first two samples and the three last samples, respectively. Further the investigation of distribution of this quantity in the various compounds conduces to the better comprehension of behavior of Pb when it is doped in similar compounds.

As it is known that the microstructural and superconducting characteristics are investigated in the present study were monitored by the electron microscope techniques TEM and SEM.

Figure 7 shows SEM micrographs taken with secondary electrons for the Ba$_{13-x}$Pb$_x$Ca$_2$Cu$_3$O$_{8+d}$ samples (x=0.2, 0.4, ...,1.0) for various Pb concentrations. It is found that for the various Pb concentrations we noticed various grain sizes from 20µm up to 50µm.
REFERENCES


11. Bokhimi X., Morales A., Garcia-Ruiz A. Crystalline structure of Ba$_2$YCu$_{0.25}$W$_{0.75}$O$_6$: a member of the new set of Ba$_2$Y$_z$CuxW$_{1-x}$O$_6$ solid solutions. Powder Diffraction 11(1), (1996), 42–44.


