Structural properties of $\text{La}_{3.5-x}\text{Ba}_{4.5+x-y}\text{Ca}_y\text{Cu}_8\text{O}_{18}$ system
$(0.2<x<0.4$ and $0.3<y<0.5)$

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Abstract. This work describes the synthesis and the structural characterization of the $\text{La}_{3.5-x}\text{Ba}_{4.5+x-y}\text{Ca}_y\text{Cu}_8\text{O}_{18}$ systems, obtained by the conventional solid-state reaction method. The samples were characterized by X-ray diffraction comparing the main signals of the experimental and theoretical diffractograms with the PCW software, revealed the obtaining of an orthorhombic structure with space group $Pmm2$ (25) and unit cell volume $V=465.5370\text{Å}^3$. The analysis by Raman spectroscopy allows to determine the main modes of vibration of the different bonds that are formed between the atoms in the synthesized perovskite structure.

1. Introduction

In the last decades have been appearing important discoveries in the field of materials, the most remarkable are in ceramic materials. Those discoveries have required a rethinking in concepts, methodologies and the use of sophisticated new experimental procedures. Reciprocally, the progressive technologic advance has increase interest in searching new components with proprieties potentially relevant in industry in order to improve processes, reduce costs and preserve the environment. These factors create the impetuous necessity to search on some continuous basis new synthesis techniques, thermic treatment techniques or apply techniques that already exist to make compounds with a collection of proprieties to meet the currently needs [1]. In this context, the combination of specific proprieties in a compound permit to have varying multifunction degrees which is a challenge in field physical-chemical in the solid state. Different physical proprieties of materials of type perovskite are linked to variables like chemical composition, purity of its phases, superficial defects, crystalline structure, morphology and sinter conditions, the control of these parameters is critic inside the production process in this type of compounds [2]. One of the most relevant applications of perovskite type materials is superconductors, where the $\text{YBa}_2\text{Cu}_3\text{O}_7$ (YBCO) system is the most important because it has a high critical temperature.

Structurally the $\text{CaLaBa}_2\text{Cu}_3\text{O}_7$ (CLBCO) presents similarities to the YBCO, becoming an important system to carry out the study of superconducting properties and the effect caused by the superconducting fluctuations. The $\text{CaLaBaCuO}_7$ was discovered in 1988 by W. T. Fu and D. M. De Leeuw [3], with studies on substitution and doping with elements of Rare Earth (RE). They observed that the CLBCO has an orthorhombic isomorph structure type $\text{YBaCuO}$, with Ca and La located on Y and Ba sites, it presents a critical temperature approximately 80K. The orthorhombic phase represents symmetric of space group $Pmm2$ (25). This type of materials is commonly used in in fields as various as in medicine for the vast majority of image scanners which use Nuclear Magnetic Resonance where those base on
superconducting magnets [3] and in train systems which works with magnet levitation. Taking into account the properties of the CLBCO 123 systems, it is intended to verify that the CLBCO system 358 presents similar proprieties to the aforementioned system further to meet with phase diagram proposed by West and collaborators for the system La$_{3.5-x}$Ba$_{4.5+y}$Ca$_y$Cu$_8$O$_{18}$ in regular conditions of temperature and pressure with 0<-$x$<0.5 and 0<-$y$<0.5. In this context, this research studies the structural properties of the La$_{3.5-x}$Ba$_{4.5+y}$Ca$_y$Cu$_8$O$_{18}$ system by means of X-ray diffraction and Raman spectroscopy obtained by the solid-state reaction method, in order to obtain a new perovskite type material with a single phase.

2. Experimental
The La$_{3.5-x}$Ba$_{4.5+y}$Ca$_y$Cu$_8$O$_{18}$ (0.2<-$x$<0.4 and 0.3<-$y$<0.5) systems, were produced by the traditional Solid-State Reaction (SSR) method from corresponding precursor oxides of La$_2$O$_3$ (99.99%), CuO (99.999%), BaCO$_3$ (99.999%) and CaCO$_3$ (99.999%) carbonates, all from Sigma-Aldrich. Initially, the precursors were heat treated to remove residual moisture for 12 hours at 200°C. The stoichiometric amounts were weighed and milled in agate mortar for 4 hours in order to obtain a more homogeneous powder. Thermal treatments initially involved a first stage at 750°C for 24 to volatilize carbonate species. Subsequently, a second heat treatment was carried out for 24 hours at 780°C in order to consolidate the crystalline phase sought. The resulting material was ground and compressed uniaxially at 5.0MPa and subjected to a sintering process at 850°C for 24 hours to achieve the final structure of the proposed system. The structural characterization of the solid was performed by X-ray diffraction using PANalytical X’Pert High Score equipment using Co Kα rad radiation (1.789Å) between 20º and 90°. The vibrational characterization of systems synthetized, were made using the Raman spectroscopy technique.

3. Results and discussion
The crystallography analysis of the La$_{3.1}$Ba$_{4.4}$Ca$_0.5$Cu$_8$O$_{18}$ and La$_{3.1}$Ba$_{4.5}$Ca$_0.4$Cu$_8$O$_{18}$ systems were based on a comparison between the experimental diffractograms obtained and the diffractograms proposed by S. Gholipour et al. [4]. These results are shown in the Figure 1(a), and allow to establish that the synthesized samples have a crystalline structure orthorhombic with a space group $Pmm2$ (25) and lattice parameters $a=3.8450Å$, $b=3.8920Å$ and $c=31.0930Å$ and $\alpha=\beta=\gamma=90°$, with a cell volume of $V=465.538Å^3$.

Figure 1. (a) Comparison of patterns of X-rays diffraction from the samples La$_{3.1}$Ba$_{4.4}$Ca$_0.4$Cu$_8$O$_{18}$ and La$_{3.1}$Ba$_{4.5}$Ca$_0.4$Cu$_8$O$_{18}$ with the theoretical pattern obtained in PCW software. (b) Ideal structure of system La$_{3.5-x}$Ba$_{4.5+y}$Ca$_y$Cu$_8$O$_{18}$ obtained with Vesta software.
According to the comparison of the experimental diffractograms with the theoretical diffractogram, it is possible to affirm that the $\text{La}_{3.1}\text{Ba}_{4.5}\text{Ca}_{0.4}\text{Cu}_{8}\text{O}_{18}$ and $\text{La}_{3.1}\text{Ba}_{4.4}\text{Ca}_{0.5}\text{Cu}_{8}\text{O}_{18}$ samples present a single phase 358, since all the signals of main intensity are adjusted to the theoretical diffraction pattern. Figure 1(b) shows the ideal structure for the $\text{La}_{3.5-x}\text{Ba}_{4.5+x-y}\text{Ca}_{y}\text{Cu}_{8}\text{O}_{18}$ system, obtained with the vesta program. The size of the crystalline domains was calculated with the Deybe–Scherrer equation taking in account the signal of major intensity in diffractogram and in average was 35nm for both samples [5].

The Figure 2 show us the Raman spectrum relevant from system $\text{La}_{3.5-x}\text{Ba}_{4.5+x-y}\text{Ca}_{y}\text{Cu}_{8}\text{O}_{18}$ which exhibits consisting broadband with the literature [6], that are link with the vibrational proprieties of the atoms in the unit cell from CLBCO-358. The spectrum was measured at 785nm which allowed us to obtain the qualitative characteristics of this spectrum that are representative of the samples of the system currently studied [7]. A bottom was presented without specific signals indicating presence of fluorescence and dispersion effects which are typical when carrying out these measurements for the aforementioned system despite the care taken during the measurements made this comparing it with previously performed work, where it is observed that there is presence of fluorescence and dispersion. The signals showed in Raman are allocated in the following way [8]. The 5 signals belong to the link oscillations Cu-O (291.5cm$^{-1}$) and Ba-O (403.5cm$^{-1}$) making an axial stretching of the same [9], the signal of major intensity (534.7 cm$^{-1}$) correspond to axial movement which origins flexion between the links La-O likewise [10], there are flexion vibrations between links Cu-O (1113cm$^{-1}$) and axial stretching of Cu-O (1235cm$^{-1}$) [11]. These signals permit determine the symmetrical structure of $\text{CaLaBaCuO-358}$. The data obtained with Raman for the $\text{La}_{3.5-x}\text{Ba}_{4.5+x-y}\text{Ca}_{y}\text{Cu}_{8}\text{O}_{18}$ system and in comparison, with the results obtained by C. Thomsen et. al. [12].

![Figure 2. Raman spectrum relevant from system $\text{La}_{3.5-x}\text{Ba}_{4.5+x-y}\text{Ca}_{y}\text{Cu}_{8}\text{O}_{18}$](image)

Some characteristics present in the spectra as mentioned correspond to the vibrations of oxygen and lanthanum atoms that are present in both the orthorhombic and tetragonal phases [13]. This the mode in 291.5cm$^{-1}$, which is absent in the tetragonal phase, has a greater intensity of both this signal and all the peaks in the orthorhombic phase of the $\text{CaLaBaCuO-358}$ system compared to the results obtained for the CLBCO-123 system [14]. The highest intensity signal appearing at 534.7cm$^{-1}$ indicates the presence
of Ca doped La$_2$CuO$_4$ (not shown). Own modes of all the vibrations in La$_2$CuO$_4$ are shown in Figure 2. In Raman, some peaks or signals that are induced by defects are formed when the oxygen bonds with the La or Ba are not completely occupied. These peaks, where the largest is at 534.7 cm$^{-1}$, were first identified as defects by de Liu et. al. [15]. The Raman spectrum is dominated by the vibrations of oxygen and copper bonds [16] so we can say that the results are similar to the results confirmed in DRX where the symmetry is orthorhombic.

4. Conclusions

The solid-state reaction method allowed to produce the samples of the La$_{3.5-x}$Ba$_{4.5+x}$Ca$_y$Cu$_8$O$_{18}$ system, demonstrating the effectiveness of synthesis method to obtain a pure phase of this material in agreement with the modelling process predicted for this sample. The analysis of Raman spectroscopy allowed us to see the main vibration types present in the CaLaBaCuO-358 system, which allows corroborating the crystal structure obtained by the X-Ray Diffraction (XRD) characterization.

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