Synthesis and characterization of RBaCo$_2$O$_{5+x}$
(R = La, Nd, Gd, Y and Ho)

N D Todorov$^1$, M V Abrashev$^1$, V G Ivanov$^1$, G V Avdeev$^2$ and S C Russev$^1$

$^1$ Faculty of Physics, University of Sofia, 1164 Sofia, Bulgaria
$^2$ Institute of Physical Chemistry, Bulgarian Academy of Sciences, 1184 Sofia, Bulgaria
E-mail: neno.todorov@gmail.com

Abstract. Ceramics of double perovskite RBaCo$_2$O$_{5+x}$ (R = La, Nd, Gd, Y and Ho) were prepared in air at different annealing conditions. The samples were characterized by optical microscopy, X-ray powder diffraction, scanning electron microscopy (SEM), energy-dispersive X-ray analysis (EDX), and micro-Raman spectroscopy. In the case of RBaCo$_2$O$_{5+x}$ (R = Gd, Y and Ho) the optical anisotropy of the tetragonal-like microcrystals observed is sufficient to determine their orientation and to obtain their polarized Raman spectra from (001)- and (100)-type oriented crystal surfaces. Due to the fact that some of the impurities observed in the ceramics have Raman spectra with intensity much larger compared to that of the main phase, special attention was paid to identify their Raman spectra. The origin of the lines observed in the polarized Raman spectra of RBaCo$_2$O$_{5+x}$ phase (R = Gd, Y and Ho) is discussed.

1. Introduction
The perovskite-like oxides and their superstructures attract the interest of the researchers for several decades because of the observation of a variety of physical phenomena in them as well their diverse physical properties. It is sufficient to note the first observations of structural second order transitions in titanates and aluminates, the discovery of high-temperature superconductivity in layered cuprates and colossal magnetoresistivity in manganites. During the last years the interest to the cobaltites with perovskite-like structure (i.e. compounds with chemical formula (R,A)CoO$_{3-\delta}$, where R is rare earth metal and A is alkaline earth metal) is also increased due to their rich structural, transport and magnetic phase diagrams [1] as well to their potential use as solid oxide fuel cell cathodes and membranes by reason of the high mobility of oxygen ions in them [2, 3]. The compounds under interest here are the double perovskites RBaCo$_2$O$_{5+x}$, $0 \leq x \leq 1$. Depending on the type of the rare earth and the annealing conditions (temperature and gas content atmosphere) several ordered structures with different oxygen content, different symmetry and unit cell can be prepared (see figure 1) [4]. Whereas the end members (for $x = 0, 1$) have simple tetragonal structure, the ordering of the oxygen vacancies in the compound with $x = 0.5$ doubles the unit cell and lowers the symmetry to orthorhombic. Tuning the oxygen content, coincident metal-insulator and ferromagnetic-paramagnetic phase transition near the room temperature can be observed [1]. Whereas large number of experimental methods were used to investigate their structural, transport and magnetic properties, there is only one paper on Raman spectroscopy of these materials [6]. Raman spectroscopy is an efficient tool for study
of the crystal structure and their changes. In this paper we study the possibilities of this method for investigation of these type of materials.

2. Experimental

Samples of RBaCo$_2$O$_{5+x}$ (R = La, Nd, Gd, Y and Ho) were prepared by a standard solid-state reaction method. The starting materials of R$_2$O$_3$, BaCO$_3$, and Co$_3$O$_4$ were weighed in the stoichiometric ratio of RBaCo$_2$O$_{5+x}$. The powders were mixed in a ball mill and calcinated at 1000 and 1050$^\circ$C for 48 h with intermediate grindings. After that the powders were pressed into tablets with diameter of 12 mm and sintered again in air at 1050$^\circ$C for additional 24 h. Finally half of the samples were cooled in the furnace to 400$^\circ$C by employing a cooling rate of 0.5$^\circ$C/min. The other half of the samples was rapidly quenched from 950$^\circ$C to room temperature. The tablets were polished using diamond pastes and then ultrasonically cleaned.

As prepared samples were observed under optical microscope Olympus BX41 equipped with $\times 100$ objective as a part of LabRAM HR800 micro-Raman spectrometer used for the Raman measurements. The Raman spectra were taken in back-scattering configuration, as the excitation source was He-Ne laser (633 nm) with a laser beam spot size of 1 – 2 $\mu$m. To prevent overheating of the samples the incident laser power was under 1 mW. The elemental analysis of the synthesized samples was carried out using scanning electron microscopy (SEM; Tescan LYRA) equipped with energy-dispersive X-ray spectrometer (EDX; Bruker). The crystalline phases were determined by X-ray powder diffraction (XRD) analysis using a Philips PW 1050 diffractometer with Cu K$\alpha$ radiation and 2$\theta$ in the range 20$^\circ$ – 90$^\circ$ with step 0.03$^\circ$ and an acquisition time for each step of 1 s. The diffraction patterns were refined with the PowderCell [7] software.

3. Results and discussion

The polycrystalline samples were analyzed initially by optical microscope. The observation of the ceramics illuminated with linearly polarized light show that for R = La and Nd, the orientation of the microcrystals is indistinguishable and the samples surface seems to be optically isotropic. For the rest samples optically anisotropic tetragonal-like microcrystals in rectangular shape can clearly be seen as shown in figure 2.

The X-ray powder diffraction analysis let us to determine the crystal phase purity of the RBaCo$_2$O$_{5+x}$ samples using a software algorithm. By variation of the phase dependent parameters, calculated powder diffraction patterns can be fitted to the experimental data. After the refinement the samples were indexed on cubic for R = La, orthorhombic for R = Nd, Gd and tetragonal for R = Y, Ho unit cells, which is consistent with the reports in the literature [3, 4, 8].
Figure 2. Optical images of (a) YBaCo$_2$O$_{5+x}$ illuminated with linearly polarized white light in the plane perpendicular to the $z$ axis (the longest side) of the delineated crystal; (b) the same crystal but the polarization of the light is in direction parallel to the $z$ axis (magnification $\times 100$).

Figure 3 can be seen that except the main phase, a perovskite-like RBa$_2$Co$_3$O$_{9-x}$ (R = La and Nd) was observed, too. These secondary phases were confirmed also by the EDX analysis. Minor impurities also exist in the Y- and Ho- samples. In figure 4 the dependence of the lattice parameters and the unit cell volume (normalized to the ideal perovskite unit cell) on the ionic radius of the rare earth element were plotted. Comparing the calculated lattice parameters and the volume of the unit cell with the ones published in the literature we can evaluate the
oxygen content in the RBaCo$_2$O$_{5+x}$ phase as follows: $x \approx 0.2$ for R = Ho and Y [9, 10], $x \approx 0.6$ for R = Gd [1], $x \approx 0.65$ for R = Nd [4, 11]. Using the empirically known dependence of the oxygen content on the type of the rare earth at equal annealing conditions, the oxygen content of La-sample also can be evaluated as $x > 0.7$ [4, 12]. Shortly, we can conclude that the main phase in Y- and Ho- samples is the tetragonal oxygen-poor RBaCo$_2$O$_{5.2}$, the one in the Gd- and Nd-samples is the orthorhombic RBaCo$_2$O$_{5.6}$, whereas the La-sample contains oxygen-rich disordered cubic perovskite (La,Ba)CoO$_{3-\delta}$.

As all atoms in the ideal stoichiometric cubic perovskite occupy sites at center of symmetry, there are no Raman-active modes in it. By this reason the observed Raman lines in the spectra of perovskite-like materials can originate by activated due to an ordering of oxygen vacancies and/or by ordering of different atoms otherwise occupying equivalent sites in the ideal perovskite. In this case the symmetry of the structure lowers and the unit cell increases. As a rule for all layered perovskites, however, the intensity of the lines in Raman spectra is usually in orders lower than the spectra of starting materials. So, in our case the Raman spectra of the main phase easily can be masked by the spectra of some impurity phase, existing in negligible concentrations in the ceramics. By this reason we have carefully measured the Raman spectra of all starting materials. Some of their spectra are presented in figure 5. It is seen that the intensity of the Raman spectra of the starting materials (and the possible impurity phases) is much stronger than the spectra of the main phase. Nevertheless, in the spectra of the main phase all lines observed are intrinsic for it.

Now we can analyze the origin of the lines observed in the spectra of the tetragonal oxygen-deficient YBaCo$_2$O$_{5.2}$. From the selection rules of the lines, their symmetry can be determined as $E_g$ for the lines at 146 cm$^{-1}$ and near 521 cm$^{-1}$, and $A_{1g}$ for the lines at 226 cm$^{-1}$ and 455 cm$^{-1}$.

**Figure 4.** The dependence of the lattice parameters of RBaCo$_2$O$_{5+x}$ and the unit cell volume on the ionic radius of the rare earth element (radius of: La$^{3+}$ and Nd$^{3+}$ is in 12-fold coordination; Gd$^{3+}$ is in 9-fold coordination; Y$^{3+}$ and Ho$^{3+}$ is in 8-fold coordination [13]).
Figure 5. Raman spectra of the starting compounds $R_2O_3$ ($R = \text{La}, \text{Nd}, \text{Gd}$) (a), $\text{BaCO}_3$ and $\text{Co}_3\text{O}_4$ (b) and $\text{YBaCo}_2\text{O}_{5+x}$ (c).

From additional measurements from a (001)-oriented micro-crystal the line at 344 cm$^{-1}$ appears to be with $B_{1g}$ symmetry. Based on the lattice dynamical calculations done for the similar tetragonal NdBaCo$_2$O$_5$ [14], the $A_{1g}$ line at 455 cm$^{-1}$ and the $B_{1g}$ line at 344 cm$^{-1}$ can be assigned to the in-phase and out-of-phase plane oxygens (both vibrations are along $z$ tetragonal axis). Lines with this symmetry and at these frequencies are typical for all layered perovskites, containing two M-O planes in the unit cell. Since the Ba, Y and O-apex atoms are in sites at center of symmetry, they cannot take part in Raman-active modes. Therefore the other lines observed can originate only by Co and O-plane vibrations. Comparing the frequencies of the observed $E_g$ line at 146 cm$^{-1}$ and $A_{1g}$ line at 226 cm$^{-1}$ with the calculated ones in [14], they can be assigned to the Co-vibrations in $xy$-plane and along $z$-direction, respectively. The origin of the broad $E_g$ line near 521 cm$^{-1}$ can be not a Raman-active mode, but rather a defect mode reflecting the oxygen non-stoichiometry. The polarized Raman spectra obtained by (100)- and (001)- oriented micro-crystals from the Ho-ceramics (not presented here) look qualitatively in the same manner. Therefore we can conclude that these spectra are typical for the tetragonal oxygen-deficient RBaCo$_2$O$_{5+x}$ structure.

4. Conclusions
The samples of double-layered perovskite RBaCo$_2$O$_{5+x}$ are synthesized and characterized. From the dependence of the crystal lattice parameters, the oxygen content is evaluated. Polarized micro-Raman spectra from (100)- and (001)- oriented microcrystal surfaces are obtained and analyzed. The lines observed in them are discussed and their origin is tentatively determined.

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