Synthesis, structure and IR absorption studies of LnBaCuCoO_5 (Ln = rare earth) oxides[†]

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Abstract. A series of oxides LnBaCuCoO_5 (Ln = Pr, Nd, Sm, Dy, Gd, Ho and Er) have been synthesized by ceramic method. The oxides crystallize in a tetragonal structure, isostructural to YBaCuCoO_5 . All the oxides in the series are semiconducting. IR spectra of these oxides show distinct absorption bands at 630 cm^{-1} , 550 cm^{-1} and 330 cm^{-1} which are assigned to E , A_2 and A_1 modes respectively. Doping of holes in these oxides, by calcium substitution in $\text{Er}_{1-x}\text{Ca}_x\text{BaCuCoO}_{5-x}$ (up to $x \approx 0.3$) was done but, these oxides did not show metallic behaviour.

Keywords. Ceramic method; rare earth oxides; IR spectra.

1. Introduction

Since the discovery of a new defect layered perovskite, YBaCuMO_5 (M = Fe and Co) (Er-rakho *et al* 1988; Barbey *et al* 1992), there has been a considerable interest in these classes of materials to understand their crystal structure and magnetic properties (Huang *et al* 1994; Mombru *et al* 1994; Caignaert *et al* 1995). Spin state and spin orientation of Co(III) (Barbey *et al* 1994) and Mössbauer studies in LnBaCuFeO_5 (Ln = rare earth ion except La) have been investigated (Pissas *et al* 1992). Further, solid solutions of $\text{YBaCu}_x\text{Co}_{2-x}\text{O}_5$ ($0 < x < 1$) (Wuuzong 1994) have been studied and in these oxides an irregular intergrowth of YBaCuCoO_5 with $\text{YBa}_2\text{Cu}_3\text{O}_7$ has been observed. In this respect, the layered 112-type oxides are interesting materials, which are built up of corner shared CuO_5 , and (Fe/Co) O_5 pyramids. Its structure can be regarded as a derivative of the high- T_c superconducting $\text{YBa}_2\text{Cu}_3\text{O}_7$ phase, achieved by removing one Ba–O layer and Cu–O chain with 50% of the remaining Cu atoms being substituted by Co or Fe. We considered worthwhile to synthesize LnBaCuCoO_5 (Ln = rare earth ion) series of oxides and study their structure and properties. Further, substitution of divalent alkaline earth ion for the lanthanide ion may lead to hole doping giving a metallic phase. Here we report synthesis, structure and properties of LnBaCuCoO_5 oxides.

2. Experimental

The samples were prepared by a ceramic method. The parent oxides Ln_2O_3 (99.6%) (Pr_6O_{11} in case of Pr), CuO (99%), Co_3O_4 (99%) and BaO_2 (99.5%) were mixed stoichiometrically, ground well and heated up to 930–1000°C with one intermittent

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Table 1. Synthetic conditions and lattice parameters of LnBaCuCoO_5 (Ln = rare earth ion).

Composition	Synthetic conditions	Lattice parameters (Å)	
		<i>a</i>	<i>c</i>
PrBaCuCoO ₅	950°C/48h	3.926(1)	7.668(7)
NdBaCuCoO ₅	950°C/48h	3.916(7)	7.658(3)
SmBaCuCoO ₅	930°C/48h	3.874(9)	7.597(5)
GdBaCuCoO ₅	930°C/48h	3.875(2)	7.587(8)
DyBaCuCoO ₅	930°C/48h	3.873(4)	7.548(4)
HoBaCuCoO ₅	930°C/48h	3.872(4)	7.538(1)
ErBaCuCoO ₅	930°C/48h	3.871(7)	7.523(8)
YBaCuCoO ₅	1000°C/48h	3.867(3)	7.571(5)

Figure 1. Powder X-ray diffraction pattern of LnBaCuCoO_5 .

grinding, and then furnace cooled. The synthetic conditions are given in table 1. Powder X-ray diffraction of these samples were recorded in a JEOL JDX-8P diffractometer. Oxygen estimation was carried out by thermogravimetric analysis (TGA) in hydrogen atmosphere. The IR spectra of these samples were recorded in a Perkin Elmer spectrometer using pressed KBr pellets. The electrical resistivity measurements were done using a four-probe method. Transmission electron microscopy of selected samples were carried out to confirm the structure.

3. Results and discussion

The powder X-ray diffraction patterns of LnBaCuCoO_5 (Ln = rare earth ions) are given in figure 1. For comparison the XRD pattern of YBaCuCoO_5 is also given. The X-ray pattern could be indexed on a tetragonal cell with $P4/mmm$ space group and the cell parameters of all the samples were obtained by least-square fitting, as summarized in table 1. These samples were synthesized at relatively lower temperatures as compared to YBaCuCoO_5 . The variation of lattice parameters, a and c as a function of rare earth ionic radii is given in figure 2. We clearly see from this figure that both a and c are increasing with increase in the rare earth ionic radii. The indexed powder X-ray diffraction data of a typical member, ErBaCuCoO_5 is given in table 2. The observed intensity matched well with the calculated values obtained by Lazy Pulverix programme. Thus, from figure 1 and tables 1 and 2, LnBaCuCoO_5 (Ln = Pr, Nd, Sm, Dy, Gd, Ho and Er) are shown to form single phase oxides which are isostructural to YBaCuCoO_5 phase. However, the lanthanum analogue of this phase could not be synthesized. When stoichiometric mixtures of La_2O_3 and the oxides were heated at $950\text{--}1000^\circ\text{C}$, a cubic like phase was obtained with $a \approx 3.94 \text{ \AA}$, probably due to mixing of La^{+3} and Ba^{+2} sites.

The TGA curve of a typical member, ErBaCuCoO_5 is given in figure 3. Oxygen estimated from the weight loss corresponds to the formula $\text{ErBaCuCoO}_{(5.006 \pm 0.003)}$.

Figure 2. The lattice parameters a and c for LnBaCuCoO_5 as a function of the rare earth ionic radii.

Table 2. Powder X-ray diffraction data for ErBaCuCoO_5

<i>h</i>	<i>k</i>	<i>l</i>	$d_{\text{obs}} (\text{\AA})$	$d_{\text{cal}} (\text{\AA})$	I_{obs}	I_{cal}
0	0	1	7.531	7.523	3	4
1	0	0	3.867	3.871	19	11
0	0	2	3.769	3.762	10	7
1	0	1	3.440	4.442	< 1	< 1
1	1	0	2.726	2.737	46	45
1	0	2	2.702	2.698	100	100
0	0	3	2.512	2.509	4	3
1	1	2	2.214	2.213	19	20
1	0	3	2.106	2.105	3	3
2	0	0	1.928	1.936	23	30
0	0	4	1.882	1.881	7	9
2	0	2	1.726	1.721	3	4
1	0	4	1.691	1.692	5	5
2	1	2	1.572	1.573	25	37
1	1	4	1.548	1.550	14	19

Figure 3. Thermogravimetric curve for ErBaCuCoO_5 .

Even after annealing these samples in oxygen atmosphere there were no significant changes in the oxygen content. From these results we believe that our samples are nearly stoichiometric LnBaCuCoO_5 .

Transmission electron microscopic studies were carried out on a typical member, ErBaCuCoO_5 , to confirm the structure. Figures 4a and b show lattice image and the corresponding diffraction pattern. The lattice image with 7.5 Å fringe spacing confirmed the layered nature. The electron diffraction pattern recorded along (001) direction indicated the tetragonal cell with lattice parameter $a \approx b \approx 3.9$ Å.

The IR spectra of LnBaCuCoO_5 samples are shown in figure 5. We can clearly see that, as the rare earth ionic size increased, intensity of absorption bands decreased. The decrease is prominent in the case of Pr and Nd. In all these oxides, three distinct absorption bands were observed at 630 cm^{-1} , 550 cm^{-1} and 330 cm^{-1} . For comparison, the IR spectra of La_2CoO_4 are given in figure 5, which agrees well with the spectra

Figure 4. a. Lattice image of ErBaCuCoO_5 with fringe spacing $7.5 \text{ \AA}$ and b. selected area diffraction pattern of image shown in a.

reported in the literature (Sreedhar and Ganguly 1990). In La_2CoO_4 , Co is octahedrally coordinated to oxygen. The absorption bands of La_2CoO_4 at 630 cm^{-1} , 510 cm^{-1} , 410 cm^{-1} and 330 cm^{-1} are assigned to in-plane stretch E_g , out of plane A_2 and two A_1 modes respectively. In the case of LnBaCuCoO_5 system, due to the loss

Figure 5. Infrared absorption spectra of LnBaCuCoO_5 .

Figure 6. Logarithm of resistivity as a function of reciprocal temperature for compounds (a) DyBaCuCoO_5 and (b) HoBaCuCoO_5 .

of octahedral symmetry one of the vibrational modes (A_1) along z-direction should disappear. Accordingly, we saw the absorption bands at 630 cm^{-1} (E), 550 cm^{-1} (A_2) and 330 cm^{-1} (A_1). One absorption band near 410 cm^{-1} disappeared. The IR spectrum of YBaCuCoO_5 was similar to LnBaCuCoO_5 oxides, indicating structural similarity amongst these oxides.

The electrical resistivity measurements were done by the four-probe method using sintered pellets. All these oxides are semiconducting. Typical $\ln(\rho)$ vs $1000/T$ plots for Ho and Dy are given in figure 6. The band gaps E_g of these oxides were in the range of 0.09 eV.

In an attempt to dope holes in these layered oxides, we synthesized the $\text{Er}_{1-x}\text{Ca}_x\text{BaCuCoO}_5$ ($0 < x < 0.3$) series of oxides at 920°C for 48 h and furnace cooled. The compositions for $x > 0.3$ were multiphasic. The powder XRD pattern could be indexed on a tetragonal cell, like the parent phase. However, there was no significant change in the resistivity of these doped compounds and they are semiconducting.

4. Conclusions

We have synthesized a series of LnBaCuCoO_5 (Ln = rare earth ion) oxides related to YBaCuCoO_5 type of phase. The unique feature of these class of materials is the presence of $(\text{Cu/Co})\text{O}_5$ corner shared pyramidal layers, which showed distinct IR absorption spectrum. An attempt to induce metallicity in this phase by hole doping was not successful.

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