Materials Research. 2011; 14(4): 472-474
DOI: 10.1590/S1516-14392011005000066

Synthesis and Characterization of Ca_2CoTaO_6, a New Monoclinically Distorted Double Perovskite

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Received: January 17, 2011; Revised: August 2, 2011

The new Ca_2CoTaO_6 double perovskite has been synthesized by a conventional solid state reaction and its unit cell parameters determined by X-ray powder diffractometry. It crystallizes in the monoclinic space group $P2_1/n$. The unit cell parameters are: $a = 5.507(2)$ Å; $b = 5.564(3)$ Å; $c = 7.798(3)$ Å; $\beta = 89.99(4)°$ and $Z = 2$. The IR spectrum of the material was recorded and is briefly discussed. Some comparisons with Ca_2CoNbO_6 and other isostructural perovskites are also performed.

Keywords: *Ca_2CoTaO_6, double perovskite, X-ray diffraction, IR spectrum*

1. Introduction

It is well-known that mixed oxides with the perovskite structure present an important number of interesting physicochemical properties and high potential for technological applications[1-3]. Double perovskites of the type $A_2BB'O_6$ containing Nb(V), Mo(VI), W(VI) or Te(VI) associated with first-row transition metal cations have shown to posses interesting magnetic properties[4-8] and are potentially useful as materials for oxide fuel cells and other similar applications[9-15]. In this context, a new perovskite of this type, Ca_2CoNbO_6, has been recently prepared and characterized[16].

As an extension of this work we have now prepared a similar double perovskite containing Ta(V) instead of Nb(V) and performed some comparisons between the two materials.

2. Experimental

Polycrystalline samples of Ca_2CoTaO_6 and Ca_2CoNbO_6 were prepared by mixing stoichiometric amounts of $CaCO_3$, Co_3O_4 and Ta_2O_5 (or Nb_2O_5). The mixtures were heated in air, in alumina crucibles, initially at 1000 °C during 8 hours. followed by multiple heatings, during other 8 hours more at 1250 °C with intermediate grinding after each step. Finally, the samples were furnace cooled to room temperature.

The obtained mixed oxides were characterized by X-ray powder diffractometry, using a continuous step scanning procedure (step size: 0.020° (in 2θ); time per step: 0.5 seconds), with a Philips PW 1710 diffractometer and monochromatic Cu-K_α radiation ($\lambda = 1.54186$ Å), using NaCl as an external calibration standard. The indexation of the powder diagrams and calculation of unit cell parameters were carried out using a locally modified version of the program PIRUM of Werner[17].

The infrared spectra were recorded with a Nicolet-Magna 550 FTIR instrument, using the KBr pellet technique. Spectral resolution was 4 cm^{-1}. Unfortunately, attempts to record the corresponding Raman spectra, using the FRA 106 Raman accessory of a Bruker IFS 66 FTIR instrument and the 1046 nm line of a solid state Nd:YAG laser for excitation, failed due to the darkness of the samples.

3. Results and Discussion

3.1. Crystallographic data and structural aspects

The prepared Ca_2CoTaO_6 and Ca_2CoNbO_6 perovskites show identical powder diagrams indicating the formation of a pair of isostructural materials. Besides, the diagram of Ca_2CoNbO_6 was identical to that previously published[16] and also to that of the isostructural Ca_2CrTaO_6[18]. The powder diagrams of the three materials present some clearly splitted reflections as well as a number of weak superstructure reflections (cf. also[16,18]).

The powder diagram of Ca_2CoTaO_6 could be clearly indexed in the monoclinic system. The refined unit cell parameters, together with other relevant crystallographic data, are shown in Table 1 and the complete indexed powder diagram is presented in Table 2. By comparison with the Rietveld refined structures of Ca_2CoNbO_6[16] and Ca_2CrTaO_6[18], one can admit that the space group of the new perovskite is also $P2_1/n$, with the Co^{III} and Ta^{V} ions distributed randomly over Wykoff positions *2c* and *2d* whereas Ca^{II} and all the O-atoms are at general Wykoff positions *4e*. Briefly, the structure is built up by two types of octahedral MO_6 polyhedra, running along the *c*-axis of the unit cell, over which the Ta(V) and Co(III) ions are distributed in a disordered way. The Ca(II) ions are located in the holes generated by this arrangement of octahedra, coordinated by twelve O-atoms.

On the other hand, and as suggested in the case of Ca_2CoNbO_6 and other related systems[16], it is possible that the material presents a slight oxygen deficiency, derived from the presence of a low percentage of Co^{II} ions at the Co^{III} sites. This supposition is supported additionally by the presence of weak bluish spots on the crucible walls after the final heating step, due probably by generation of small amounts of the $CoAl_2O_4$ spinel.

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Table 1. Crystallographic data of Ca_2CoTaO_6.

a (Å)	b (Å)	c (Å)	β (°)	Vol. ($Å^3$)	Space group	Z	$\delta_{calc.}$ ($g.cm^{-3}$)
5.507(2)	5.564(3)	7.798(3)	89.99(4)	238.94(20)	$P2_1/n$	2	5.78

Table 2. Indexed powder pattern of Ca_2CoTaO_6.

h k l	$d_{obs.}$ (Å)	$d_{calc.}$ (Å)	I/I_o
1 0 1	4.550	4.498	5
1 1 0	3.933	3.913	85
1 1 1	3.523	3.536	5
1 1 2	2.800	2.800	100
2 0 0	2.759	2.752	45
0 0 3	2.599	2.597	5
–2 0 1	2.5646	2.5631	4
2 1 0	2.4688	2.4663	6
2 1 1	2.3741	2.3755	4
–1 0 3	2.3114	2.3142	5
0 2 2	2.2661	2.2640	6
1 1 3	2.1910	2.1923	5
–1 1 3	2.1402	2.1367	6
2 2 0	1.9605	1.9563	55
2 0 3	1.9294	1.9268	4
3 0 1	1.8006	1.8013	7
–3 0 1	1.7722	1.7701	32
–3 0 2	1.6334	1.6350	30
0 2 4	1.5965	1.5957	45
3 2 1	1.5113	1.5120	4
2 2 4	1.3993	1.4000	17
2 0 5	1.3796	1.3794	10
–1 4 1	1.3268	1.3266	10
–1 0 6	1.2530	1.2531	20

The unit cell parameters of Ca_2CoTaO_6 are very close to those of Ca_2CoNbO_6, as expected from the fact that Shannon and Prewitt's radii for both Nb(V) and Ta(V) in octahedral coordination are identical[19].

3.2. Infrared spectra

The FT-IR spectra of both, Ca_2CoTaO_6 and Ca_2CoNbO_6 samples, are also totally similar and present a very simple spectral pattern, as usually found in perovskite materials[1,20]. The spectrum of one of the prepared Ca_2CoTaO_6 samples is shown in Figure 1.

IR and Raman spectra for Sr_2LnTaO_6 materials (with Ln = trivalent lanthanides, Y(III) and In(III)), which are also isostructural to Ca_2CoTaO_6 and Ca_2CoNbO_6, have recently been investigated[21] and also theoretically analyzed[22].

In all cases, two groups of bands, together with a certain number of weak shoulders, could be clearly identified. Measured band positions for Ca_2CoTaO_6 and Ca_2CoNbO_6 are shown in Table 3.

The very strong higher energy band is assigned to the antisymmetric stretching vibration (ν_3 of an O_h-symmetry species) of the MO_6 octahedra containing the Co(III) and Ta(V) ions and is surely dominated by the Ta-O motions, which involves the stronger metal-oxygen bonds. The second strong band, at 370 cm^{-1}, can be assigned to the antisymmetric deformation (ν_4 of an O_h-symmetry species) of these same octahedra.

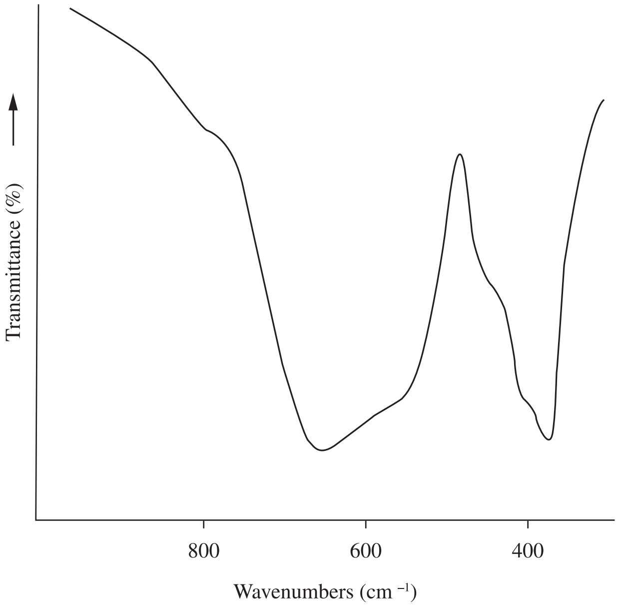

Figure 1. FTIR spectrum of one of the prepared Ca_2CoTaO_6 samples in the spectral range between 900-300 cm^{-1}.

Table 3. FTIR spectra of Ca_2CoTaO_6 and Ca_2CoNbO_6 (band positions in cm^{-1}).

Ca_2CoTaO_6	Ca_2CoNbO_6	Approximate assignment
823 sh	806 sh	
660 vs, 558 sh	652 vs, 540 sh	ν_{as} (MO_6)
463 sh, 440 sh, 371 vs	466 sh, 440 sh, 370 vs	δ_{as} (MO_6)

vs: very strong; sh: shoulder.

Only slight energy differences are observed between the band positions of Ca_2CoTaO_6 and Ca_2CoNbO_6, in agreement with their practically identical unit cell dimensions and M-O bond strengths. The determined band positions are also comparable to those measured in the Sr_2LnTaO_6 materials[21].

4. Conclusions

Ca_2CoTaO_6 constitutes a new example of a monoclinically distorted double perovskite. Its unit cell parameters are close to those of the recently reported isostructural Ca_2CoNbO_6 material. The very simple two-band infrared spectra of both compounds are also totally similar and resemble that of other perovskite materials. In order to go deeper and to provide more details about this compound, further studies should be conducted.

Acknowledgements

This work has been supported by the Universidad Nacional del Centro de la Provincia de Buenos Aires, the Universidad Nacional de La Plata and the Consejo Nacional de Investigaciones Científicas y Técnicas de la República Argentina. E.J.B. is a member of the Research Career from this organization.

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