

## Synthesis and Characterization of $\text{Ca}_2\text{CoTaO}_6$ , a New Monoclinically Distorted Double Perovskite

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The new  $\text{Ca}_2\text{CoTaO}_6$  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  $\text{P2}_1/\text{n}$ . The unit cell parameters are:  $a = 5.507(2)$  Å;  $b = 5.564(3)$  Å;  $c = 7.798(3)$  Å;  $\beta = 89.99(4)^\circ$  and  $Z = 2$ . The IR spectrum of the material was recorded and is briefly discussed. Some comparisons with  $\text{Ca}_2\text{CoNbO}_6$  and other isostructural perovskites are also performed.

**Keywords:**  $\text{Ca}_2\text{CoTaO}_6$ , 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<sup>1-3</sup>. Double perovskites of the type  $\text{A}_2\text{BB}'\text{O}_6$  containing Nb(V), Mo(VI), W(VI) or Te(VI) associated with first-row transition metal cations have shown to possess interesting magnetic properties<sup>4-8</sup> and are potentially useful as materials for oxide fuel cells and other similar applications<sup>9-15</sup>. In this context, a new perovskite of this type,  $\text{Ca}_2\text{CoNbO}_6$ , has been recently prepared and characterized<sup>16</sup>.

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  $\text{Ca}_2\text{CoTaO}_6$  and  $\text{Ca}_2\text{CoNbO}_6$  were prepared by mixing stoichiometric amounts of  $\text{CaCO}_3$ ,  $\text{Co}_3\text{O}_4$  and  $\text{Ta}_2\text{O}_5$  (or  $\text{Nb}_2\text{O}_5$ ). 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 2 $\theta$ ); time per step: 0.5 seconds), with a Philips PW 1710 diffractometer and monochromatic  $\text{Cu-K}\alpha$  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<sup>17</sup>.

The infrared spectra were recorded with a Nicolet-Magna 550 FTIR instrument, using the KBr pellet technique. Spectral resolution was 4  $\text{cm}^{-1}$ . 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  $\text{Ca}_2\text{CoTaO}_6$  and  $\text{Ca}_2\text{CoNbO}_6$  perovskites show identical powder diagrams indicating the formation of a pair of isostructural materials. Besides, the diagram of  $\text{Ca}_2\text{CoNbO}_6$  was identical to that previously published<sup>16</sup> and also to that of the isostructural  $\text{Ca}_2\text{CrTaO}_6$ <sup>[18]</sup>. The powder diagrams of the three materials present some clearly splitted reflections as well as a number of weak superstructure reflections (cf. also<sup>16,18</sup>).

The powder diagram of  $\text{Ca}_2\text{CoTaO}_6$  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  $\text{Ca}_2\text{CoNbO}_6$ <sup>[16]</sup> and  $\text{Ca}_2\text{CrTaO}_6$ <sup>[18]</sup>, one can admit that the space group of the new perovskite is also  $\text{P2}_1/\text{n}$ , with the  $\text{Co}^{\text{III}}$  and  $\text{Ta}^{\text{V}}$  ions distributed randomly over Wyckoff positions  $2c$  and  $2d$  whereas  $\text{Ca}^{\text{II}}$  and all the O-atoms are at general Wyckoff positions  $4e$ . Briefly, the structure is built up by two types of octahedral  $\text{MO}_6$  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  $\text{Ca}_2\text{CoNbO}_6$  and other related systems<sup>16</sup>, it is possible that the material presents a slight oxygen deficiency, derived from the presence of a low percentage of  $\text{Co}^{\text{II}}$  ions at the  $\text{Co}^{\text{III}}$  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  $\text{CoAl}_2\text{O}_4$  spinel.

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**Table 1.** Crystallographic data of  $\text{Ca}_2\text{CoTaO}_6$ .

a (Å)	b (Å)	c (Å)	$\beta$ (°)	Vol. (Å <sup>3</sup> )	Space group	Z	$\delta_{\text{calc.}}$ (g.cm <sup>-3</sup> )
5.507(2)	5.564(3)	7.798(3)	89.99(4)	238.94(20)	P2 <sub>1</sub> /n	2	5.78

**Table 2.** Indexed powder pattern of  $\text{Ca}_2\text{CoTaO}_6$ .

h k l	d <sub>obs.</sub> (Å)	d <sub>calc.</sub> (Å)	I/I <sub>o</sub>
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  $\text{Ca}_2\text{CoTaO}_6$  are very close to those of  $\text{Ca}_2\text{CoNbO}_6$ , as expected from the fact that Shannon and Prewitt's radii for both Nb(V) and Ta(V) in octahedral coordination are identical<sup>19</sup>.

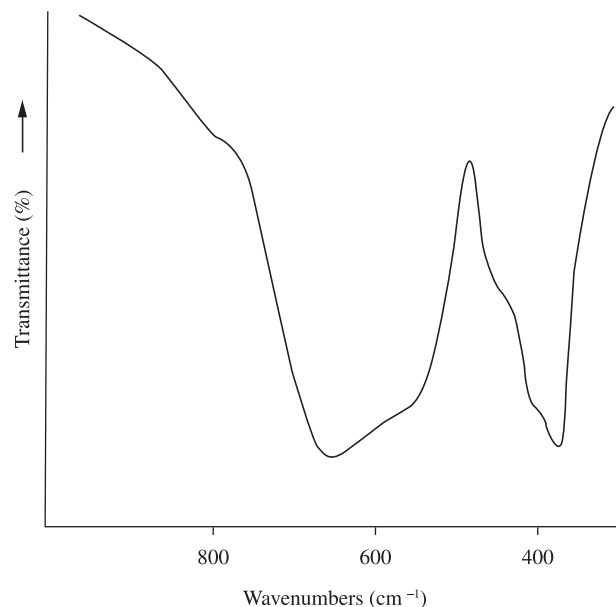
### 3.2. Infrared spectra

The FT-IR spectra of both,  $\text{Ca}_2\text{CoTaO}_6$  and  $\text{Ca}_2\text{CoNbO}_6$  samples, are also totally similar and present a very simple spectral pattern, as usually found in perovskite materials<sup>1,20</sup>. The spectrum of one of the prepared  $\text{Ca}_2\text{CoTaO}_6$  samples is shown in Figure 1.

IR and Raman spectra for  $\text{Sr}_2\text{LnTaO}_6$  materials (with Ln = trivalent lanthanides, Y(III) and In(III)), which are also isostructural to  $\text{Ca}_2\text{CoTaO}_6$  and  $\text{Ca}_2\text{CoNbO}_6$ , have recently been investigated<sup>21</sup> and also theoretically analyzed<sup>22</sup>.

In all cases, two groups of bands, together with a certain number of weak shoulders, could be clearly identified. Measured band positions for  $\text{Ca}_2\text{CoTaO}_6$  and  $\text{Ca}_2\text{CoNbO}_6$  are shown in Table 3.

The very strong higher energy band is assigned to the antisymmetric stretching vibration ( $\nu_3$  of an  $\text{O}_h$ -symmetry species) of the  $\text{MO}_6$  octahedra containing the Co(III) and Ta(V) ions and is surely dominated by the Ta-O motions, which involves the stronger

**Figure 1.** FTIR spectrum of one of the prepared  $\text{Ca}_2\text{CoTaO}_6$  samples in the spectral range between 900-300  $\text{cm}^{-1}$ .**Table 3.** FTIR spectra of  $\text{Ca}_2\text{CoTaO}_6$  and  $\text{Ca}_2\text{CoNbO}_6$  (band positions in  $\text{cm}^{-1}$ ).

$\text{Ca}_2\text{CoTaO}_6$	$\text{Ca}_2\text{CoNbO}_6$	Approximate assignment
823 sh	806 sh	
660 vs, 558 sh	652 vs, 540 sh	$\nu_{\text{as}}(\text{MO}_6)$
463 sh, 440 sh, 371 vs	466 sh, 440 sh, 370 vs	$\delta_{\text{as}}(\text{MO}_6)$

vs: very strong; sh: shoulder.

metal-oxygen bonds. The second strong band, at 370  $\text{cm}^{-1}$ , can be assigned to the antisymmetric deformation ( $\nu_4$  of an  $\text{O}_h$ -symmetry species) of these same octahedra.

Only slight energy differences are observed between the band positions of  $\text{Ca}_2\text{CoTaO}_6$  and  $\text{Ca}_2\text{CoNbO}_6$ , 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  $\text{Sr}_2\text{LnTaO}_6$  materials<sup>21</sup>.

## 4. Conclusions

$\text{Ca}_2\text{CoTaO}_6$  constitutes a new example of a monoclinically distorted double perovskite. Its unit cell parameters are close to those of the recently reported isostructural  $\text{Ca}_2\text{CoNbO}_6$  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.

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