Preparation and IR-spectroscopic characterisation of Cd$_2$InNbO$_6$ perovskite oxide

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The paper presents results concerning the synthesis of a double perovskite in the CdO-In$_2$O$_3$-Nb$_2$O$_5$ system. The lattice parameter of the mixed oxide was estimated by means of a hard sphere model in order to determine if the formation of the double perovskite is favoured in the above system. The reaction evolution was monitored by means of thermal analysis, X-ray diffraction and infrared spectroscopy. The results confirm the formation of the double perovskite and are close to those indicated by the proposed model.

1. Introduction

The literature presents many studies dealing both the synthesis and HTS applications for different double perovskites based on niobium and 3rd main group elements A$_2$MNbO$_6$ (where A is a divalent cation and M = Al, Ga) [1-4]. For the same series of compounds there are fewer papers dealing with indium containing oxides [5] but the interest has grown up [6, 7] since investigations have revealed their potential application as visible light driven photocatalysts for the hydrogen production from water [8]. In this context, the aim of the present work is to evaluate the preparation possibility of a similar compound containing cadmium as A^{2+} cation (Cd$_2$InNbO$_6$) and if feasible to lower the synthesis temperature comparing with the above products.

2. Experimental

The following high purity materials have been used as reagents for the solid-state synthesis: Nb$_2$O$_5$, In$_2$O$_3$ and CdCO$_3$. These materials were intimately mixed in the stoichiometric ratio corresponding to the nominal composition Cd$_2$InNbO$_6$, pressed into pellets and submitted to different thermal treatments in air. The synthesis was monitored by thermal analysis, XRD and IR spectroscopy. The density of the final sample was experimentally determined by the picnometric method.

A MOM-Budapest derivatograph, with the concomitant recording of T, TG, DTG and DTA curves, have been used. In all cases, the same sample weight (100 mg) and standard substance (Al$_2$O$_3$) were maintained. The analyses were performed in air up to 1000 °C/min at a heating rate of 10°C/min. The formation of final products was studied by means of powder diffraction method, using a DRON-2 diffractometer with Mo Kα radiation, and by infrared spectroscopy. The diffractometer was calibrated using standard samples of silicon dioxide. The data were processed using CELLREF software version 3 [9]. The IR spectra were recorded on a Digilab FTS 2000 instrument, using the KBr pellet technique.

3. Results and discussion

3.1. The hard sphere model

Taking into account that previous studies indicated the formation of both perovskite and pyrochlore phases in the Cd$_2$MNbO$_6$ systems (M – trivalent ion) [10], we have performed a theoretical calculation, based on the ionic radii [11] and using a hard sphere approximation [1], in order to determine the average lattice parameter for the perovskite Cd$_2$GaNbO$_6$ phase as follows:

$$a_A = 2(R_{Cd} + R_O)/\sqrt{2} \qquad (1)$$

$$a_B = R_{In} + R_{Nb} + 2R_O \qquad (2)$$

$$a_{calc} = (a_A + a_B)/2 \qquad (3)$$

where R are the ionic radii of each ion involved in the structure, a$_A$ and a$_B$ are the calculated lattice parameters based on A (i.e. 12-coordinated Cd^{2+}) and B (i.e. 6-coordinated In^{3+} and Nb^{5+}) cations, and a$_{calc}$ is the average calculated lattice parameter. Accordingly, the expected value of the pseudo-cubic lattice parameter for the double perovskite would be of 8.072Å and a corresponding calculated theoretical density of 4.02 g/cm^3.

The literature also defines a tolerance factor (4) that is correlated with the perovskite structure [12, 13]:

$$T = a_A/a_B \qquad (4)$$

Accordingly, the formation of a perovskite requires $1.03 > T > 0.71 \div 0.89$ but only the materials with T in the range $0.985 \div 1.03$ have a cubic structure. Compounds with lower values generally have a lower symmetry due to the tilting of BO$_6$ octahedra [14]. The oxide studied in the present paper has a calculated tolerance factor of 0.904 and consequently we did not expected to find a cubic structure for it.

3.2 TG analysis and thermal treatments

The thermogravimetric data for reagents and reaction intermediaries are listed in Table 1.

The thermogravimetric results obtained with the initial reaction mixture indicated the development of complex volatilisation processes for temperatures over 350 °C. Therefore, we decided to perform a presinterisation of the reaction mixture for nine hours at 300 °C. The presintered sample (1) was submitted again to the thermal analysis. The weight loss was much smaller in this case suggesting a further presinterisation at a higher temperature (7h/500°C). A new thermal analysis of the as treated sample (presintered 2) has shown the same small weight loss, normally assigned to the oxygen loss that could be eliminated by subsequent annealing in oxygen [2,4]. Consequently, the sample was ground, pressed again and submitted to a new thermal treatment for eight hours at 1000 °C. The processed sample has shown a macroscopic monophasic aspect, fact also confirmed by the XRD.

Table 1. Thermogravimetric data of the reagents and presintered samples

No.	Substance	Weight variation (%)		Temp. field (°C)	Observations
		Calc.	Found		
1.	Nb$_2$O$_5$	-	-2	840-1000	It occurs the partial reduction to NbO$_2$ [15].
2.	In$_2$O$_3$	-	-	20-900	The literature indicates a reversible reduction at about 850°C followed by a slow sublimation of the formed oxide [16]. In$_2$O$_3$ $\Leftrightarrow$ In$_2$O + O$_2$
3.	CdCO$_3$	-25.52	-25	285-390	
4.	4 CdCO$_3$ + In$_2$O$_3$ + Nb$_2$O$_5$	-14.27 - -	-14.5 -7 -23	185-340 450-555 690-837	The derivatogram showed three losses steps. The first one corresponds to the CdCO$_3$ decomposition. The other two suggest complex volatilisation processes.
5.	4 CdCO$_3$ + In$_2$O$_3$ + Nb$_2$O$_5$	-14.27	-14.5	185-310	The heating was stopped at 310°C and maintained for 60 minutes. No further weight losses have been noticed.
6.	Presintered (1)	-	-4.5	300-1000	The weight loss was of 1.5% at 500°C.
7.	Presintered (2)	-	-4	300-1000	

3.3. XRD analysis

The lines of the starting materials were not identified in the XRD spectrum and the search in the JCPDF files did not revealed the presence of any known mixed oxides that can be formed in the system CdO-In$_2$O$_3$-Nb$_2$O$_5$ [17]. The analysis evidenced as the main phase (over 95%) an orthorhombic structure with the unit cell parameters a = 5.191 Å, b = 5.356 Å and c = 7.3187 Å, space group symmetry Pnmb (Table 2). This is in excellent agreement with literature data that reported the orthorhombic space group Pnma for the similar compound Ca$_2$InNbO$_6$ [8].

As can be seen, there is an acceptable correlation between the expected and the calculated values of the unit cell parameters. On the other hand, the experimental density of the sample (4.26 g/cm^3) was also close to the calculated one.

Table 2. Miller indices for Cd$_2$InNbO$_6$ mixed oxide

No.	H	K	L	2θ observed	2θ calculated	2θ difference
1.	0	1	2	13.5980	13.5082	0.0898
2.	2	0	0	15.7210	15.7381	-0.0171
3.	1	2	0	17.1050	17.1738	-0.0688
4.	0	0	4	22.3850	22.3977	-0.0127
5.	3	1	2	27.3950	27.3785	0.0165
6.	1	4	0	31.8020	31.8133	-0.0113
7.	0	1	6	34.7720	34.7689	0.0031
8.	1	1	6	35.6640	35.6997	-0.0357
9.	3	4	0	39.2160	39.2137	0.0023
10.	2	4	4	41.7720	41.7365	0.0355

3.4. IR spectroscopy

The infrared spectrum of the material presented three well-defined bands (see Fig. 1). This is in good agreement with what is systematically found for a perovskite structure in accordance with group theory predictions [18].

In materials of this type, important vibrational couplings between the different coordination polyhedra present in structure may be expected. Taking into account that In-O and Nb-O bonds of the MO_6 octahedra are involving metal cations of charges +3 and +5, these are stronger than those belonging to the 12-coordinated Cd(II)-O units [3]. Therefore, on the basis of this argument, one expects to find the MO_6 octahedra dominating the spectroscopic behaviour.

The asymmetric stretching and bending modes of the MO_6 octahedra, usually dominate the IR spectra of perovskite materials [19]. Therefore, in the present case, the strong band from 436 cm^{-1} is involving the asymmetric bending mode of the MO_6 octahedra whilst the other strong broad band from 542 cm^{-1} can be assigned to the asymmetric stretching mode of the MO_6 octahedra. The two well-defined IR bands in the 400-650 cm^{-1} region, has also been found in a great number of $A_2BB'O_6$ perovskite-type materials and they were assigned in the same way [20, 21]. The shoulder observed at 702 cm^{-1} also suggests the overlapping of InO_6 and NbO_6 stretching bands with the displacement toward higher frequencies of the NbO_6 bands (Nb^{+5} is lighter and smaller than In^{+3}) [3].

Fig. 1. IR spectrum of the final sample

Finally, the broad band from 926 cm^{-1} can be assigned to the originally IR inactive symmetric stretching mode (A_{1g}) of the NbO_6 octahedra, activated by symmetry lowering. This assignment is also supported by the fact that in the Raman spectra of different ordered $A_2BB'O_6$ perovskites [21,22] or perovskite-type materials [19], a strong line related to this mode, has been usually observed in the same frequency range.

Several perovskite-type oxides and specially the niobium containing compounds may present corner-shared and edge-shared octahedra [19,23,24]. In the case of and edge-shared NbO_6 octahedra the symmetric stretching vibrations are usually observed in the 850-1000 cm^{-1} region, whereas in corner connected octahedra these vibrations are observed in the 750-850 cm^{-1} region [25,26]. In the present study, the symmetric stretching vibrations from 926 cm^{-1}, strongly support the possible existence of edge-connected NbO_6 octahedra but this fact must also be proved by cation distribution studies.

Table 3. Lattice misfit between different HTS and Cd$_2$InNbO$_6$

Compound	Lattice parameters (Å)/normalised values			Mismatch (%)		
	a	b	c	ε_a	ε_b	ε_c
YBCO	3.827	3.877	11.708 / 3.903	4.07	2.32	6.25
TBCCO (1245)	3.850	3.850	22.300 / 3.717	4.65	1.64	1.56
BSCCO (2212)	5.393	5.393	30.523 / 3.815	3.75	0.69	4.09
BSCCO (2223)	5.391	5.391	37.102 / 3.710	3.71	0.65	1.37
Cd$_2$InNbO$_6$	5.191 / 3.671	5.356 / 3.787	7.3187 / 3.659	-	-	-

3.5. Lattice matching with HTS

Matthews and Klokholm have defined the epitaxial misfit in a 'pseudomorphic' film in perfect registration at the interface with its substrate at room temperature as:

$$\varepsilon_a = (a_{film} - a_{substr})/\, a_{film} \qquad (5)$$

where a_{film} and a_{substr} are the lattice parameters of the film and the substrate [27]. According to relation (5), Table 2 compares lattice parameters of some usual high temperature superconductors [28] with those of Cd$_2$InNbO$_6$.

All c parameters were normalised for the simple primitive unit cells. On the other hand, although the substrate and YBCO, respectively TBCCO (1245), lattices are distorted differently from the simple pseudocubic cell, a direct comparison of their ab planes can be made dividing the a and b values of Cd$_2$InNbO$_6$ by $\sqrt{2}$, because the superconductor unit cell contains only half as many atoms in the plane. This normalisation gives a test for the condition in which the same number of atoms per unit area exists for both sides of the superconductor-substrate interface. Despite the fact that the normalisation is an approximation, since the space groups are not the same, other authors also used it in order to compare how different perovskite-type space groups compounds meet the unit cells at the film-substrate interface [1].

The data presented in Table 2 indicate that the misfit between Cd$_2$InNbO$_6$ and the analysed superconductors have very low values (similar or even better than other acknowledged HTS substrates), suggesting the possible use of the material with this purpose.

4. Conclusions

The attempts to synthesize mixed oxides in the system CdO-In$_2$O$_3$-Nb$_2$O$_5$, lead to the formation of the double perovskite Cd$_2$InNbO$_6$. The compound was obtained in milder conditions than corresponding oxides from the same series [2,3]. The results of XRD and IR analyses were in good agreement with the theoretical data indicating an orthorhombic double perovskite structure.

The material presents a good lattice matching with some well-known superconductors but further studies must to be performed in order to determine the cation distribution and the electric properties requested by a HTS substrate application.

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