PREPARATION OF Cd_2GaNbO_6 PEROVSKITE OXIDE: A POSSIBLE SUBSTRATE FOR HIGH T_C SUPERCONDUCTORS

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The paper presents results concerning the synthesis of a double perovskite in the CdO-Ga_2O_3-Nb_2O_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 studies concerning both the synthesis and HTS applications for different gallium based mixed oxides [1-3]. Among these, the gallium-niobium double perovskites (A_2GaNbO_6 - with Ca and/or Sr as A cations) appeared to be promising materials from the viewpoint of producing single crystals as possible substrates for HTS. In this context, the aim of the present work is to evaluate the possibility to prepare of a similar compound containing cadmium as A^{2+} cation and to try to to lower the synthesis temperature, when compar with the above products.

2. Experimental

The following high purity materials have been used as reagents for the solid-state synthesis: Nb_2O_5, Ga_2O_3 and $CdCO_3$. These materials were intimately mixed in the stoichiometric ratio corresponding to the nominal composition Cd_2GaNbO_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_2O_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 Co $K\alpha$ radiation, and by infrared spectroscopy. The diffractometer was calibrated using standard samples of silicon dioxide. The data were processed using DICVOL and CELLREF software [4,5]. The IR spectra were recorded on a Digilab FTS 2000 instrument, using the KBr pellet technique.

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3. Results and discussion

3.1. The hard sphere model

Based on the ionic radii [6] and using a hard sphere approximation [2], we have calculated the theoretical average lattice parameter for the Cd_2GaNbO_6 material as follows:

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

$$a_B = R_{Ga} + R_{Nb} + 2R_O \tag{2}$$

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

where R are the ionic radius of each ion involved in the structure, a_A and a_B are the calculated lattice parameters based on A (i.e. Cd^{2+}) and B (i.e. Ga^{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 7.273Å and a corresponding calculated theoretical density of 5.03 g/cm^3.

The literature also defines a tolerance factor (4) that is correlated with the perovskite structure [7,8]:

$$T = a_A/a_B \tag{4}$$

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 [9]. The oxide studied in the present paper has a calculated tolerance factor of 0.841 and consequently we did not expected to find a cubic structure for it.

3.2. The TG analysis and XRD

The thermogravimetric data are listed in Table 1. The DTA curve for the reaction mixture indicated that 50% of the reaction enthalpy corresponding to the carbonate decomposition is missing. The cause might be either the difference between the thermal conductivities of the reagents from the mixture, either the presence of a chemical reaction accompanied by an exothermic effect.

Table 1. Thermogravimetric data of the reagents.

No.	Substance	Weight variation (%)		Temp. field (°C)	Observations
		Calc.	Found		
1.	Nb_2O_5	-	-2	840-1000	It occurs the partial reduction to NbO_2 [10].
2.	Ga_2O_3	-	-	20-920	
3.	$CdCO_3$	+25.52	+25	285-390	The peak of the corresponding endothermic effect due is at 368 °C.
4.	$4\,CdCO_3 + Ga_2O_3 + Nb_2O_5$	+15.4	+15	300-375	The endothermic effect corresponding to the $CdCO_3$ decomposition, evaluated from the DTA, is only 50% from the value expected from stoichiometry.

According to the thermogravimetric results we decided to perform a presinterisation of the reaction mixture for eight hours at 800 °C. The temperature was chosen in order to avoid both the

possible niobium reduction and the cadmium volatilisation. On the other hand, the difference between the expected and the found thermal effect, from the DTA curve recorded for the reaction mixture, indicated a possible formation of a mixed oxide.

The as presintered sample had a multiphase aspect and consequently, it was ground, pressed again and submitted to a new thermal treatment for six hours at 1100°C. The processed sample has shown a macroscopic monophasic aspect, fact also confirmed by the XRD (see Fig. 1). The weight loss during the heating indicated a final formula $Cd_2GaNbO_{5.5}$ for the synthesised oxide. However, a subsequent annealing in oxygen at about 750°C eliminates the oxygen vacancies [3].

The XRD evidenced as the main phase (over 90%) an orthorhombic structure with the unit cell parameters a = 5.154 Å, b = 5.598 Å and c = 7.317 Å. The lines of the starting materials were not identified in the spectrum [11]. The search in the JCPDF files did not revealed the presence of any known mixed oxides that can be formed in the system CdO-Ga_2O_3-Nb_2O_5.
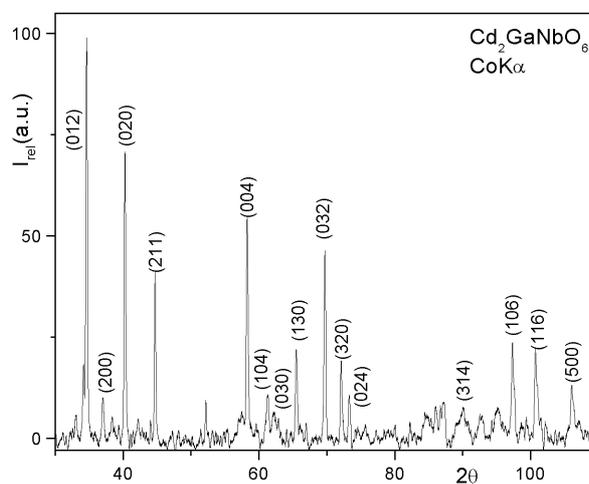

Fig. 1. XRD spectrum of the final sample.

As can be seen, there is a quite good correlation between the expected and the calculated values of the unit cell parameters. On the other hand, the experimental density of the sample (4.96 g/cm^3) was very close to the calculated one.

3.3. The IR spectroscopy

The infrared spectrum of the material presented three well-defined bands (see Fig. 2). This is in good agreement with what is systematically found for a perovskite structure in accordance with group theory predictions [12].

In materials of this type, important vibrational couplings between the different coordination polyhedra present in structure may be expected. The asymmetric stretching and bending modes of the MO_6 octahedra, usually dominate the IR spectra of perovskite materials [13]. Therefore, in the present case, the strong band from 426 cm^{-1} is involving the asymmetric bending mode of the NbO_6 octahedra whilst the other strong broad band from 576 cm^{-1} can be assigned to the asymmetric stretching mode of the NbO_6 octahedra. The same spectral pattern, with two strong and 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 [14-17]. Finally, the weak band from 904 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 [15-17] or perovskite-type materials [13], 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 [13, 18-20]. 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 [21, 22]. In the present study, the symmetric stretching vibrations from 904 cm^{-1} support the possible existence of edge-connected NbO_6 octahedra but this fact must also be proved by cation distribution studies.
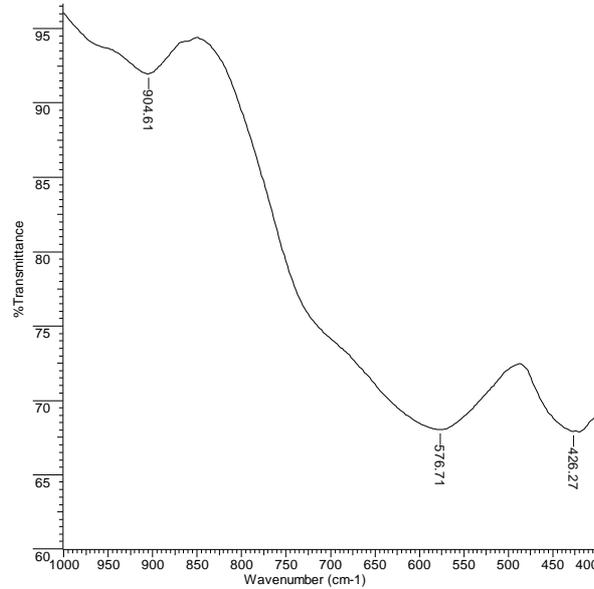

Fig. 2. IR spectrum of the final sample.

3.4. 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:

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

where a_{film} and a_{substr} are the lattice parameters of the film and the substrate [23]. According to relation (5), Table 2 compares lattice parameters of some usual high temperature superconductors [24] with those of Cd_2GaNbO_6.

Table 2. Lattice misfit between different HTS and Cd_2GaNbO_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	4.78	-2.09	6.25
TBCCO (1245)	3.850	3.850	22.300 / 3.717	5.35	-2.80	1.56
BSCCO (2212)	5.393	5.393	30.523 / 3.815	4.43	-3.80	4.09
BSCCO (2223)	5.391	5.391	37.102 / 3.710	4.41	-3.69	1.37
Cd_2GaNbO_6	5.154 / 3.644	5.598 / 3.958	7.317 / 3.659	-	-	-

The 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$_2$GaNbO$_6$ 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$_2$GaNbO$_6$ and the analysed superconductors have reasonable low values (similar or better than other acknowledged HTS substrates), suggesting the possible use of the material to this purpose.

4. Conclusions

The attempts to synthesize mixed oxides in the system CdO-Ga$_2$O$_3$-Nb$_2$O$_5$, lead to the formation of the double perovskite Cd$_2$GaNbO$_6$. 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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