Impact of Cations Nature of Double Perovskite Ca_2BWO_6 on Structure and Magnetic Properties

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The aim of this work is to study the perovskite-type oxide Ca_2BWO_6 materials, where B = Cr, La and Sm, obtained by the sol–gel citrate-combustion method. The nature of the B-site cations influences the structure and properties of these compound. The synthesis progress was evaluated using X-ray diffraction and the structure of the samples was characterized by the Fourier transform infrared spectroscopy. In our case, the tolerance factor decrease with increasing of the ionic radius B leads to the structural distortion different from the cubic one. The magnetic properties were evaluated by a SQUID magnetometer and they are discussed in relationship with their compositions. From experimental data, it was noticed that all compound are ferromagnetic.

Keywords: double-perovskite, sol–gel citrate, FT-IR spectroscopy, X-ray diffraction, magnetic properties

The general formula for oxides type perovskite is ABO_3, where A represents an electropositive cation and B represents a transition metal ion [1]. They have some flexibility in the chemical composition and the crystal structure; the control of their crystal structure and properties are possible with the combination of many cations. The modification of structural and magnetic properties by changing the A, B' and/or B" site cations has gained interest in recent years in order to better understand the mechanism of colossal magnetoresistance [2].

In general, the size of A ion influences the crystal symmetry significantly while that of the B ion does not change the symmetry, but changes the lattice volume proportionally [3, 4]. Depending on the valences and relative ionic radii of all the ions involved, the B' and B'' ions are either random or in an ordered arrangement. The crystal system of double perovskite is cubic, orthorhombic, or monoclinic, because the B (B') - cation arrangement is limited to be a random type. Since the B cation generally determines the physical properties of perovskites, different kinds of B' and B'' ions should show a variety of the electronic and magnetic properties of these double perovskites [5, 6]**.**

In order to improve the properties of double perovskites and to obtain the appropriate products for different applications, various synthesis techniques such as sol–gel [7] have been developed. The sol–gel and its variants, including sol–gel autocombustion, has been shown to have great potential in the preparation of metal oxides with the perovskite structure for advanced applications [8].

The objective of this investigation was to prepare by citrate combustion method a series of double perovskite oxides Ca_2BWO_6 (B = Cr, La and Sm) for the first time. Also, we presented the variation of the structural characteristics and magnetic properties with the size of this three trivalent in the B-site cations.

Experimental part

Synthesis

We have prepared our samples of Ca_2BWO_6 using the sol–gel autocombustion method. The starting materials were $Ca(NO_3)_2 \cdot 4H_2O$, $Cr(NO_3)_3 \cdot 9H_2O$, $La(NO_3)_3$, $Sm(NO_3)_3 \cdot 6H_2O$, $(NH_4)_6W_7O_{24} \cdot 4H_2O$ and citric acid as the combustion agent. The metallic precursors and citric acid were dissolved in distilled water and the mixtures were gradually heated up to 80°C under continuous stirring in a water bath in order to obtain a viscous gel. The resulting mixtures were stirred for the 4 h at 80°C for concentrating solutions by slow evaporation The gels was then dried in the air up to 220°C, until that occurs autocombustion.

The powders obtained from autocombustion were then heated in air at 350°C/7h and 500°C/7h. After that, the compounds were slowly cooled, then ground, shaped by uniaxial pressing at 150 kPa into pellets. Presintering was done in air at 750°C/ 7h and 900°C/7h. The samples were slowly cooled, ground, pressed with radial gradient into pellets of 10 mm diameter and 2 mm thickness. The samples were sintered in the air, with a heating rate of 5°C/min at 1100°C/24 h and 1200°C/24 h.

After repeating this procedure with grinding, pelletizing and firing, only single-phase perovskite was obtained. The phase formation of the double perovskite Ca_2BWO_6 and analysis of crystalline structure was monitored by using a Fourier transform infrared (FTIR) spectra and X-ray diffraction technique.

Characterization

X-ray diffraction (XRD) patterns of the sample were recorded with a SHIMADZU LabX6000 diffractometer equipped with a graphite monochromator and CuKα radiation ($\lambda = 1.5406$ A) with a scan step of 0.02° and a counting time of 1 s/step, for $2\theta \in (20\text{-}80)°$.

FT-IR spectra were obtained with wave number range 4000-400 cm^{-1} using a JASCO 660 PLUS spectrophotometer on the KBr pellets.

The magnetic properties were studied using a Quantum Design MPMS-XL superconducting quantum interference device (SQUID) magnetometer. The sample was packed into teflon tape packet and field and zero field cooled magnetizations were measured on a Quantum Design SQUID magnetometer.

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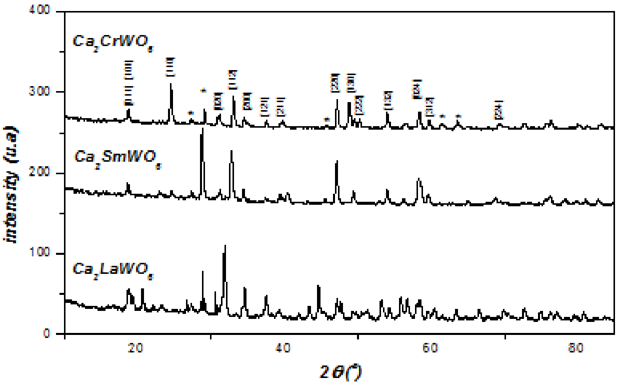

Fig. 1. X-ray diffraction patterns of Ca$_2$BWO$_6$

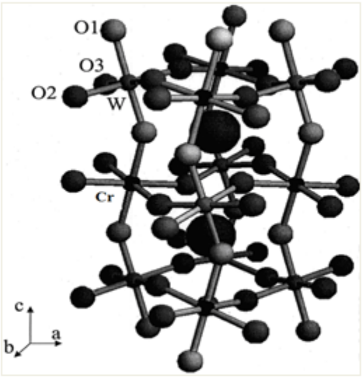

Fig. 2. The crystal structure of Ca$_2$BWO$_6$ (B = Cr)

Table 1
UNIT CELL PARAMETERS CALCULATED FROM SPUDS FOR Ca$_2$BWO$_6$ SINTERED AT 1200°C

Compound	rB^{2+} (Å)	*t* space group	Cell parameter (Å)	*V* (Å^3)	*β* (°)
Ca$_2$CrWO$_6$	0.52	0.9445 P*bnm*	a = 5.3826 Å, b = 5.5076 Å, c = 7.6971 Å	229.906	90.0016
Ca$_2$SmWO$_6$	0.964	0.8646 P21/n	a = 5.5121 Å, b = 5.8996 Å, c = 8.0381 Å,	262.964	89.8709
Ca$_2$LaWO$_6$	1.061	0.8480 P21/n	a = 5.5247 Å, b = 5.9856 Å, c = 8.0949Å	269.204	90.1970

Results and discussions

Figure 1 shows X-ray powder diffraction for Ca$_2$BWO$_6$ (B = Cr, La and Sm) obtained by the sol-gel citrate-combustion at 1200°C.

The strongest reflection peak at 2θ of around 30°, assigned to the (112), (110) and (220) the XRD diffraction planes, was identified in the pattern of each sample, confirming the formation of the double perovskites phase [9]. The observed peaks can be fitted to an orthorhombic unit cell with P*bnm* space group in the case of Ca$_2$BWO$_6$ (B = Cr). and a monoclinic structure with the space group P2$_1$/n for Ca$_2$BWO$_6$ (B = Sm and La.) The crystal structure of Ca$_2$BWO$_6$ (B = Cr) are illustrated in figure 2.

Starting from orthorhombic space group P*bnm* and monoclinic space group P2$_1$/n we have calculated with SPuDS program some unit cell parameters tolerance factor (*t*), latice parameters, cell volume (*V*), cell angle (β) (table 1).

We observed that with increasing of the B site cationic effective ionic radii in series ($r_{Cr}^{3+} < r_{Sm}^{3+} < r_{La}^{3+}$) takes place a monotonic increase of lattice parameters and thus a decrease of the tolerance factor wich determines the transition from the orthorhombic structure. The distortion of ideal cubic structure of the double perovskite it depends on tilt angle and the tolerance factor. The compound presents a structure with a lower symmetry when the tolerance factor value is smaller than the unity.

In our case (fig. 3) the tolerance factor decreases with the size of cation B: with increasing of the ionic radius in the serie ($r_{Cr}^{3+} < r_{Sm}^{3+} < r_{La}^{3+}$).

The FTIR spectra of the perovskite structure have three strong adsorption bands characteristic between 850 - 400 cm^{-1}, which are usually used to identify the perovskite phase formation [11].

The IR spectra of the compounds Ca$_2$BWO$_6$ (fig. 4) present the characteristic band of the perovskite structure, two at high-wavenumber range (around 800 cm^{-1} and 600 cm^{-1}) and one at a lower range of wavenumber (around

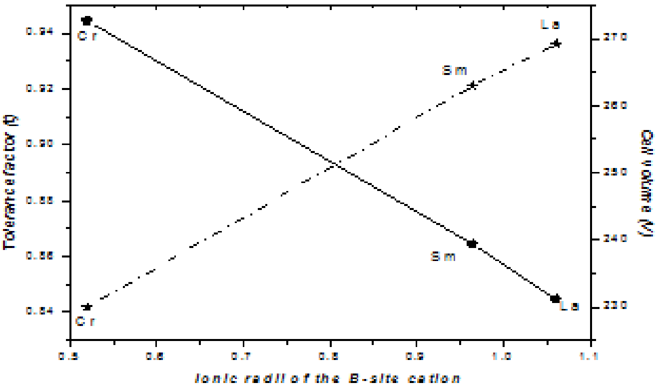

Fig. 3. The variation of the tolerance factor (*t*) and cell volume (*V*) according to the ionic radii of the B site cation (r_B^{3+})

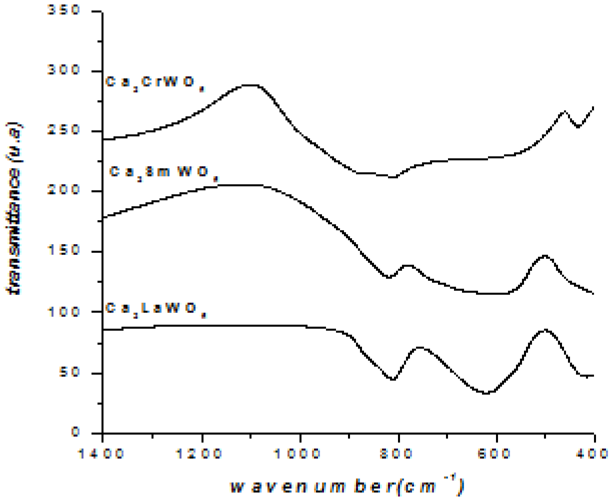

Fig. 4. FT-IR spectra recorded for the Ca$_2$BWO$_6$ powders sintered at 1200°C

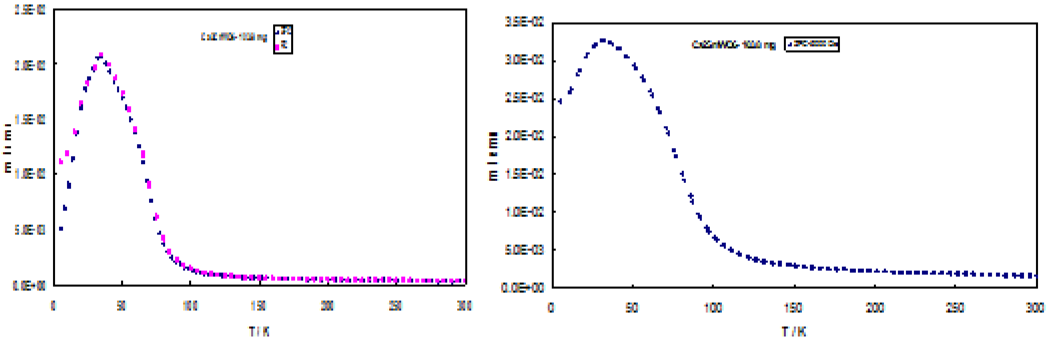

Fig. 5. Variation of the specific magnetization with temperature foe a) Ca_2CrWO_6 and b) Ca_2SmWO_6

430 cm^{-1}). The strong high energy band centered at about 660 cm^{-1} can surely by assigned to the antisymmetric stretching mode of WO_6 octahedra due to higher charge of this cation, a band at 840 cm^{-1} which can eventually be assigned to the symmetric stretching vibration of these octahedra and the strong IR-band at around 450cm^{-1} wich can be assigned to the $W(B)O_6$ deformation.

For all the compounds Ca_2BWO_6 (with B = Cr, Sm and La) by decreasing *t* (tolerance factor) with increasing the size of cation B a low displacement of bands into at high wavenumber range was observed.

In figure 5 are presented the plots of magnetization against temperature for Ca_2BWO_6 (B = Cr and Sm). It is observed that for all compounds the magnetization decrease with increasing temperature and all compounds are ferromagnetics.

The origin of magnetism in the double perovskite still is discussed controversially. Historically, the ferromagnetism in the system Sr_2FeMoO_6 has been explained in terms of an antiferromagnetic superexchange interaction between the Mo^{5+} ($5d^1$) spin and the Fe^{3+} ($3d^5$) spins [12].

The Curie temperature for our compound Ca_2CrWO_6, Tc = 150 K is very similar to that reported in the literature for the compound [13]. In our case due to the monoclinic distortion in Ca_2BWO_6, the B-O-B2 bonding angle deviates significantly from 180°. This results in a reduction of the hopping integral, in a weaker delocalization of the W 5d electron and, in a weakening of the magnetic exchange. As a direct consequence, Curie temperature and the magnetic moment induced at the W are reduced in Ca_2BWO_6.

Conclusions

We have performed the synthesis of Ca_2BWO_6 (B = Cr, Sm and La) double perovskites by the sol–gel autocombustion method with citric acid as the combustion agent. The synthesis method selected proved to be quite good, although in order to achieve the formation of perovskite phase without impurities is required fairly high temperature sintering.

We made a detailed analysis of the influence of cation nature of the position B on the structural and magnetic characterization of the double perovskite. FT-IR spectra and XRD patterns confirmed the double-perovskites phase formation for all obtained materials. Cell parameters and tolerance factor are influenced by the size of the B-site cation as resulted from the SPuDS software. On the other hand, the perovskite with the cation B = Cr proved to be the best position for cavity type B.

All compounds are ferromagnetics and magnetic properties are indirectly influenced by the distortion degree of the lattice and degree of ordering cations B/W.

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