JOURNAL OF SOLID STATE CHEMISTRY **80**, 40–44 (1989)

Infrared Absorption Investigations of the ALa_3MgCoO_8 (A = Ca, Sr, Ba) Oxides

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Received October 27, 1988; in revised form January 30, 1989

An infrared absorption investigation of the ALa_3MgCoO_8 samples (A = Ca, Sr, Ba) with K_2NiF_4-type structure has allowed the authors to evaluate the local distortion of the (CoO_6) octahedron. In this set of materials of composition similar to that of the perovskite layers the local distortion can be explained by chemical bonding competition along the c-axis.

Introduction

The ALa_3MgCoO_8 (A = Ca, Sr, Ba) samples have been prepared using high oxygen pressures. The oxygen stoichiometry was determined indirectly by iodometric titration for cobalt ions, which was confirmed to be trivalent for all of the samples. It is assumed that the stoichiometry of cations is not changed during the sample preparation at high temperature (*1*, *2*).

Powder X-ray diffraction patterns indicate that the structures have the K_2NiF_4-type unit cell (a_0, c_0). The presence of some weak superlattice lines show the existence of an enlarged unit cell ($a = a_0\sqrt{2}$, $c = c_0$) (Table I) resulting from a long-range Mg–Co ordering within the perovskite-type layers.

In the K_2NiF_4 lattice the c_0/a_0 ratio is in first approximation dependent on two factors: (i) the size effect of the nine-coordinated cations along the c-axis (A, La), and (ii) the structural distortion of the MO_6 octahedra in the perovskite layers.

If we compare the $SrLa_3MgCoO_8$ and La_4LiCoO_8 oxides where Sr^{2+} and La^{3+} have close sizes (d_{Sr-O} = 2.688 Å and d_{La-O} = 2.584 Å with Sr^{2+} and La^{3+} in coordination 9) (*3*), the increase of the c_0/a_0 ratio (3.27 to 3.33) (Table I) could be attributed to an enhancement of the structural elongation of the CoO_6 octahedra. Such a phenomenon should result from the decrease of the covalency of the competing M–O bond from Mg–O to Li–O (Fig. 1) (*4*). In the ALa_3MgCoO_8 series (A = Ca, Sr, Ba) the competing Mg–O bond is always present, so that the c_0/a_0 ratio depends on the steric or size effect (d_{Ca-O} = 2.547 Å, d_{Sr-O} = 2.668 Å, d_{Ba-O} = 2.818 Å, Ca^{2+}, Sr^{2+}, Ba^{2+} being all in coordination 9) (*3*).

Competition between the A–O and Co–O bonds along the c-axis could lead to a varia-

0022-4596/89 $3.00

TABLE I

CRYSTALLOGRAPHIC PARAMETERS FOR SOME Co(III) OXIDES WITH THE K_2NiF_4-TYPE STRUCTURE

	a_0 (Å)	c_0 (Å)	$a = a_0\sqrt{2}$ (Å)	c_0/a_0
$CaLa_3MgCoO_8$	3.825	12.37	5.409	3.23
$SrLa_3MgCoO_8$	3.837	12.54	5.426	3.27
$BaLa_3MgCoO_8$	3.871	12.75	5.474	3.29
$SrLaCoO_4$	3.80	12.51		3.33
La_4LiCoO_8	3.783	12.61	5.350	3.33

tion of the (CoO_6) elongation (Fig. 1) (*4*). For the same ALa_3MgCoO_8 set (A = Ca, Sr, Ba) the elongation of the (CoO_6) octahedron depends actually on two factors: steric effect and chemical bonding along the c-axis. The aim of the present IR absorption study is to evaluate such a local distortion.

Infrared Absorption Investigation

The IR spectra for the polycrystalline samples ALa_3MgCoO_8 (A = Ca, Sr, Ba) in CsBr pellets were obtained at 25°C as given in Fig. 2.

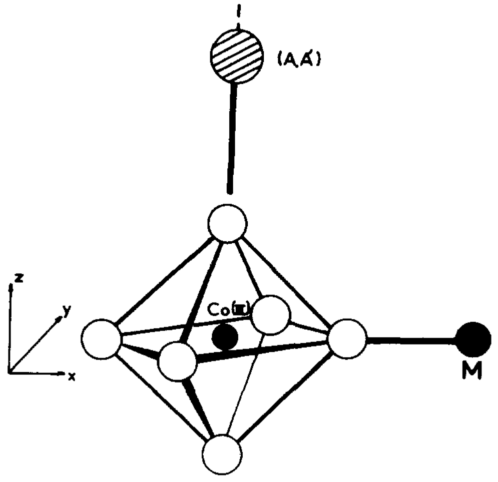

FIG. 1. Chemical bonding competition in the xOy plane and along the Oz axis in the K_2NiF_4-type structure.

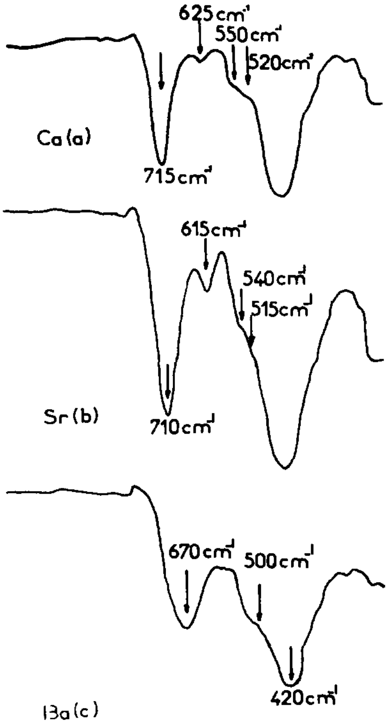

FIG. 2. IR spectra for the series ALa_3MgCoO_8 [A = Ca (a), Sr (b), Ba (c)].

In ordered perovskites of the type $A_2BB'O_6$, the shift of oxygen ions toward the more highly charged B cation was observed (*5–9*). Blasse *et al.* reported that such a highly charged BO_6 octahedron acts as an independent group (*10, 11*). Similarly, with perfectly symmetrical surroundings in the xy-plane (Fig. 1), the oxygen ions are expected to be shifted toward the Co^{3+} ion because of its high charge. Although an exact IR analysis for ALa_3MgCoO_8 (A = Ca, Sr, Ba) oxides should be carried out in terms of the full crystal group (*12*), we assume that the binding forces in the CoO_6 octahedron are large compared to the MgO_6 octahedron, and the CoO_6 octahedron is decoupled from the remainder of the lattice. In this case the internal (CoO_6) and external modes should be sufficiently separated.

Group theoretical considerations for the elongated and the undistorted (MO_6) octahedron, with respectively D_{4h} and O_h symmetry, lead to 15 normal vibration modes in the D_{4h} symmetry,

$$\Gamma D_{4h} = 2A_{1g} + B_{1g} + B_{2g} + E_g + 2A_{2u} + B_{2u} + 3E_u,$$

and also 15 in O_h symmetry,

$$\Gamma O_h = A_{1g} + E_g + 2T_{1u} + T_{2g} + T_{2u}.$$

From these representations we can deduce the list of normal modes grouped according to the IR and Raman activities of the fundamental vibrations (Table II). Therefore, we may expect either five bands or two bands in the IR absorption spectra of the (CoO_6) octahedra for the respective D_{4h} and O_h symmetry. Lowering of the local symmetry will increase the number of infrared active modes, and IR spectroscopy can evaluate thus the evolution of the local (MO_6) distortion.

In the IR spectra of the ALa_3MgCoO_8 phases (A = Ca, Sr, Ba), the band located in the region 670–715 cm^{-1} is at too high a frequency to represent a contribution from the Co–O bonds (internal modes). It can be attributed to the A–O bonds along the c-axis. As expected there are relatively large shifts of this band toward lower wavenumbers as the A cation (Ca, Sr, Ba) gets heavier. This indicates a decreasing bond strength of A–O from Ca to Ba, which induces a strengthening of the competing axial Co–O bond.

The Co–O asymmetric vibration band splits into a doublet with $\bar{\nu}$ = 620 and 540 cm^{-1} in $CaLa_3MgCoO_8$ and $SrLa_3MgCoO_8$. Such a splitting suggests a D_{4h} symmetry of each isolated (CoO_6) octahedron. In comparison for $BaLa_3MgCoO_8$, it is limited to a single strong shoulder ($\bar{\nu}$ = 500 cm^{-1}). One may deduce that the (CoO_6) octahedron is much closer to a pure O_h symmetry as the A cation becomes more basic from Ca to Ba. It had been confirmed that the shoulders below 400 cm^{-1} are attributed to the other external modes (*10*), which can be assigned if normal mode analyses of full crystal groups are performed. But those modes are believed not to alter our conclusion significantly.

TABLE II

INFRARED AND RAMAN ACTIVITIES OF THE FUNDAMENTAL VIBRATIONS

Symmetry	Infrared active	Raman active	Inactive
D_{4h}	$2A_{2u}$, $3E_u$	$2A_{1g}$, B_{1g}, B_{2g}, E_g	B_{2u}
O_h	$2T_{1u}$	A_{1g}, E_g, T_{2g}	T_{2u}

Even though the c_0/a_0 ratio, which is determined by X-ray diffraction analysis, is increased by substitution of Ba (3.29) for Ca (3.23), which implies the strong tendency of tetragonal elongation in CoO_6 octahedron, such a tendency seems to be strongly compensated by the contraction in the axial Co–O bond due to the gradual increase of basicity from Ca to Ba (increase in covalent bonding character of Co–O bond). In fact, the IR investigation points out a decrease of the local (CoO_6) elongation when the A cation becomes larger. Such a phenomenon results from competition along the c-axis between weakening A–O and strengthening Co–O bonds. The X-ray diffraction study indicates, however, that the steric effect of the alkali earth cation is the prevailing factor for the c_0/a_0 variation and *low-spin Co(III) → high-spin Co(III) transition.*

The transition from a low-spin ($^1A_{1g}$) to a high-spin ($^5T_{2g}$) ground state of Co(III) had been studied in perovskite oxides such as $TCoO_3$ (*13*) (T = rare earth) or K_2NiF_4-type oxides such as $SrLaCoO_4$ (*14*) and La_4LiCoO_8 (*15*).

For O_h symmetry the energy of the cubic field term vs q/B can be given in a Tanabe–Sugano diagram (*16*).

For a strong D_{4h} elongation a splitting of the high-energy $^3T_{2g}$ term can be achieved (Fig. 3). The $^3B_{2g}$ term has an energy close

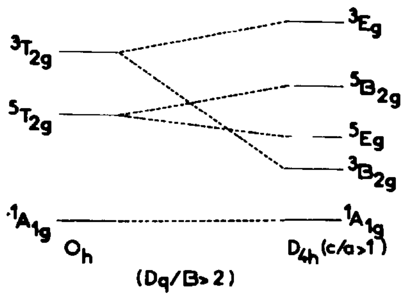

FIG. 3. Evolution of the relative stabilities of the spectroscopic terms vs structural elongation for a d^6 configuration in octahedral surroundings.

to that of the $^1A_{1g}$ term. If the local elongation of the (CoO_6) octahedron is small such an intermediate electronic configuration should have a higher energy (*15*).

The magnetic susceptibility measured with a Faraday balance between 4.2 and 800 K is given for each ALa_3MgCoO_8 phase (Fig. 4). The maximum of χ_M^{-1} observed at about 475 K(Ca), 400 K(Sr) and 380 K(Ba) is the result of an electronic transition of Co(III) from the diamagnetic $^1A_{1g}$ ground term to the paramagnetic $^3B_{2g}$ ($^3T_{2g}$) and/or ^5E_g ($^5T_{2g}$) terms.

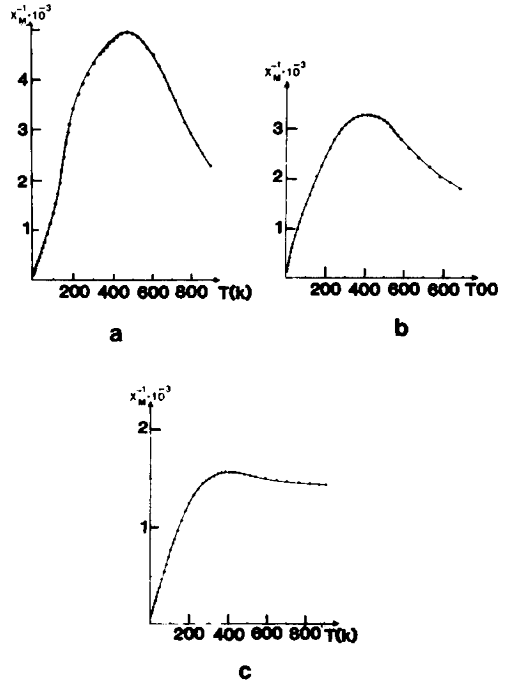

FIG. 4. Reciprocal molar susceptibility vs temperature for the series ALa_3MgCoO_8 [A = Ca (a), Sr (b), Ba (c)].

From the magnetic data a recent spin-transition study of the $SrLa_3MgCoO_8$ phase based on the model proposed by Schlichter and Drickamer (*17*) confirmed the existence of the $^1A_{1g} \rightarrow {}^5T_{2g}$ transition (*1*).

Because of the size difference between the low-spin and high-spin Co(III) species ($r_{Co(III)LS} = 0.50$ Å (*13*) and $r_{Co(III)HS} = 0.63$ Å (*18*)), the $^1A_{1g} \rightarrow {}^5T_{2g}$ transition depends on (i) the steric effect and (ii) the value of the local crystal field for cobalt. Due to increasing basicity from Ca to Ba, this local crystal field should decrease slightly.

The evolution of the spin-transition temperature from $CaLa_3MgCoO_8$ (475 K) to $BaLa_3MgCoO_8$ (380 K) implies that the lattice dilation associated with the A cation expansion is predominant on the expected Co–O bond effect in initiating the LS → HS transition.

On the contrary the smaller elongation of the (CoO_6) octahedron has the opposite influence, as it should make the Jahn–Teller effect which is associated with the LS → HS transition more difficult. We may conclude that the A size effect is largely prevailing on the influence of the higher symmetry observed for the (CoO_6) octahedron as the A cation is enlarged.

Conclusion

An infrared spectroscopic study of the ALa_3MgCoO_8 oxides (A = Ca, Sr, Ba) with the K_2NiF_4-type structure has led to an evaluation of the local influence of the size of the A cation. This evaluation and the strengthening of the Co–O bond along the c-axis are discussed as factors accounting for the variation of the c_0/a_0 ratio and for the temperature of the LS → HS transition.

The first one is in both cases the leading factor.

Acknowledgment

The authors thank Professor Paul Hagenmuller for valuable participation in the discussions.

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