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Spectroscopic study of spinel $ZnCr_2O_4$ obtained from mechanically activated $ZnO–Cr_2O_3$ mixtures

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Abstract

A mixture of starting ZnO and Cr_2O_3 powders in equimolar quantities was mechanically activated by grinding using a high energy vibro-mill for 0, 40 and 80 min. The spinel $ZnCr_2O_4$ was prepared from activated mixtures by a conventional solid-state reaction at the temperature of 900 °C during 240 min. Raman scattering (RS) and Far-infrared (IR) spectroscopy were applied to study the local structure of zinc chromium oxide spinels. We report on an analysis of the vibrational spectra of the spinel $ZnCr_2O_4$ structure using both the classical factor-group theory (O_h^7 spectroscopic symmetry) and a local environmental model. The structural modifications were studied on the basis of vibrations of ZnO_4 tetrahedral and CrO_6 octahedral units building the crystal lattice. The RS and IR line intensities and positions remained in good agreement with the *Fd*3*m* space group. The broadness of IR and Raman bands and the fact that more vibration modes than expected were observed, may be attributed to certain disorder in the crystal symmetry of cubic spinel $ZnCr_2O_4$. Formation of the defect spinel structure can be assigned to mechanical activation of the starting oxide mixture.

Keywords: Milling; Defects; Spectroscopy; Spinels

1. Introduction

Spinel and spinel-like are attractive subjects for continuous scientific interest and have been deeply investigated in materials sciences, because of their physico-chemical properties.

Vibrational spectroscopy has been widely applied in solid state chemistry because it can provide information on structural characteristics of inorganic solids.[1] Few studies have been reported regarding spectroscopic measurements, i.e. Raman scattering and IR of $ZnCr_2O_4$ spinels.[2–8] Analysis of the vibrational spectra of many spinels is complicated by disordering of the cations and sample history.[3,9,10] The existence of defects leads to the formation of local charge-uncompensated defects responsible for the spectroscopic features of this material. It is obvious that the defects may cause disturbance of the crystal lattice.[11] It was recently reported that redox reactions, catalytic and sensory activity are much better of non-stoichiometric or doped spinels than of stoichiometric ceramics.[9,11] Because determination of the local structure seems one of the key issues for understanding electrochemical properties, vibrational spectroscopy can be applied to provide information on structural characteristics of $ZnCr_2O_4$.

In this study, we have systematically investigated the effects of mechanical activation of starting powder mixtures of $ZnO–Cr_2O_3$ on the spinel structure of $ZnCr_2O_4$ by spectroscopic methods.

2. Experimental procedure

$ZnCr_2O_4$ spinel was synthesized according to a previously described method.[12] Mixtures of starting ZnO (Merck, p.a. 99%) and Cr_2O_3 (Fluka, p.a. 99%) powders in equimolar quantities were used in the experimental procedures. Mechanical activation was performed by grinding (dry) a conventionally prepared mixture of powders, in a continual regime in a vibro-mill with steel rings (CUP Mill Type MN 954/3 KHD HUMBOLDT WEDAG AG) in air. The grinding times were 0, 40 and 80 min, and samples were denoted as ZC-00, ZC-40 and ZC-80 according to the time of activation, respectively. The mixtures were additionally pressed at 125 MPa into cylindrical compacts (with no binder) 10 mm in diameter. Calcinations were carried out in a furnace (Lenton Tube furnace LTF) at a temperature of 900 °C for 4 h in

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air. Afterwards, the samples were cooled down in the furnace to room temperature.

The room temperature Raman spectra of $ZnCr_2O_4$ samples were recorded on a Raman-laser spectrometer equipped with a Jobin-Yvon U1000 double-monochromator, using the 488 and 514.5 nm line of an argon-ion laser (the average power was about 50 mW) in the back-scattering geometry. Standard photon-counting techniques were used for detection. In order to attain a better signal-to-noise ratio, approximately 20 spectra were averaged. Far-infrared reflection spectra were recorded at 300 K in the spectral range from 70 to 700 cm^{-1} using a BOMEM spectrometer.

3. Results and discussion

It is now commonly accepted that normal AB_2O_4 spinel exhibits a cubic structure, with space group $Fd3m$ (Z = 8). In this structure, the anions form a cubic close-packed sub lattice of oxygen surrounded by tetrahedral and octahedral sites. The anionic array is described by the monovariant equivalent position $32e^u$ point symmetry $3m$. The actual value of the free parameter u (commonly known as the oxygen positional parameter) shows a slight deviation from 1/4, the ideal value for cubic-closest packing. Cations occupy only 1/8 of the tetrahedrally coordinated sites (8a Wyckoff position) and 1/2 of the octahedrally coordinated sites (16d Wyckoff position). There are then only two geometrical parameters to optimize: the lattice parameter a and the anion position parameter u.

By means of the group theory, it is possible to calculate the number of Raman- and IR-active phonons allowed for a certain crystal structure, thus providing useful information about the breakdown of crystal symmetry through various defective chemistry processes. Analysis of the vibrational spectra of spinel $ZnCr_2O_4$ can be made by the classical factor-group theory using the O_h^7 spectroscopic symmetry. However, it is also convenient to analyse Raman and infrared spectra in terms of localized vibrations. Considering the spinel structure constituted by CrO_6 octahedra and ZnO_4 tetrahedra, the molecular approach assumes that elemental units are weakly connected.[8] The approximately close cubic packed array of oxide ions incorporates CrO_6 octahedra sharing two opposite corners with ZnO_4 tetrahedra[13] (see Fig. 1). The CrO_6 is regular only for an ideal geometry ($u = 0.25$), whereas the ZnO_4 tetrahedron is always regular. In our case, the oxygen parameter u takes approximately the same value of about 0.26 for all samples.[12] It is interesting to notice that each oxygen is fourfold coordinated with one Zn and three Cr nearest neighbors.

The full cubic cell of spinel is redundant since only two octants of the cell which lie along the main body diagonal are really different.[2] The full cell contains 56 atoms, but the smallest Bravais cell contains only of 14 atoms. As a result, one should expect 42 vibrational modes. The factor group analysis predicts the following modes in the spinel structure:

$$\Gamma = A_{1g}(R) + E_g(R) + F_{1g}(in) + 3F_{2g}(R) + 2A_{2u}(in) + 2E_u(in) + 4F_{1u}(IR) + F_{2u}(in)$$

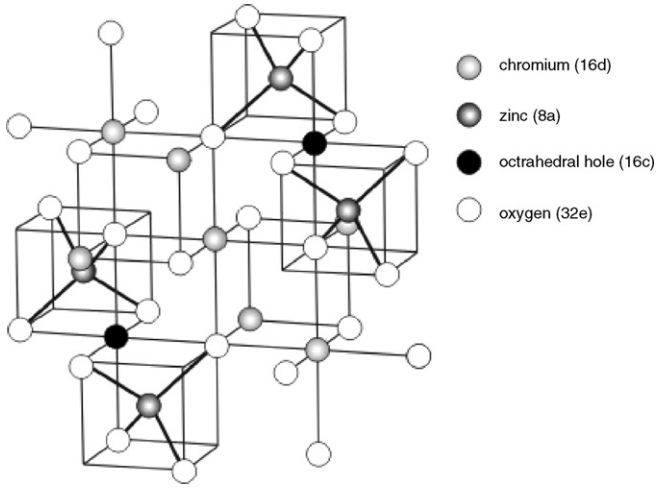

Fig. 1. Schematic representation of the spinel structure of $ZnCr_2O_4$.

where (R) represents Raman-active vibrations, (IR) infrared-active vibration and (in) are inactive modes. In a normal, non-defective $ZnCr_2O_4$ spinel and without mode couplings, selection rules suggest that only five modes should be Raman active and four modes infrared active.[2]

Non-stoichiometry, the presence of vacancies, interstitial cations, and defects in general, may result in activation of new phonon modes not predicted by group theory. Therefore, a complication of the spectra as compared with that of a single crystal is expected to occur due to some disorder and a wide grain-size distribution in the sample.

An octahedrally coordinated molecule of the CrO_6 type possesses only three Raman-active modes $\nu_1(A_{1g}) + \nu_2(E_g) + \nu_5(F_{2g})$. As distortions are generally imposed on the CrO_6 group, the symmetry is lowered and a greater number of possible fundamental modes become Raman active.

Fig. 2 shows the Raman-active modes of $ZnCr_2O_4$ spinels measured in the spectral region between 150 and 900 cm^{-1} at ambient conditions. A common feature of these spectra is the

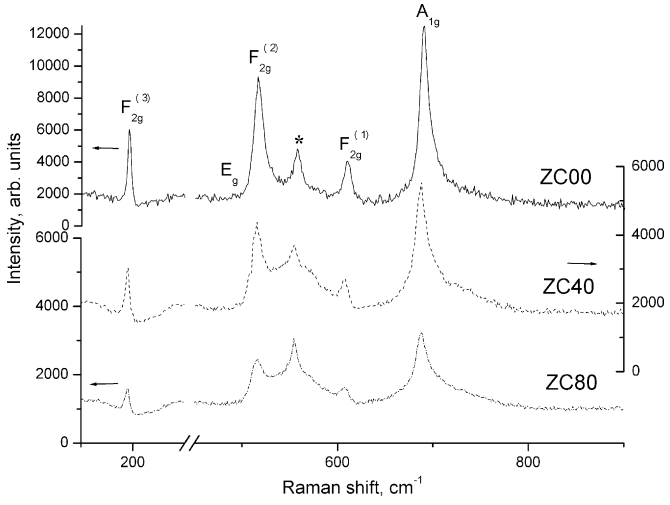

Fig. 2. Raman spectra of the $ZnCr_2O_4$ cubic spinels of ZC00, ZC40 and ZC80 samples collected at room temperature.

Table 1
Position (in cm^{-1}), symmetry and assignments of the Raman- and IR-active modes of the spinel $ZnCr_2O_4$

Raman (cm^{-1})	IR (cm^{-1})	Symmetry species	Assignment
	185	F_{1u} (ν_4)	δ(O–Cr–O)
195		$F_{2g}^{(3)}$	δ(Zn–O)
	367	F_{1u} (ν_3)	ν(Zn–O)
490		E_g	ν_s(Cr–O) + ν_s(Zn–O)
	497	F_{1u} (ν_2)	ν(Cr–O)
516		$F_{2g}^{(2)}$	ν(Cr–O)
556		*	
609		$F_{2g}^{(1)}$	ν_s(Cr–O)
	615	F_{1u} (ν_1)	ν_{as}(Cr–O)
690		A_g	ν_s(Cr–O)

presence of a group of strong bands between 500 and 700 cm^{-1} and low-wave number bands below 250 cm^{-1} with a weaker intensity. Spectroscopic data giving the phonon features are summarized in Table 1. These modes are in agreement with the previous measurements and calculations using different models.[8]

According to lattice dynamics calculations and the general spectral features of spinel oxides, assignments are as follows. In spinel oxides, energies in the spectral region 600–700 cm^{-1} are characteristic of vibrations involving the motion of oxygen atoms inside the octahedral unit CrO_6.[2,3] The Raman band located at about 690 cm^{-1} is viewed as the symmetric Cr–O stretching vibration of CrO_6 groups. This high-wave number band is assigned to the A_{1g} species in the O_h^7 spectroscopic symmetry. Its broadness is related to the cation–anion bond lengths and polyhedral distortion occurring in $ZnCr_2O_4$.

In our previous work we performed a detailed X-ray structural analysis of $ZnCr_2O_4$ synthesized from previously mechanically activated mixtures of starting ZnO and Cr_2O_3 powders.[12] This work shows that the lattice parameters of the cubic spinel depended on the preparation conditions, i.e. the time of activation. These changes are associated with the non-stoichiometry and defect structure of spinel. The experimental data presented in this study indicating that clusters formed from Zn^{2+} and Cr^{4+} defects on octahedral sites are the dominating defect present in these spinel structures.[11,12]

As the chromium ions of the spinel structure exhibited a charge disproportionation such as $Zn[Cr^{3+}Cr^{4+}]O_4$, there are isotropic $Cr^{4+}O_6$ octahedra and locally distorted $Cr^{3+}O_6$ octahedra due to the presence of Cr^{4+} defects on octahedral sites. Thus, we expect to observe stretching vibrations of $CrO_6{}^{9-}$ and $CrO_6{}^{8-}$ octahedra which provide the broadness of the A_{1g} mode in mechanically activated samples ZC40 and ZC80 (see Fig. 2).

The modification of the Raman scattering efficiency, i.e. decrease of the Raman peak intensity, could be attributed to the electronic properties of $ZnCr_2O_4$. It is a fact that $Zn[Cr^{3+}Cr^{4+}]O_4$ is a small-polaron semiconductor, in which electron hopping occurs between the two oxidation states of chromium ions. An increase in conductivity, i.e. higher concentration of carriers, reduced the optical skin depth resulting in a decrease in Raman scattering intensity in mechanically activated samples ZC40 and ZC80.

The peak at 609 cm^{-1} of the $F_{2g}^{(1)}$ mode in this region is not well separated in samples ZC40 and ZC80 because of its lower intensity. In the localized vibrational approach, it is speculated that the intensity of the Raman shoulder is closely related to the chromium average oxidation state in the spinel phase.

The RS peak with medium intensity located at 516 cm^{-1} has the $F_{2g}^{(2)}$ symmetry, while the very broad band located at 490 cm^{-1} has the E_g symmetry. The peak located at 195 cm^{-1} has the $F_{2g}^{(3)}$ symmetry.

The band at 556 cm^{-1} is an unexpected mode. The origin of this mode remains unclear, it could be Raman-active due to the cation disorder. As the volume Zn/Cr cation ratio in spinel increases, with increasing time of activation, the lattice constant increases monotonously.[12] This indicates that cation–oxygen bonding in the ZnO_4 tetrahedron and CrO_6 octahedron gets worse leading to expansion of the spinel framework, i.e. reduction of crystal symmetry. In this compound, zinc partly substitutes for chromium on octahedral 16d sites with a concomitant increase in the Cr-ion oxidation state to maintain the charge neutrality. The cubic lattice shrinks, as the result of a combined effect of the increase in the average oxidation state in chromium ions and of the substitution of chromium by zinc on the octahedral sites. As a result, a breakdown in the Raman and IR selection rules is expected, which may explain the observation of broad-band (somewhat disordered) and the fact that more vibrational modes than expected are observed in cubic $ZnCr_2O_4$. Taking into account that the samples were prepared from mechanically activated mixture of ZnO and Cr_2O_3 in high-temperature procedure, they most likely result from cationic disorder that induces a breakdown of the translation symmetry.

In the earlier literature, the infrared-active modes were interpreted as vibrations of the tetrahedron and octahedron units of the spinel structure. But, now it is accepted that complex vibrations of the entire lattice are the atomic displacement contributing to the infrared spectra of spinel phases and therefore vary considerably from compound to compound, depending on the masses, charges and chemical properties of the ions.[5,7] This

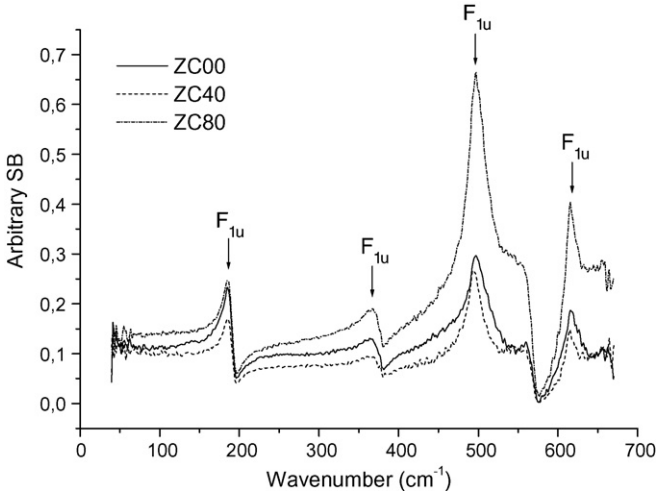

Fig. 3. Far-IR reflectivity spectrum of spinel samples ZC00, ZC40 and ZC80 recorded at room temperature.

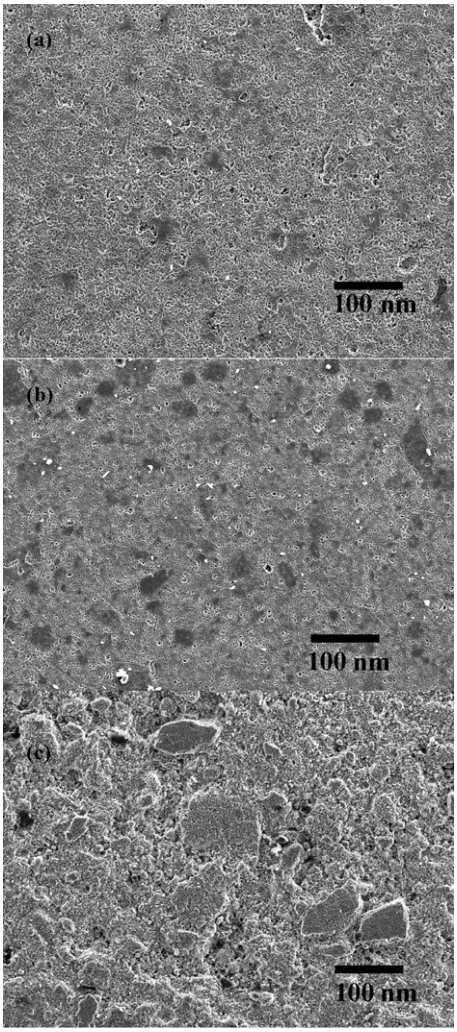

Fig. 4. SEM micrographs of samples (a) ZC00, (b) ZC40 and (c) ZC80.

is because the infrared-active modes all belong to the same symmetry species, F_{1u}, and can interact strongly with one another (see Table 1).

The two high-frequency IR bands ν_1 and ν_2 essentially depend (in shape and position) on the stoichiometry and chemical nature of the octahedral, chromium cation and thus are essentially related to vibrations of lattice octahedral groups. The two low-frequency bands ν_3 and ν_4 must be assigned to complex vibrations involving the simultaneous participation of both cations, tetrahedral and octahedral.[5,8,10]

As we can see in Fig. 3, in $ZnCr_2O_4$ spinels, the expected four phonon bands[5,7] are centered at 185, 367, 497 and 615 cm^{-1}. The two higher frequency modes are very intense, while other two are quite weak. The high-frequency bands of IR reflection spectrum of $ZnCr_2O_4$ located at 497 and 615 cm^{-1} involve mainly displacement of oxide anions relative to the chromium cations along the direction of the octahedral chains, although the vibrations are rather more complex than simple Cr–O stretching to which these bands are often loosely assigned. Whereas the low-frequency bands at 185 and 367 cm^{-1} also involve displacements of all ions in the lattice but derive predominantly from cooperative vibrations of Cr and Zn ions, respectively.

A careful analyses of the spectral shape of IR reflections in the optical phonon resonance region can be used to get information on the intergranular to grain ratio, which are related to the quality of sintered samples.[14] The use of IR spectroscopy for analysis of grain shape and aggregate composition of microcrystals is based on the theory of average dielectric constants (TADC).[14,15] This theory enables analysis of the aggregate composition using estimated packing density. The height of the main peak is a measure of growth of the crystalline grains.[14] The micrograph of sample ZC80 (see Fig. 4(c)) showed crystal aggregation differing from the relatively homogeneous microstructure with small grains in the samples ZC00 and ZC40 (see Fig. 4(a) and (b)). These observations suggest that sample ZC80 has a rather high fraction of big crystalline grains, which magnify the effective dielectric constant and thus the reflectance.

4. Conclusions

This work shows various aspects of the vibrational features of $ZnCr_2O_4$ spinel. Raman and IR data show that it is possible to study the lattice dynamics of $ZnCr_2O_4$ spinel using either the conventional factor group theory or the localized vibrational approach. The internal modes of polyhedral entities of the structure are clearly identified despite the strong interactions between them in the solid-state structure. The vibrational stretching modes of the octahedral cations are associated with the high-wave number band, while vibrational modes in the low frequency region, below 300 cm^{-1} are assigned to the vibrations of zinc cations against the neighboring oxygen anions.

The infrared and Raman spectra of the $ZnCr_2O_4$ spinel were dependent on the sample preparation conditions. Formation of the defect spinel structure is due to mechanical activation of the starting oxide mixture. Vibrational spectra are strongly influenced by various structural parameters such as the connection between CrO_6 octahedra, the zinc site occupancy, structural distortion, the average chromium state and aggregate composition of microcrystals. A loss of translation invariance certainly occurs, due to a combined effect of the increase in the average oxidation state in chromium ions and substitution of chromium by zinc on the octahedral sites. As an experimental result, a breakdown in the Raman and IR selection rules is observed in the spectra. The broadness of IR and Raman bands and the fact that more modes than expected are attributed to disorder in the cationic sublattice of cubic $ZnCr_2O_4$.

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