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Studies of Spinels
VII. Order–Disorder Transition in the Inverse Germanate Spinels $Zn_{2-x}(Co, Ni)_xGeO_4 (x \simeq 1)$

J. PREUDHOMME AND P. TARTE

University of Liège, Institute of Chemistry, B-4000 Sart-Tilman par Liege 1, Belgium

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A series of germanate spinels $Zn_{2-x}(Ni, Co)_xGeO_4$ has been synthesized and investigated by X-ray diffractometry and infrared spectroscopy. Synthesis at 1200°C leads to cubic phases characterized by an inverse, disordered distribution of Ge and bivalent cations (essentially Ni or Co) over the octahedral sites; however, the presence of some short-range order is suggested by the infrared spectrum. Tempering at an appropriate temperature (between 800 and 900°C, depending on the Co/Ni ratio) leads to tetragonal spinel phases, corresponding to the 1 : 1 order between Ge and bivalent cation on octahedral sites. The transformation is sluggish and proceeds at a significant rate only in a narrow temperature range, just below the transition temperature. A comparison with the behavior of known inverse, ordered titanate spinels shows that, within the family of inverse II–IV spinels $M_2^{II}M^{IV}O_4$, the ratio of the octahedral cationic radii $r_{M^{II}}/r_{M^{IV}}$ is one of the factors determining the order–disorder transition temperature, and the importance of the tetragonal distortion.

Introduction

The investigation of the pseudobinary systems Ni_2GeO_4–Zn_2GeO_4 and Co_2GeO_4–Zn_2GeO_4 led Reinen to the conclusion that three phases, separated by large immiscibility gaps, are present in these systems: a Ni- (or Co-) rich phase with the Ni_2GeO_4 (or Co_2GeO_4) normal spinel structure; a Zn-rich phase with the Zn_2GeO_4 phenacite structure; and a phase of intermediate composition Zn_{2-x}(Co or Ni)$_x GeO_4$ with x somewhat variable, but not very different from unity.

This phase also has a spinel structure, but with a cation distribution which is probably inverse (tetrahedral Zn and octahedral Ge), as deduced from the electronic spectra of the Co and Ni cations (*1*). The octahedral coordination of germanium, and hence the inverse cation distribution, has been confirmed by ir spectroscopy (*2*, *3*), and accordingly, we have investigated the possibility of order–disorder transitions in this family of spinels.

Experimental

All phases were synthesized by conventional solid-state reactions: the appropriate amounts of oxides or carbonates are ground and mixed, and progressively heated in covered platinum crucibles up to 1200°C. If necessary, grinding and heating were repeated until no change is observed in the X-ray powder diagram. All samples were first

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air quenched from 1200°C, and later submitted to a more or less slow cooling from 950 down to 350°C, so as to induce the cation ordering. For reasons which will be indicated below, this slow cooling was finally replaced by a tempering at constant temperature (between 900 and 750°C, depending on the chemical composition). This tempering was carried out, either in air (covered platinum crucibles), or in sealed silica tubes containing a small pressure (20–30 mm Hg) of gaseous HCl.

The cation ordering was investigated by both ir spectroscopy and X-ray diffractometry. For this family of compounds, the latter method is considerably more sensitive than the former to the ordering process since, except for the small-angle region, there is no overlapping of the diffraction peaks of the ordered (tetragonal) and disordered (cubic) phases. Precise (to 0.001 Å) unit cell parameters were deduced from high-angle diffraction peaks (731–553, 800, 751–555, and 662 for the cubic, disordered spinels; C.G.R. diffractometer; Co$K\alpha$ monochromatized radiation); no internal standard was used.

Infrared spectra were obtained with a Beckman IR 12 spectrophotometer (1200–250 cm^{-1} region; KBr discs) and a Polytec FIR 30 interferometer (300–20 cm^{-1} region; polythene discs).

Results

Limiting Compositions

After Reinen (*1*), the compositions giving a single, inverse spinel phase are as follows:

$Zn_{2-x}Ni_xGeO_4$: $0.70 \leq x \leq 0.95$

$Zn_{2-x}Co_xGeO_4$: $(1.1)^1 \leq x \leq 1.4$

These limits apply to samples quenched from 1150°C. The homogeneity field is slightly larger by quenching from 1200°C.

Our own results are in nearly perfect agreement with Reinen's data. Likewise, for these limiting compositions, our values of the unit cell parameter a_0 are in good agreement with the data published by Navrotsky (*4*).

Cation Ordering and Cubic-Tetragonal Transition

In view of the octahedral coordination of germanium, these spinels are similar to the inverse titanate spinels $M_2^{II}TiO_4$ (= M^{II} [M^{II}Ti]O_4) which present at least for M^{II} = Mg, Zn, Mn) the well-known 1 : 1 ordering of the octahedral cations, leading to a tetragonal cell characterized by a $\simeq a_{sp}/2^{1/2}$ and $c \simeq a_{sp}$ (diagonal cell) (*5*).

Cation ordering has been obtained for all phases $Zn_{2-x}(Co, Ni)_xGeO_4$ with the inverse spinel structure. Despite numerous attempts and various thermal conditions, no ordering was observed with the corresponding compounds $ZnCoTiO_4$, $ZnNiTiO_4$, $ZnCoSnO_4$, or $ZnNiSnO_4$, all of which contain octahedral M^{4+}.

For both cubic and tetragonal phases, the unit cell parameters of these inverse germanates are essentially determined by the Ni percentage (with respect to the sum Zn + Co), and not by the relative amounts of Zn and Co (Fig. 1).

For the cubic, disordered, phase the a_{cub} parameter decreases regularly when the Ni content increases; for the tetragonal, ordered, phase, the a_{tetr} parameter (plotted as $a \cdot 2^{1/2}$ in Fig. 1) also decreases, but c_{tetr} slightly *increases* with the Ni content; the tetragonal distortion is the highest for the Co compounds, and the lowest for the Ni compounds.

Temperature and Kinetics of Ordering

The order–disorder transition temperature is near 770°C for Mn_2TiO_4 (*6*), and near 500°C for Zn_2TiO_4 (*7, 8*) and Mg_2TiO_4 (*9*). The cation ordering is fairly rapid for Mn_2TiO_4, but much slower for Zn_2TiO_4 and

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[1] Estimated from Fig. 7 in Ref. (*1*).

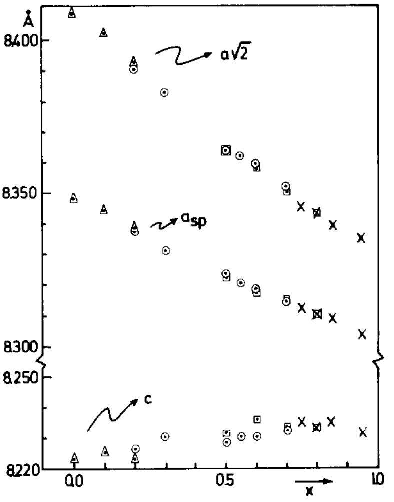

FIG. 1. Relationship between unit cell dimensions for both cubic and tetragonal phases, and the nickel content x. For the tetragonal phases, the quantity $a \cdot 2^{1/2}$ (rather than a) has been used for ease of comparison. Triangles: $Zn_{0.8}Co_{1.2-x}Ni_xGeO_4$ ($0.0 \leq x \leq 0.2$). Circles: $Zn_{1.0}Co_{1.0-x}Ni_xGeO_4$ ($0.2 \leq x \leq 0.7$). Squares: $Zn_{1.2}Co_{0.8-x}Ni_xGeO_4$ ($0.5 \leq x \leq 0.8$). Crosses: $Zn_{2-x}Ni_xGeO_4$ ($0.75 \leq x \leq 0.95$).

Mg_2TiO_4. According to these data, we tried to induce cation ordering in the germanates by a moderately rapid cooling from 900 to 700°C (in 4 days by steps of 50°C), followed by a much slower cooling from 700 to 400°C (in 2 months by steps of 20 and 10°C). All these attempts failed, and it was finally realized that kinetic factors play an essential role here: the ordering proceeds at a significant rate only in a narrow temperature range, slightly below the transition temperature. Even in favorable temperature conditions (near 800°C for Co-rich phases; near 880°C for Ni-rich phases), the ordering process takes several days or even several weeks (against a few hours in Mn_2TiO_4). Conversely, some of the ordered phases were submitted to a progressive heating, so as to determine the disordering temperature. A brief summary of these experiments is given in Table I. Three experimental facts emerge from these data:

(i) There is no abrupt transition temperature: we always find a small temperature range (20–30°C) in which the two phases (ordered and disordered) are able to coexist. For a given temperature, no further change is observed in the system after 7 days; thus this seems to correspond to true

TABLE I

INFLUENCE OF THE CHEMICAL COMPOSITION (Co/Ni PERCENTAGE) ON THE ORDER–DISORDER TRANSITION TEMPERATURE

Thermal treatment	Compositions (all ordered) $Zn_{0.8}Co_{1.2}GeO_4$	$Zn_{1.0}Co_{0.5}Ni_{0.5}GeO_4$	$Zn_{1.2}Co_{0.3}Ni_{0.5}GeO_4$	$Zn_{1.25}Ni_{0.75}GeO_4$
4 days 840°C	Ordered	Ordered	Ordered	Ordered
4 days 860°C	Beginning of disorder	Ordered	Ordered	Ordered
4 days 880°C	Strongly disordered	Ordered	Ordered	Ordered
3 days 900°C	Totally disordered	Ordered	Ordered	Ordered
4 days 925°C		Totally disordered	Beginning of disorder	Ordered
3 days 940°C			Totally disordered	Partly disordered
3 days 960°C				Totally disordered

equilibrium conditions. Billiet (*10*) has noticed a similar behavior in the case of Zn_2TiO_4.

(ii) The transition temperature range increases slightly, but significantly when cobalt is replaced by nickel.

(iii) Near the transition temperature, the disordering is slow, and no peak is observed by differential thermal analysis.

Factors Influencing the Kinetics of Ordering

Influence of gaseous HCl in a closed system. Since the kinetics of ordering is related to the mobility of the cations, it was assumed that a chemical agent such as HCl would increase this mobility through an equilibrium such as:

$$Zn_{2-x}Co_xGeO_4 + 8\ HCl \rightleftarrows (2-x)ZnCl_2 + x\ CoCl_2 + GeCl_4 + 4\ H_2O.$$

This type of reaction is well known as a means of obtaining monocrystals of various oxides by chemical transport in a temperature gradient; it has been used for obtaining monocrystals of the normal spinels Ni_2GeO_4 and Co_2GeO_4 (unpublished results from this laboratory). However, no temperature gradient was used in the present experiments, so as to avoid compositional changes due to possible selective transport.

In accordance with expectations, we have noticed a rather beneficial influence of the presence of HCl. First, for a given composition and a given temperature, the ordering proceeds at a higher rate; and second, the high-angle diffraction peaks are very sharp; this is not always the case for the ordered phases obtained in the absence of HCl. No composition change has been observed.

Influence of the cations. The rate of ordering slightly increases with increasing Zn content (i.e., $Zn_{0.9}Co_{1.1}GeO_4$, or $Zn_{1.25}Ni_{0.75}GeO_4$ are more rapidly ordered than $Zn_{0.7}Co_{1.3}GeO_4$, or $Zn_{1.05}Ni_{0.95}GeO_4$, respectively), and strongly decreases when Co is replaced by Ni ($Zn_{0.8}Co_{1.2}GeO_4$ is fully ordered after 1 month at 800°C; but the same treatment leaves $Zn_{1.05}Ni_{0.95}GeO_4$ fully disordered).

On the other hand, the introduction of either Cu or Ti in the structure seems to hinder the ordering process. Phases such as $Zn_{0.8}(Co_{1.2-x}Cu_x)GeO_4$, or $Zn_{0.8}Co_{1.2}(Ge_{1-x}TI_x)O_4$ may be obtained in the ordered state for $x = 0.05$, but remain fully disordered for $x = 0.20$. It must be pointed out, however, that the ordering temperature of Zn_2TiO_4 is much lower (between 500 and 550°C) and that, accordingly, ordering of Ti-containing phases will possibly occur at temperatures which are lower than those necessary for the pure germanates.

Infrared Spectra

A brief account of these spectra has been given elsewhere (*2, 3*). The most conspicuous features are as follows:

(i) The unique band observed near 700 cm^{-1} in the ir spectra of normal germanate spinels $M_2^{II}GeO_4$, and corresponding to the GeO_4 antisymmetric stretch (*11*), is replaced here by a group of bands in the 650–550 cm^{-1} region. As a first approximation, these bands may be assigned to vibrations of the lattice of GeO_6 octahedra.

(ii) The spectrum of the ordered phases is not drastically different from that of the disordered ones; in this latter case, the moderate complexity of the spectrum suggests the existence of some kind of local ordering.

Discussion

1 : 1 Octahedral Ordering in Inverse II–IV Spinels

We must first point to the perfect analogy between the spinels under consideration, and the high-pressure form of Zn_2GeO_4.

The phenacite → spinel transformation of this compound under high pressure was first evidenced by Rooymans (*12*), and further investigated by Syono *et al.* (*13*). They found two spinel phases, depending on T–P conditions: either a cubic one with a = 8.3499 (3) Å; or a tetragonal one with a = 5.937 (1) and c = 8.254 (1) Å; this is to be compared with our own results on $Zn_{0.8}Co_{1.2}GeO_4$: a_{cubic} = 8.348 Å; a_{tetr} = 5.946, c_{tetr} = 8.223 Å. Such analogies add strong support to the hypothesis that the tetragonal distortion in Zn_2GeO_4 is most probably due to the ordering of Zn^{2+} and Ge^{4+} ions in the octahedral sites of the spinel lattice (*13*). Likewise, the tetragonal distortions are fairly similar: $c/a\ 2^{1/2}$ = 0.983 and 0.978 for Zn_2GeO_4 and $Zn_{0.8}Co_{1.2}GeO_4$, respectively.

The factors determining the amount of distortion are not well known, but the existing data on inverse II–IV spinels suggest that one of these factors is the ratio of the ionic radii of the cations participating to the order (Fig. 2).

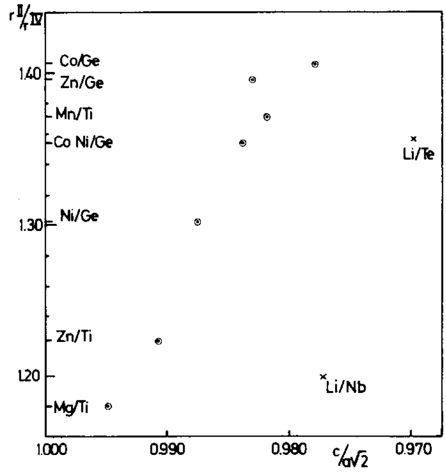

FIG. 2. Relationship between the ratio of the octahedral cationic radii $r_{M^{II}}/r_{M^{IV}}$ and the tetragonal distortion $c/a\ 2^{1/2}$ for the ordered $M^{II}\ [M^{II}M^{IV}]O_4$ spinels. The crosses are related to $Li[LiTe]O_4$ and $Zn[LiNb]O_4$ to show the influence of the valencies of the cations.

TABLE II

CORRELATION BETWEEN THE TRANSITION TEMPERATURE OF INVERSE II–IV SPINELS AND THE RATIO OF THE OCTAHEDRAL CATIONIC RADII

Compound	Transition temperature (°C)	r_{II}/r_{IV}
Mg_2TiO_4	About 500	1.190
Zn_2TiO_4	500–550	1.223
Mn_2TiO_4	770	1.372
$Zn_{0.8}Co_{1.2}GeO_4$	860–900	1.406
$Zn_{1.25}Ni_{0.75}GeO_4$	940–960	1.302

Two comments can be made about this figure:

(i) The I–II–V and I–VI spinels Zn $[LiNb]O_4$ and Li $[LiTe]O_4$ fall well outside the relation given by the II–IV spinels. Thus, the valency difference between ordering cations is another essential factor determining the importance of the tetragonal distortion.

(ii) Within the II–IV spinels, the correlation between ionic radii ratio and tetragonal distortion is clear, but the significant scattering of the points suggests that some other factors must also be taken into account. One of these could be the electronic structure of the cations, but the small number of existing data does not allow a detailed discussion of this point.

Transition Temperature

Among the spinels possessing (or able to possess) 1 : 1 octahedral order, the possibility and ease of ordering are clearly, although qualitatively, related to the valence difference between ordering cations: $Li[LiTe]O_4$ and $Zn[LiNb]O_4$ are known in the ordered state only; on the contrary, all inverse II–IV spinels are known in the disordered state, and some of them only can be ordered; and finally, all inverse II–III spinels are known in the disordered state only.

This trend is also true for other types of ordering (e.g., 1 : 1 tetrahedral and 3 : 1 octahedral), and is readily explained by the fact that the ordering minimizes electrostatic repulsion forces (*14*).

Now, if we keep this factor constant by considering a given family, namely, the II–IV inverse spinels, we find a rough correlation between the ordering temperature and the ratio of the octahedral cationic radii (Table II): the transition temperature decreases when the octahedral ionic radii become more similar. This should be simply considered as a qualitative trend, since other factors are certainly playing a significant role. Among these, we should probably consider the unit cell volume: to a smaller unit cell volume should be associated a larger lattice energy and possibly a higher transition temperature; this would explain the apparently abnormally high transition temperature of the nickel compounds.

Such considerations would also explain why the stannate spinels (such as Mg_2SnO_4, Zn_2SnO_4, Co_2SnO_4 . . .) have never been obtained in an ordered state: owing to the larger ionic radius of Sn^{4+}, the r^{II}/r^{IV} ratio is still smaller for stannates than for titanates, and, if the correlation suggested by Table II is valid, the transition temperature of stannates should be well below 400°C, a temperature range in which the cation mobility is probably negligible. A cell volume effect would act in the same direction, and still lower the transition temperature. The kinetic aspects of the transition will not be discussed here, because of the lack of quantitative data.

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