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SYNTHESIS AND CRYSTALLOGRAPHIC STUDY OF $Cd_xNi_{1-x}Ga_2O_4$ SPINELS **

$CdGa_2O_4$, $NiGa_2O_4$ and four mixed spinels $Cd_xNi_{1-x}Ga_2O_4$ ($x=0.25$, 0.50, 0.70 and 0.85) were prepared, in polycrystalline form, by solid state reaction (at 1273 K) in mixtures of CdO, NiO and Ga_2O_3. X-ray diffraction analysis was used to determine the lattice parameter, a_o, oxygen parameter, u, and cation distribution for each spinel. The lattice parameter was found to increase, almost linearly, from $a_o=826.1$ pm for $x=0$ up to $a_o=860.1$ pm for $x=1$; the u parameter also increases continously, from 0.385 up to 0.392, along the same composition range. Ni^{2+} ions were found to occupy octahedral sites in all cases, whilst the Cd^{2+} ion showed a pronounced tetrahedral preference. The Ga^{3+} distribution changes with the composition parameter x; thus, the proportion of tetracoordinated Ga^{3+} decreases from 46% down to 7,5% as x is raised from 0 to 1.

1 — INTRODUCTION

The distribution of cations among the available tetrahedral and octahedral sites in spinels is governed by their relative site preference energy [1-9], and the equilibrium configuration is a function of temperature, pressure and composition [10-15]. Thus, in a binary spinel (with only two different cations) the ionic partition can only be modified through changes of either temperature or pressure (or both), and the available cation distribution range is often quite small. However, in mixed spinels (with more than two cations) gradual changes in chemical composition often bring about substantial variations in cation distribution [15-17]; hence, solid solution formation between two end menbers, affords a particularly good opportunity to explore the relative preference of different cations for the tetrahedral or ocatahedral coordination.

The present paper reports the results of a structural investigation, by X-ray diffraction, of the mixed spinels $Cd_xNi_{1-x}Ga_2O_4$. The Ni^{2+} ion is known to have a strong octahedral preference [3,4,18], whilst Cd^{2+} shows a pronounced tetrahedral preference in binary oxidic spinels [2,8]. Thus, the degree of inversion of the mixed spinels $Cd_xNi_{1-x}Ga_2O_4$ is expected to increase markedly on passing from $CdGa_2O_4$ to $NiGa_2O_4$.

RUDDORFF and REUTER [19], DATTA and ROY [20], and HUBER [21], among others, have studied the structure of the simple $CdGa_2O_4$ spinel. $NiGa_2O_4$ has been studied by GREENWALD *et. al.* [22], and by PLYUSCHEV *et. al.* [23], among others.

2 — EXPERIMENTAL

SPECIMEN PREPARATION

Pure $CdGa_2O_4$, pure $NiGa_2O_4$ and four $Cd_xNi_{1-x}Ga_2O_4$ ($x=0.25$, 0.50, 0.70 and 0.85) solid solutions have been investigated. The starting materials were Ga_2O_3 and NiO, supplied by «Koch-Light Laboratories» with a nominal purity of 99.99% or higher, and CdO Merck «pro analysi». To prepare the spinels, the appropriate amounts of the component oxides were mixed, and fired in air at 1273 K. To avoid losses of CdO, which is appreciably volatile at 1273 K, an additional amount of this oxide was placed in the reaction tube and kept at a temperatu-

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re slightly higher than the reacting oxide mixture, thus providing a local atmosphere saturated with cadmium oxide vapour. More details of the experimental set up will be given elsewhere [24].

The progress of the reaction was followed by X-ray diffraction. When the diffractograms showed no trace of the initial oxides the samples were heated at 1273 K for 24 hours and quenched in liquid nitrogen.

X-RAY ANALYSIS

Lattice parameters and diffraction intensities were obtained using a Philips X-ray diffractometer equipped with a graphite crystal monochromator and scintillation counter. CuK_α radiation was used throughout. Lattice parameter values were determined from diffractograms obtained at room temperature (294 ∓ 5 K) using NaCl ($a_o = 564.02$ pm) as an internal standard, a scanning rate of $1/4^\circ$ $min^{-1}(2\theta)$ and a time constant of 4 s. Diffraction intensities were determined from the number of impulses accumulated in the counter; allowance for background was made by counting the intensity at each side of every diffraction line over a time interval long enough to attain a small statistical error [25]. 12-18 diffraction lines were measured for each spinel.

3 — RESULTS AND DISCUSSION

Mean values of the lattice parameter, a_o, calculated from six diffraction lines for each sample, are shown in Table 1. A continuous increase in a_o with the composition parameter x may be observed. This fact, and the observed absence in the diffractograms of other crystalline phases apart from the spinel one, provide clear evidence of the formation of a series of solid solutions between $CdGa_2O_4$ and $NiGa_2O_4$

Table 1
Lattice parameters, a_o, for $Cd_xNi_{1-x}Ga_2O_4$ spinels

x	a_o (pm)
0	826.1
0.25	836.0
0.50	844.2
0.70	850.6
0.85	855.7
1	860.1

The ionic radius of Cd^{2+} is 38% greater than the corresponding value for the Ni^{2+} ion [26], this explains the observed increase of a_o as the composition parameter is raised, from $x=0$ to $x=1$, in $Cd_xNi_{1-x}Ga_2O_4$. The a_o value found for $NiGa_2O_4$ ($a_o = 826.1$) is very close to those of $a_o = 825.8$ pm reported by GREENWALD *et. al.* [22], and $a_o = 826.2$ pm given by the NBS [32]. For $CdGa_2O_4$ the present value ($a_o = 860.1$ pm) agrees with those of $a_o = 860.2$ pm and $a_o = 860.1$ pm givem by DATTA and ROY [20] and by OTERO AREAN [27], respectively; the value of $a_o = 839$ pm reported by RUDDORFF and REUTER [19] appears to be too small, the discrepancy could be due to a slight deviation from stoichiometry.

The oxygen parameter, u, and cation distribution for each spinel were determined applying a Monte Carlo computer program [28] to the method proposed by FURUHASHI *et. al.* [29]. This method is based on the linear relationship:

$$\ln(I^{obs}_{hkl} / I^{cal}_{hkl}) = \ln k - 2B_{eff} (\sin \theta_{hkl} / \lambda)^2 \qquad (1)$$

where I^{obs}_{hkl} are the experimentally observed intensities, I^{cal}_{hkl} the intensities calculated for different diffraction lines and simulated structures, k is a scale factor, B_{eff} the temperature factor, θ_{hkl} the diffraction angle and λ the wavelenght of the radiation used. The computer program takes into account the Lorentz-polarization and multiplicity factors. Atomic scattering factors were calculated according to the equation:

$$f(\lambda^{-1} \sin \theta) = \sum_{i=1}^{4} a_i \exp(-b_i \lambda^{-2} \sin^2\theta) + c \qquad (2)$$

using the coefficients, and corrections for anomalous scattering, given in the International Tables [30]. The Monte Carlo computer program applies Furuhashi's method 70 times to each spinel; in each run a value of the random error, following the impulse count statistics [25], is added to the experimentally determined counter readings corresponding both to the diffraction lines and to the background intensity. The average values obtained for the oxygen parameter and cation distribution, corresponding to each spinel, are shown in Table 2; numbers in brackets indicate the standard deviation of each parameter, in units of the last significant figure. The absolute value of the linear regression

Table 2

Oxygen Parameter, u, and cation distribution for $Cd_xNi_{1-x}Ga_2O_4$ spinels

x	u	Tetrahedral			Octahedral		
		Cd^{2+}	Ni^{2+}	Ga^{3+}	Cd^{2+}	Ni^{2+}	Ga^{3+}
0	0.3855(2)	—	0.080(4)	0.920(4)	—	0.920(4)	1.080(4)
0.25	0.3850(15)	0.250(5)	0.049(9)	0.701(11)	0.000(5)	0.701(9)	1.299(11)
O.50	0.3873(3)	0.500(5)	0.002(3)	0.498(7)	0.000(5)	0.498(3)	1.502(7)
0.70	0.3905(2)	0.663(3)	0.000(1)	0.337(3)	0.037(3)	0.300(1)	1.663(3)
0.85	0.3913(20)	0.749(11)	0.002(35)	0.249(46)	0.101(11)	0.148(35)	1.751(46)
1	0.3924(2)	0.850(3)	—	0.150(3)	0.150(3)	—	1.850(3)

coefficient found in the adjustment of equation (1) fell, in all cases, between 0.85 and 0.97.

The oxygen parameter (Table 2) was found to increase continuously with cadmium content, from 0.3855 in $NiGa_2O_4$ to 0.3924 in $CdGa_2O_4$. The slight decrease observed in $Cd_{0.25}Ni_{0.75}Ga_2O_4$ ($u = 0.3850$) is not considered to be significant. The large ionic radius of Cd^{2+}, 80 pm in four-fold ccordination [26], together with the observed fact that this cation occupies preferentially tetrahedral sites, must be responsible for the increased value of u as x is raised. It is well known that the tetrahedral interstice expands more rapidly than the octahedral one when u increases. The former is in fact larger than the latter for $u > 0.3875$. The results for $CdGa_2O_4$ and $NiGa_2O_4$ (Table 2) are close to the values of $u = 0.390$ and $u = 0.387$ given by GARCÍA DÍAZ [31] and GREENWALD *et. al.* [22], respectively, for these two compounds.

As shown in Table 2, the Ni^{2+} ion occupies almost exclusively octahedral sites. This is indeed the behaviour to be expected from a d^8 ion, which must find a considerable stabilization in octahedral interstices through crystal field effects [3-5]. For Cd^{2+} and Ga^{3+} (d^{10} ions) convalency effects should result, according to GOODENOUGH and LOEB [2], and BLASSE [8], in a preference for the tetrahedral coordination. The experimental results show that such a preference is greater in the case of Cd^{2+}. This is why $CdGa_2O_4$ is only 15% inverted. The combined effects of Ni^{2+} and Cd^{2+}, the former anchored in octahedral sites and latter occupying tetrahedral sites, condition the behaviour of Ga^{3+} whose coordination symmetry is strongly dependent on the composition parameter x. Thus, the proportion of tetracoordinated Ga^{3+} decreases continuously as x is raised, from 45% in $NiGa_2O_4$ down to 7.5% in $CdGa_2O_4$.

Table 2 shows that $NiGa_2O_4$ is, very nearly, a totally inverse spinel (at 1273 K), which agrees with the results found by GREENWALD *et. al.* [22] and by PLYUSCHEV *et. al.* [23]. For $CdGa_2O_4$ we have found an inversion degree of 15% (at 1273 K). Previously reported values are: 0% (RUDDORF and REUTER [19]), 22.5% (HUBER [21]) and 16% (GARCÍA DÍAZ [31]).

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Short title:

CRYSTALLOGRAPHIC STUDY OF $Cd_xNi_{1-x}Ca_2O_4$ SPINELS

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