JOURNAL OF SOLID STATE CHEMISTRY 60, 1–5 (1985)

Structural Study of Copper–Nickel Aluminate ($Cu_xNi_{1-x}Al_2O_4$) Spinels

C. OTERO AREÁN AND J. S. DÍEZ VIÑUELA

Departamento de Química Inorgánica, Facultad de Química, Oviedo, Spain

Received December 4, 1984; in revised form March 19, 1985

$CuAl_2O_4$, $NiAl_2O_4$, and three ternary spinels $Cu_xNi_{1-x}Al_2O_4$ have been prepared, in polycrystalline form, by solid-state reaction of mixtures of CuO, NiO, and Al_2O_3 at 1223 K. X-Ray powder diffractometry, coupled with adequate computational methods, allowed determination of the unit-cell length, oxygen positional parameter, and cation distribution for each compound. Interdependence of these structural parameters is closely analyzed on the ternary oxide spinels. The one-electron difference between the Cu^{2+} and Ni^{2+} ions was found to be enough to render them distinguishable by X-ray powder diffraction. © 1985 Academic Press, Inc.

Introduction

Investigation of cation distribution in spinels, among tetrahedral and octahedral sites, is a suitable method to gain knowledge about the various factors which determine coordination preferences in the structural chemistry of oxides. Cation site preferences in binary spinels are well documented (*1–3*), but ternary spinels (i.e., spinels with three kinds of cations) are not so well understood. A number of studies (*4–9*) have recently emphasized the need for understanding the cation distribution in these more complex systems about which much remains to be known.

Ternary spinels are particularly useful model systems in solid-state structural chemistry, since gradual changes in chemical composition produce variations in cation distribution (*4, 10*) which allow investigation of the physical and chemical properties connected with the coordination symmetry of different cations. Such studies are also relevant to the many technological applications of oxide spinels.

The present paper reports on a structural investigation of the ternary spinels $Cu_xNi_{1-x}Al_2O_4$. X-Ray powder diffraction has been used to determine the unit-cell length a_0, the oxygen parameter u, and the cation distribution as a function of composition. The oxygen parameter quantifies the distortion of the anion sublattice. When cations fit perfectly the tetrahedral interstices, the oxide ions form an ideal cubic close-packed array, and $u = 0.375$. In most spinels, however, $u > 0.375$ as a result of small displacements of the anions in the [111] direction, which allows expansion of the tetrahedral sites (*11*). Knowledge of the oxygen parameter is necessary for a full understanding of cation distribution since u, together with a_0, defines the sizes of the tetrahedral and octahedral interstices.

The $Cu_xNi_{1-x}Al_2O_4$ system can be regarded as a solid solution between the binary spinels $CuAl_2O_4$ and $NiAl_2O_4$ · $CuAl_2$

0022-4596/85 $3.00

O_4 has been previously studied by Cooley and Reed (*12*), Pepe *et al.* (*13*), and Díez Viñuela *et al.* (*9*), among others. Structural characterization of $NiAl_2O_4$ was reported by Furuhashi *et al.* (*14*), Porta *et al.* (*4*), and Otero Areán *et al.* (*15*), among others.

Experimental

Specimen preparation. $CuAl_2O_4$, $NiAl_2O_4$, and three $Cu_xNi_{1-x}Al_2O_4$ (x = 0.25, 0.50, and 0.75) spinels were prepared in polycrystalline form by solid-state reaction at 1223(±20) K of the parent oxides (CuO, NiO, and α-Al_2O_3) mixed in the appropriate proportions; these starting materials were supplied by Koch-Light Laboratories with a nominal purity of 99.99%.

To facilitate reaction the samples were periodically removed from the furnace and ground. This also allowed the progress of the reaction to be followed by X-ray diffraction. When the diffractograms showed no traces of the parent oxides (typically after 300 hr), the samples were reheated to 1223 K for a further 30 hr to ensure total conversion to spinel. They were then rapidly immersed in liquid nitrogen to quench the cation distribution equilibrium.

X-Ray diffraction. Lattice parameters and diffraction intensities were determined with a Philips powder diffractometer equipped with a graphite crystal monochromator (on the diffracted beam) and scintillation counter. Cu*Kα* radiation was used throughout. Lattice parameter values were determined from diffractograms obtained at room temperature (294 ± 5 K) using NaCl (a_0 = 564.02 pm) as an internal standard. Diffraction intensities were obtained from the number of pulses accumulated in the counter during the 2θ scanning of each line at 0.125° $\min^{-1}$. Allowance for background intensities was made by setting the goniometer at each side of every diffraction line and accumulating enough pulses to have only a small statistical error (*16*).

Results

Lattice Parameter

The X-ray diffractogram of each sample could be indexed completely as a single cubic-phase spinel. The a_0 values, obtained from several diffraction lines with $2\theta > 40°$ are shown in Table I, along with the corresponding standard deviations, s. It is seen that there is a continuous variation of a_0 with the composition parameter x. This, taken together with the results of phase analysis reported above, shows that $CuAl_2O_4$ and $NiAl_2O_4$ form a complete series of solid solutions at 1223 K.

Also shown in Table I are the deviations from the Végard law (*17, 18*), Δa_0, and from the corresponding law of additivity of unit-cell volumes (*19*), ΔV. The values of Δa_0 and ΔV were calculated by subtracting from the experimentally observed values of a_0 and V (unit-cell volume) those obtained from the linear relationships

$$a_0 = x(a_{0,\mathrm{CuAl_2O_4}}) + (1 - x)(a_{0,\mathrm{NiAl_2O_4}}) \quad (1)$$

$$V = x(V_{\mathrm{CuAl_2O_4}}) + (1 - x)(V_{\mathrm{NiAl_2O_4}}). \quad (2)$$

Oxygen Parameter and Cation Distribution

The intensities of the (220), (311), (400), (422), (333, 511), (440), (620), (533), (622), (642), (553, 731), (800), (660, 822), (555, 751), (662), (840), (931), and (844) diffraction lines were measured for each sample. From these intensity values, the oxygen pa-

TABLE I

LATTICE PARAMETER OF $CuAl_2O_4$, $NiAl_2O_4$, AND $Cu_xNi_{1-x}Al_2O_4$ SPINELS

x	a_0 (pm)	s	Δa_0 (pm)	$10^3\Delta V$ (nm³)
0	805.0	0.05	—	—
0.25	805.3	0.05	−0.4	−0.9
0.50	805.9	0.05	−0.6	−1.1
0.75	806.8	0.04	−0.4	−0.7
1	807.9	0.03	—	—

rameter and cation distribution of each spinel were calculated following a modified version (*20*) of the method proposed by Furuhashi *et al.* (*14*). This method is based on the fact that when a simulated structure coincides with the actual structure of the sample a linear relationship between $\ln(I^{\mathrm{obs}}_{hkl}/I^{\mathrm{calc}}_{hkl})$ and $\sin^2\theta_{hkl}/\lambda^2$ must be obtained, according to the equation (*21*)

$$\ln(I^{\mathrm{obs}}_{hkl}/I^{\mathrm{calc}}_{hkl}) = \ln K - 2B_{\mathrm{eff}}\sin^2\theta_{hkl}/\lambda^2, \quad (3)$$

where I^{obs}_{hkl} is the experimentally observed intensity, $I^{\mathrm{calc}}_{hkl} = |FF^*|Lpm$, K is a scale factor, B_{eff} the temperature factor, θ_{hkl} the diffraction angle, and λ the wavelength of the radiation used. Atomic scattering factors were calculated according to the equation and coefficients given in the International Tables for X-Ray Crystallography, and corrections for anomalous scattering (as shown in the same tables) were also incorporated.

The values obtained for the oxygen parameter u and cation distribution of each spinel are shown in Table II. Numbers in parentheses indicate the standard deviation of each parameter in units of the last significant figure. These deviations were calculated applying a Monte Carlo method described elsewhere (*20*). The linear regression coefficient r of Eq. (3) was never smaller than $r^2 = 0.81$.

Discussion

In a crystalline compound containing distorting ions (such as d^9 Cu^{2+}) regularly arranged on a lattice the interaction between the distortions can lead, at sufficiently low temperatures, to the trapping of each distortion in a fixed orientation to the others, giving rise to a cooperative Jahn–Teller effect (*22, 23*). However, the X-ray diffractograms of $CuAl_2O_4$ and the other copper-containing spinels did not reveal any departure from the cubic symmetry. The temperature of preparation (1223 K) was evidently high enough to preclude any cooperative effect.

For the cubic $CuAl_2O_4$ spinel we have found a lattice parameter $a_0 = 807.9$ pm and an oxygen parameter $u = 0.3867$, in agreement with the values $a_0 = 807.8$ pm, $u = 0.386$ reported by Cooley and Reed (*12*). The inversion parameter γ, defined as the fraction of divalent ions in octahedral sites, is $\gamma = 0.35$ (Table II) and corresponds to the temperature of 1223 K from which the spinel was quenched. This is entirely consistent with the values $\gamma = 0.32$ (at 886 K) and $\gamma = 0.36$ (at 1468 K) given by the above-mentioned authors.

The unit-cell length found for $NiAl_2O_4$ ($a_0 = 805.0$ pm) agrees closely with the value of 804.78 pm reported by Porta *et al.* (*4*). The inversion parameter is $\gamma = 0.844$ (Table

TABLE II

OXYGEN PARAMETER AND CATION DISTRIBUTION IN $Cu_xNi_{1-x}Al_2O_4$ SPINELS

Mole fraction of Cu^{2+}, x	Oxygen parameter, u	Cation distribution					
		Tetrahedral sites			Octahedral sites		
		Cu^{2+}	Ni^{2+}	Al^{3+}	Cu^{2+}	Ni^{2+}	Al^{3+}
0	0.3798(3)	—	0.156(2)	0.844(2)	—	0.844(2)	1.156(2)
0.25	0.3824(2)	0.23(4)	0.04(5)	0.73(1)	0.02(4)	0.71(5)	1.27(1)
0.50	0.3844(2)	0.35(2)	0.01(2)	0.64(1)	0.15(2)	0.49(2)	1.36(1)
0.75	0.3861(2)	0.51(2)	0.01(3)	0.48(1)	0.24(2)	0.24(3)	1.52(1)
1	0.3867(4)	0.649(5)	—	0.351(5)	0.351(5)	—	1.649(5)

Note. Mean values are given, with standard deviations in parentheses.

II) and is to be compared with $\gamma = 0.84$ and $\gamma = 0.78$ determined by Furuhashi *et al.* (*14*) and by Porta *et al.* (*4*), respectively. Our previous value (*15*) for a sample of $NiAl_2O_4$ quenched from 1273 K is $\gamma = 0.836$. The sample described in the present paper was quenched from 1223 K; a small temperature effect is observed. The oxygen parameter $u = 0.3798$ (Table II) is consistent with the value $u = 0.379$ reported by Furuhashi *et al.* (*14*). Porta *et al.* (*4*) have not determined this parameter for $NiAl_2O_4$.

Table I shows that a_0 increases continuously as the copper content of the spinels is increased. This is a direct consequence of the larger volume of Cu^{2+} compared with Ni^{2+}. According to Shannon (*24*) the ionic radii of Cu^{2+}, Ni^{2+}, and Al^{3+} in tetrahedral (tet) and octahedral (oct) coordination are: $Cu_{tet} = 57$ pm, $Cu_{oct} = 73$ pm, $Ni_{tet} = 55$ pm, $Ni_{oct} = 69$ pm, $Al_{tet} = 39$ pm, $Al_{oct} = 53.5$ pm.

More quantitatively, it is also seen in Table I that the a_0 values for the ternary spinels $Cu_xNi_{1-x}Al_2O_4$ ($0 < x < 1$) lead to a negative deviation from a linear variation of either the lattice parameter or the unit-cell volume. Inspection of Table II shows that the replacement of Ni^{2+} by Cu^{2+} is not a simple matter of the latter ion occupying the sites previously taken by the former. As x increases there is a marked positional change. The tetrahedral sites acquire a larger proportion of divalent ions, while Al^{3+} ions are transferred from tetrahedral to octahedral sites. This can explain in finer detail the observed variation of a_0.

The tetrahedral bond length, d_{AO} (distance between the center of a tetrahedrally coordinated cation and the center of the nearest anions) is given by

$$d_{AO} = \sqrt{3}(u - 0.25)a_0 \qquad (4)$$

and the octahedral bond length, d_{BO} is

$$d_{BO} = [3u^2 - (11u/4) + (43/64)]^{1/2}a_0. \qquad (5)$$

Using the values of a_0 and u given in Tables I and II, and taking 138 pm as the radius of the O^{2-} ion (*24*), Eqs. (4) and (5) lead to values of d_{AO}, d_{BO}, r_{tet}, and r_{oct} given in Table III, where r_{tet} and r_{oct} are the mean sizes of the tetrahedral and octahedral interstices, respectively. It is now seen that the octahedral interstices in $NiAl_2O_4$ ($r_{oct} = 59$ pm) are too large to accommodate an increasing proportion of Al^{3+} ($r_{oct} = 53.5$ pm) in the $Cu_xNi_{1-x}Al_2O_4$ spinels. To stabilize the octahedrally coordinated Al^{3+} ion, r_{oct} must decrease when x is increased, which is indeed observed in the last column of Table III. This is accomplished through (i) an increasing value of the oxygen parameter, and (ii) an increase of a_0 smaller than what would correspond to a linear variation between the values for $NiAl_2O_4$ and $CuAl_2O_4$, thus explaining the above-mentioned negative deviation. The increasing value of u also allows the expansion of the tetrahedral sites (Table III) needed to accommodate the progressively larger proportion of the more voluminous, divalent ions with tetrahedral coordination.

The standard deviations in the cation distribution results for Cu^{2+} and Ni^{2+} given in Table II show that the one-electron difference between these two cations is enough to render them distinguishable by X-ray diffraction. This was also proved to be the case for the ion pairs Cu^{2+}/Zn^{2+} in Cu_xZn_{1-x}

TABLE III

MEAN LENGTHS OF THE TETRAHEDRAL (d_{AO}) AND OCTAHEDRAL (d_{BO}) BONDS AND SIZES OF THE CORRESPONDING INTERSTICES IN $Cu_xNi_{1-x}Al_2O_4$ SPINELS

x	d_{AO} (pm)	d_{BO} (pm)	r_{tet} (pm)	r_{oct} (pm)
0	181	197	43	59
0.25	184	196	46	58
0.50	187	194	49	56
0.75	190	193	52	55
1	191	193	53	55

Al_2O_4 spinels (*20*) and Cu^{2+}/Ga^{3+} in $CuGa_2O_4$ (*25*).

Table II shows that the spinel $NiAl_2O_4$ is 84% inverted. The strong octahedral preference of Ni^{2+} (a d^8 ion) can be ascribed to well-known crystal field stabilization effects. According to Dunitz and Orgel (*26*) the octahedral stabilization energy of Ni^{2+} amounts to 86 kJ $mole^{-1}$; therefore, the high degree of inversion found for $NiAl_2O_4$ is readily explained. In the ternary spinels $Cu_xNi_{1-x}Al_2O_4$ the percentage of octahedrally coordinated Ni^{2+} is even higher than in $NiAl_2O_4$; thus, 95% of the Ni^{2+} ions occupy octahedral sites in $Cu_{0.25}Ni_{0.75}Al_2O_4$, and 98% in $Cu_{0.5}Ni_{0.5}Al_2O_4$. It should be remembered that anion polarization effects favor an ionic partition where the divalent ions occupy tetrahedral sites (*27, 28*). The presence of tetrahedrally coordinated Cu^{2+} in the ternary spinels allows Ni^{2+} to occupy almost exclusively octahedral sites while maintaining tetrahedrally coordinated divalent ions to benefit from the stabilization due to polarization effects.

References

1. G. Blasse, *Philips Res. Rep. Suppl.* No 3 (1964).
2. C. Glidewell, *Inorg. Chim. Acta* **19,** 445 (1976).
3. J. K. Burdett, G. D. Price, and S. L. Price, *J. Amer. Chem. Soc.* **104,** 92 (1982).
4. P. Porta, F. S. Stone, and R. G. Turner, *J. Solid State Chem.* **11,** 135 (1974).
5. S. M. Zhilyakov, V. V. Ivolga, V. J. Mal'tsev, and E. P. Naiden, *Sov. Phys. Solid State* **19,** 1817 (1977).
6. K. Seshan, A. L. Shashimohan, D. K. Chakrabarty, and A. B. Biswas, *Phys. Status Solidi A* **68,** 97 (1981).
7. T. O. Mason and H. K. Bowen, *J. Amer. Ceram. Soc.* **64,** 86 (1981).
8. P. Porta, A. Anichini, and A. Guglietti, *Gazz. Chim. Ital.* **113,** 595 (1983).
9. J. S. Díez Viñuela, C. Otero Areán, and F. S. Stone, *J. Chem. Soc. Faraday Trans. 1* **79,** 1191 (1983).
10. F. C. Romeijn, *Philips Res. Rep.* **8,** 321 (1953).
11. E. W. Gorter, *Philips Tech. Rep.* **9,** 295 (1954).
12. R. F. Cooley and J. S. Reed, *J. Amer. Ceram. Soc.* **55,** 395 (1972).
13. F. Pepe, P. Porta, and M. Schiavello, *in* "Proceedings, 8th International Symposium on Reactivity of Solids (Gothenburg, 1976)" (J. Wood, O. Lindqvist, C. Helgesson, and N. G. Vannerberg, Eds.), p. 183, Plenum, New York (1977).
14. H. Furuhashi, M. Inagaki, and S. Naka, *J. Inorg. Nucl. Chem.* **35,** 3009 (1973).
15. C. Otero Areán, M. L. Rodríguez Martínez, and A. Mata Arjona, *Mater. Chem. Phys.* **8,** 443 (1983).
16. H. P. Klug and L. E. Alexander, "X-Ray Diffraction Procedures: For Crystalline and Amorphous Materials," p. 361, Wiley, New York (1974).
17. L. Végard, *Z. Phys.* **5,** 17 (1921).
18. L. Végard and H. Dale, *Z. Kristallogr.* **67,** 148 (1928).
19. E. an Zen, *Amer. Mineral.* **41,** 523 (1956).
20. C. Otero Areán, J. S. Díez Viñuela, J. M. Rubio González, and A. Mata Arjona, *Mater. Chem.* **6,** 165 (1981).
21. A. J. C. Wilson, *Nature (London)* **150,** 152 (1964).
22. E. Prince, *Acta Crystallogr.* **10,** 554 (1957).
23. E. Pytte, *Phys. Rev. B* **3,** 3503 (1971).
24. R. D. Shannon, *Acta Crystallogr. Sect. A* **32,** 751 (1976).
25. F. S. Stone, C. Otero Areán, J. S. Díez Viñuela, and E. Escalona Platero, *J. Chem. Soc. Faraday Trans. 1* **81,** 1255 (1985).
26. J. D. Dunitz and L. E. Orgel, *J. Phys. Chem. Solids* **3,** 318 (1957).
27. J. Smit, F. K. Lotgering, and R. P. van Stapele, *J. Phys. Soc. Jpn.* **17,** 268 (1962).
28. J. Smit, *Solid State Commun.* **6,** 745 (1968).