

## X-ray study of some spinels containing gallium and manganese

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**Abstract.** The ternary oxides  $\text{CrMnGaO}_4$ ,  $\text{NiMnGaO}_4$ ,  $\text{CuMnGaO}_4$  and  $\text{ZnMnGaO}_4$ , crystallize in the cubic spinel structure with lattice parameter  $a=8.41 \pm 0.02 \text{ \AA}$ ,  $8.34 \pm 0.02 \text{ \AA}$ ,  $8.36 \pm 0.02 \text{ \AA}$  and  $8.32 \pm 0.02 \text{ \AA}$ , respectively. The oxidation state of manganese in these spinels was determined x-ray spectroscopically. The site distribution was determined from the structural properties and calculated site preference energies of cations in the lattice. The ionic structures were found to be  $\text{Ga}^{3+} [\text{Mn}^{2+} \text{Cr}^{3+}] \text{O}_4^{2-}$ ,  $\text{Ga}^{3+} [\text{Cu}^{2+} \text{Mn}^{3+}] \text{O}_4^{2-}$ ,  $\text{Mn}^{2+} [\text{Ga}^{3+} \text{Ni}^{3+}] \text{O}_4^{2-}$  and  $\text{Zn}^{2+} [\text{Mn}^{3+} \text{Ga}^{3+}] \text{O}_4^{2-}$ .

**Keywords.** X-ray spectroscopy; spinel structure;  $\text{CrMnGaO}_4$ ;  $\text{NiMnGaO}_4$ ;  $\text{CuMnGaO}_4$ ;  $\text{ZnMnGaO}_4$ .

### 1. Introduction

The binary and ternary oxides having spinel structure have attracted wide attention in recent years, because of their remarkable electrical and magnetic properties which depend upon the oxidation states and location of the cations at the tetrahedral (A) and octahedral (B) sites in the lattice. In this paper we report results obtained on the ionic structures of the spinels  $\text{CrMnGaO}_4$ ,  $\text{NiMnGaO}_4$ ,  $\text{CuMnGaO}_4$  and  $\text{ZnMnGaO}_4$  by using x-ray diffraction and x-ray spectroscopic techniques. Among the several methods (Mathur *et al* 1947 and O'Keeffe 1961) for determining the valency of ions, x-ray spectroscopy is the most suitable method (Kulkarni *et al* 1971) because of its specificity. Out of the four spinels studied in this work some information is already available (Bongers 1957 and Robbins *et al* 1966) about the compounds  $\text{NiMnGaO}_4$ ,  $\text{CuMnGaO}_4$  and  $\text{ZnMnGaO}_4$ . The spinel  $\text{CrMnGaO}_4$  has been prepared for the first time.

### 2. Experimental

*Preparation and identification:* The oxides  $\text{MeMnGaO}_4$ , where  $\text{Me}=\text{Cr}$ ,  $\text{Ni}$ ,  $\text{Cu}$  and  $\text{Zn}$ , were prepared (Economos 1956) by mixing the reacting oxides of analar grade in stoichiometric proportions under acetone. The mixtures were heated in a platinum crucible in an electrically operated furnace for several hours at  $900^\circ\text{C}$ . In order to avoid the random distribution (Millar 1968) of the ions in the lattice the samples were cooled slowly to room temperature in about 8–10 hr.

The formation of the oxides was confirmed from their powder patterns taken on a 57.3 mm Debye-Scherrer camera using filtered copper radiation. The observed  $1/d^2$  values for the various atomic planes, obtained from the measurements on the diffraction patterns are given in table 1 along with the observed intensities of the

**Table 1.** X-ray diffraction data of the spinels

<i>hkl</i>	$1/d^2$		Intensity		<i>hkl</i>	$1/d^2$		Intensity	
	Obs.	Cal.	Obs.	Cal.		Obs.	Cal.	Obs.	Cal.
CrMnGaO <sub>4</sub> $a=8.41\pm 0.02$ Å					CuMnGaO <sub>4</sub> $a=8.36\pm 0.02$ Å				
111	0.0456	0.0424	<5	<3	111	0.0444	0.0429	<5	<3
220	0.1148	0.1130	35	34.2	220	0.1139	0.1144	30	31.2
311	0.1574	0.1554	100	100	311	0.1584	0.1574	100	100
400	0.2288	0.2260	15	13.3	400	0.2298	0.2289	15	14.1
422	0.3419	0.3391	15	13.5	422	0.3460	0.3434	15	10.98
511 } 333 }	0.3838 0.3815	0.3815	25	24.7 } 8.2 }	511 } 333 }	0.3872 0.3863	0.3863	25	22.41 } 7.98 }
440	0.4528	0.4521	45	44.7	440	0.4590	0.4579	45	41.9
531	0.4916	0.4945	<5	<3	533	0.6161	0.6153	10	10.4
533	0.6056	0.6076	10	10.8	642	0.7931	0.8013	5	5.8
731	0.8309	0.8336	15	13.6	731	0.8417	0.8442	15	13.3
555	1.0584	1.0597	<5	<3	800	0.9192	0.9158	5	6.7
931	1.2795	1.2858	15	12.1	555	1.0694	1.0732	<5	<2
844	1.3490	1.3564	30	28.1	931	1.3002	1.3022	15	12.0
951	1.5049	1.5109	20	17.0	844	1.3679	1.3737	30	28.2
					951	1.5278	1.5311	20	18.0
NiMnGaO <sub>4</sub> $a=8.34\pm 0.02$ Å					ZnMnGaO <sub>4</sub> $a=8.32\pm 0.02$ Å				
111	0.0451	0.0429	<5	<3	111	0.0451	0.0433	<5	<3
220	0.1172	0.1144	20	20.6	220	0.1163	0.1156	30	30.4
311	0.1607	0.1573	100	100	311	0.1605	0.1589	100	100
222	0.1742	0.1716	10	7.3	400	0.2308	0.2312	15	13.0
400	0.2328	0.2288	30	24.7	422	0.3476	0.3468	10	11.8
422	0.3470	0.3432	10	7.6	511 } 333 }	0.3896 0.3901	0.3901	25	24.3 } 8.1 }
511 } 333 }	0.3885 0.3861	0.3861	30	23.4 } 7.8 }	440	0.4621	0.4624	45	42.5
440	0.4634	0.4576	45	43.2	620	0.5791	0.5780	5	4.7
620	0.5739	0.5720	5	5.0	533	0.6229	0.6213	10	10.4
533 } 622 }	0.6218 0.6149	0.6149	15	10.5	642	0.8116	0.8092	5	5.7
444	0.6887	0.6864	<5	<3	731	0.8494	0.8525	15	13.4
642	0.8110	0.8008	5	6.1	555	1.0806	1.0837	20	19.0
731	0.8539	0.8437	15	13.6	844	1.3873	1.3872	30	30.0
800	0.9208	0.9152	5	6.9	951	1.5394	1.5461	20	19.4
660	1.0340	1.0296	<5	<3					
555	1.0782	1.0725	<5	<3					
840	1.1477	1.1440	5	3.5					
931	1.3090	1.3013	15	12.8					
844	1.3776	1.3728	35	29.9					
862	1.4901	1.4872	10	7.3					
951	1.5356	1.5301	20	19.4					

diffraction lines. Also included in the table are the  $1/d^2$  values calculated from the mean lattice parameter 'a'. Our data show that CrMnGaO<sub>4</sub>, NiMnGaO<sub>4</sub>, CuMnGaO<sub>4</sub> and ZnMnGaO<sub>4</sub> have cubic spinel structure (space group  $Fd\bar{3}m$ ) with  $a=8.41\pm 0.02$  Å,  $8.34\pm 0.02$  Å,  $8.36\pm 0.02$  Å and  $8.32\pm 0.02$  Å respectively.

**Table 2.** The site distribution in the spinels

Spinel	A Site occupied by		$I_{220}/I_{422}$		$I_{422}/I_{400}$	
			Calc.	Obs.	Calc.	Obs.
CrMnGaO <sub>4</sub>	(i)	Ga <sup>3+</sup>	2.53	2.33	1.01	1.0
	(ii)	Mn <sup>2+</sup>	2.73		0.43	
NiMnGaO <sub>4</sub>	(i)	Ga <sup>3+</sup>	2.50	2.0	0.88	0.33
	(ii)	Mn <sup>2+</sup>	2.70		0.30	
CuMnGaO <sub>4</sub>	(i)	Ga <sup>3+</sup>	2.84	2.0	0.78	1.0
	(ii)	Cu <sup>2+</sup>	3.02		0.54	
ZnMnGaO <sub>4</sub>	(i)	Ga <sup>3+</sup>	2.56	3.0	0.91	0.66
	(ii)	Zn <sup>2+</sup>	2.51		0.90	

The intensities of various observed reflections were calculated using the formula

$$I_{hkl} \propto |F_{hkl}|^2 P \frac{1 + \cos^2 \theta}{\cos \theta \sin^2 \theta}$$

where the symbols have their usual meaning. The most intense reflection was always from the (311) planes which was given an arbitrary intensity 100. The relative intensities for all the planes were calculated using (311) reflection as the standard. These calculations were carried out for an ideal close packing i.e., the oxygen ion parameter to be equal to 3/8. The calculated intensities are in good agreement with the observed intensities. In order to determine the site distribution, the intensity ratios  $I_{220}/I_{422}$  and  $I_{422}/I_{400}$ , were calculated and compared with the observed ratios for different possible cation distributions in all these spinels (table 2). The Ga<sup>3+</sup> ions in CrMnGaO<sub>4</sub> and CuMnGaO<sub>4</sub>, Zn<sup>2+</sup> ions in ZnMnGaO<sub>4</sub>, and Mn<sup>2+</sup> ions in NiMnGaO<sub>4</sub> occupy the A sites. The site preference energies for these cations given by various workers (McClure 1957, Dunitz *et al* 1957 and Miller 1959) also support our observations. In case of NiMnGaO<sub>4</sub> alone, one could not distinguish between occupation of A sites by either Mn<sup>2+</sup> or Ga<sup>3+</sup> ions on the basis of site preference energies.

*X-ray spectroscopic study:* A Machlett sealed x-ray tube with a copper target was used as a source of white radiation for x-ray absorption work throughout this study. A Cauchois type Blokhin (1962) bent crystal x-ray spectrograph of 400 mm diameter, equipped with a mica crystal with (100) as reflecting planes was used to record the spectra of manganese in manganese metal, in the spinels and in some compounds of well known valencies. The exposure times varied from 8 to 12 hr for obtaining a good contrast. The x-ray spectroscopic results are given in table 3. The wavelength of K absorption limit for manganese metal reported by Cauchois and Hulubei (1947) is also included in table 3 for comparison. From the observed chemical shifts for the manganese ion in the four spinels it is found using Kunzl's law (Kunzl 1932) that manganese is in the divalent state in CrMnGaO<sub>4</sub> and NiMnGaO<sub>4</sub> and in trivalent state in CuMnGaO<sub>4</sub> and ZnMnGaO<sub>4</sub>. We have not studied the absorption spectra of Zn and Ga in the spinels because these ions have most stable valencies two and three (Remy 1956) respectively. It was not possible to record the K absorption spectra

**Table 3.** Wavelengths of the K-absorption edges of manganese

Absorber	Valency	Wavelength X.U.	Chemical shift X.U.
Mn metal [Cauchois and Hulubei (1947)]	—	1892.54	—
Mn metal (Present work)	—	1892.6	—
MnCl <sub>2</sub> · 4H <sub>2</sub> O	2	1890.9	1.7
MnO	2	1890.8	1.8
MnCO <sub>3</sub>	2	1891.1	1.5
Mn <sub>2</sub> O <sub>3</sub>	3	1888.9	3.7
Mn <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	3	1889.1	3.5
MnO <sub>2</sub>	4	1887.6	5.0
CrMnGaO <sub>4</sub>	—	1890.7	1.9
NiMnGaO <sub>4</sub>	—	1890.6	2.0
CuMnGaO <sub>4</sub>	—	1888.8	3.8

of Cu and Ni because of the interference with the Cu K<sub>β5</sub> and W L<sub>α</sub> lines in the spectra.

### 3. Discussion

*Ionic Structure of CrMnGaO<sub>4</sub>:* The possible charge distributions for this spinel are (i) Cr<sup>3+</sup> Mn<sup>2+</sup> Ga<sup>3+</sup> O<sub>4</sub> and (ii) Cr<sup>2+</sup> Mn<sup>3+</sup> Ga<sup>3+</sup> O<sub>4</sub>. Our x-ray spectroscopic results given in table 3 show that manganese ions are in the divalent state, in this spinel, thus ruling out the second valence structure. As shown earlier the gallium ions are at the A sites. Hence we may write the ionic structure of this spinel as Ga<sup>3+</sup> [Mn<sup>2+</sup> Cr<sup>3+</sup>] O<sub>4</sub>.

*Ionic Structure of NiMnGaO<sub>4</sub>:* The possible valance structures for this spinel are (i) Ni<sup>2+</sup> Mn<sup>3+</sup> Ga<sup>3+</sup> O<sub>4</sub> and (ii) Ni<sup>3+</sup> Mn<sup>2+</sup> Ga<sup>3+</sup> O<sub>4</sub>. From magnetic studies Bongers (1957) has found that the manganese ion is in the trivalent state in this spinel. Our x-ray spectroscopic results given in table 3 clearly show that manganese ions are divalent in this spinel, ruling out the first charge distribution. Also the lattice parameter and intensities are found to agree well with the second valance structure. As has already been shown the manganese ions occupy the A sites. Hence, we may write the ionic structure of the spinel as Mn<sup>2+</sup> [Ga<sup>3+</sup> Ni<sup>3+</sup>] O<sub>4</sub>.

*Ionic Structure of CuMnGaO<sub>4</sub>:* The possible charge distributions in this spinel are (i) Cu<sup>2+</sup> Mn<sup>3+</sup> Ga<sup>3+</sup> O<sub>4</sub> and (ii) Cu<sup>+</sup> Mn<sup>4+</sup> Ga<sup>3+</sup> O<sub>4</sub>.

Our x-ray spectroscopic results (table 3) indicate that the valency of manganese ions is three in this spinel, which is found to agree with those of Bongers (1957). However, there is a difference about the cation distribution: Bongers believes that Cu<sup>2+</sup> ions occupy A sites while our results (table 2) indicate that the Ga<sup>3+</sup> ions are in the A sites. The relative site preference energies and the observed lattice parameter favour this site distribution. It is rather difficult to explain the symmetry of this spinel in which the B sites are occupied by the two distorting ions Cu<sup>2+</sup> and Mn<sup>3+</sup>. The tetragonal-

cubic transition temperature of this oxide lies below the room temperature; the manganese ions are in the low spin state and the number of  $\text{Cu}^{2+}$  ions in the B sites are insufficient to cause any distortion. Hence, we may write the ionic structure of the spinel as  $\text{Ga}^{3+} [\text{Cu}^{2+} \text{Mn}^{3+}] \text{O}_4$ .

*Ionic Structure of  $\text{ZnMnGaO}_4$* : Bongers (1957) found that there is a distortion of lattice with  $c > a$  in this spinel. But, our x-ray diffraction data given in table 1 show that this spinel is cubic. The difference could be due to the difference in the method of preparation as pointed out by Millar (1968): sudden quenching of the sample gives rise to random distribution of cations at different sites which lowers down the symmetry of the lattice. As shown earlier  $\text{Zn}^{2+}$  ions occupy the A sites in this spinel; hence, we may write the ionic structure as  $\text{Zn}^{2+} [\text{Mn}^{3+} \text{Ga}^{3+}] \text{O}_4$ .

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