



Indian J. Phys. **68A** (4), 393–395 (1994)

I J P A
- an international journal

X-ray intensities and structural studies of the spinel MgCr_2O_4

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Received 1 February 1994, accepted 11 April 1994

Abstract : Assignment of space group for the compound MgCr_2O_4 aroused many controversies. Compound being cubic spinel, usual assigned space group is $Fd\bar{3}m$. But critical study of MgCr_2O_4 showed some additional reflections, which are not permitted by space group $Fd\bar{3}m$. Grimes suggested the space group $F\bar{4}3m$ for the same. A comparative study of X-ray intensities of the compound by using both the space groups $Fd\bar{3}m$ and $F\bar{4}3m$ is carried out in the present work.

Keywords : Cubic spinel, intensity calculations, space group assignment

PACS Nos. : 61.10.My, 61.50.Em, 61.66.Fn

A group of oxides with formula XY_2O_4 with crystal structure of either MgAl_2O_4 or Mn_3O_4 is known as spinel. These spinel structures are cubic or tetragonal unit cells respectively, which have similar atomic arrangements in a unit cell. The space group associated with the cubic structure is $Fd\bar{3}m$ (MgAl_2O_4) in which B-sites have $3m$ point symmetry [1]. Many binary spinels containing Mg^{+2} are studied by various workers and explained the results on the basis of previously well-tested space group $Fd\bar{3}m$. Later on, critical study of MgCr_2O_4 [2-5] is carried out indicating that there are some additional reflections which are not permitted by space group $Fd\bar{3}m$. These extra reflections are linked [6-9] with displacement of B-cations (Cr^{+3}) along $[1,1,1]$ direction which in effect reduces the point symmetry to $3m$ with space group $F\bar{4}3m$. The oxides of Mg^{+2} found to be controversial due to iso-electronic scattering with O^{-2} for X-rays.

It is interesting to know that all compounds with XY_2O_4 need not have spinel structure e.g. BeAl_2O_4 , MgSi_2O_4 etc. So complete structure along with exact space group can only be known if atomic positions are determined by systematic matching of intensities. Intensity depends upon scattering powers of the atomic centre and vary with ' λ ' and ' T '. Assuming

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effect of 'T' to be very small, one can estimate intensities sufficiently accurate for the purpose of structure determination. We calculated intensities for the cubic spinel MgCr_2O_4 using both the space group $\text{Fd}\bar{3}\text{m}$ and $\text{F}\bar{4}3\text{m}$.

Intensity for non-zero reflections can be computed using the formula

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

where symbols have usual meanings.

The amplitude of structural factor $[F_{hkl}]$ is obtained from the expression

$$|F_{hkl}| = \left[(f_r A_r)^2 + (f_r B_r)^2 \right]^{1/2}.$$

The values of A and B factors for space groups $\text{F}\bar{4}3\text{m}$ and $\text{Fd}\bar{3}\text{m}$ are first calculated [10].

The intensities for all the observed planes are then calculated. Values of I/I_{max} (observed), I/I_{max} (for $\text{Fd}\bar{3}\text{m}$) and I/I_{max} (for $\text{F}\bar{4}3\text{m}$) for all the planes are listed in the Table 1.

Table 1. A comparative study of the intensities

hkl	Observed I/I_{max}	I/I_{max} (cal) ($\text{Fd}\bar{3}\text{m}$)	I/I_{max} (cal) ($\text{F}\bar{4}3\text{m}$)
220	14	11.97	11.93
311	100	100.00	100.00
222	14	10.56	10.60
400	55	52.99	52.95
422	4	3.26	3.66
511	40	25.27	38.82
440	55	38.82	38.82
531	14	10.48	10.50
620	40	13.08	13.08

Our results based on both the space groups show that the changes in the intensities are very small and one can not be sure enough to say that the compound possesses the space group $\text{F}\bar{4}3\text{m}$. There appears to be a large degree of difference between the report in the intensities of MgCr_2O_4 . The most intense plane for 440 then 311 plane may not be due to displacement of Cr^{+3} ions as suggested earlier, but may be due to the ordering of cations and formation of superlattice and/or constructing interference of Mg^{+2} and O^{-2} ions which are isoelectronic and have similar scattering powers. So there is no necessity of changing the

space group from Fd3m to F $\bar{4}$ 3m. Some of the forbidden reflections may be explained on the basis of superlattice formation just like alloys.

Acknowledgments

One of the authors is thankful to Inter University Consortium for DAEF, Indore for providing financial aid.

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