Acta Cryst. (1975). A**31**, 820

Thermal Expansion of Natural Spinel, Ferroan Gahnite, Magnesiochromite, and Synthetic Spinel

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(*Received* 1 *April* 1975; *accepted* 28 *May* 1975)

The lattice parameters of natural spinel, ferroan gahnite, magnesiochromite, and synthetic spinel at elevated temperatures have been determined. The results are: spinel $a_t = 8{\cdot}0870 + 35{\cdot}24 \times 10^{-6}t + 45{\cdot}73 \times 10^{-9}t^2$, $22 < t < 840$°C; ferroan gahnite $a_t = 8{\cdot}1050 + 54{\cdot}35 \times 10^{-6}t + 10{\cdot}53 \times 10^{-9}t^2$, $22 < t < 845$°C; magnesiochromite $a_t = 8{\cdot}2965 + 56{\cdot}82 \times 10^{-6}t + 8{\cdot}08 \times 10^{-9}t^2$, $22 < t < 823$°C, synthetic spinel $a_t = 8{\cdot}0821 + 45{\cdot}79 \times 10^{-6}t + 35{\cdot}69 \times 10^{-9}t^2$, $26 < t < 800$°C, where a_t is the lattice parameter in Å at t°C. Expressions for thermal expansions are derived. The replacement of magnesium cations by zinc and iron and of Al_2O_3 by Cr_2O_3 in spinel decreases the mean thermal expansion in the range of temperatures covered, but increases the lattice parameters.

Introduction

Little has been published on the thermal expansions of natural minerals, as can be seen from the data summarized by Skinner (1966). The mean thermal expansion coefficients of synthetic spinel, gahnite and magnesiochromite have been measured by Beals & Cook (1957), who measured interplanar d_{420} spacing for each of the test temperatures between 20 to 1200°C. The thermal expansion of the spinel at elevated temperatures was measured dilatometrically by Rigby, Lowell & Green (1946) and Nielsen & Leipold (1963). No thermal-expansion data for natural spinels are available in the literature. This work, therefore, was undertaken to measure precisely the lattice parameters of natural spinel, ferroan gahnite, magnesiochromite, and synthetic spinel and to calculate the thermal expansion coefficients.

Experimental

Specimens of natural spinel, ferroan gahnite, and magnesiochromite were selected and checked for homogeneity and single phase with an X-ray diffraction technique. Properties determined by Horai & Simmons (1969), as well as the density of these samples are given in Table 1. The chemical composition of each sample was determined with a microprobe and these analyses along with that of the synthetic spinel are given in Table 2. From the analyses the formulas $Mg_{0{\cdot}93}Fe_{0{\cdot}07}Al_2O_4$, $Zn_{0{\cdot}49}Fe_{0{\cdot}38}Mg_{0{\cdot}13}Al_2O_4$, and $Mg_{0{\cdot}34}Fe_{0{\cdot}42}(Cr_2O_4)_{0{\cdot}76}{\cdot}24MgAl_2O_4$ can be calculated for spinel, ferroan gahnite, and magnesiochromite respectively.

Table 2. *Microprobe analyses of the materials*

	Spinel natural	Gahnite	Magnesio-chromite	Spinel synthetic
Al_2O_3	71·7	56·8	12·3	71·5
TiO_2	–	–	0·2	–
Cr_2O_3	0·1	–	57·0	–
FeO	3·7	16·1	14·9	–
MgO	25·7	3·2	15·3	28·3
ZnO	–	23·3	–	–
	101·2	99·4	99·7	99·8

We used a Norelco wide-range goniometer with an MRC high-temperature diffractometer attachment. Thin-film sample mounts were found to be most suitable for this work. High-purity aluminum and silicon

Table 1. *Characterization of experimental materials*

Mineral name Location	Spinel (natural) Antsiriki Madagascar	Ferroan gahnite Guffey, Colorado	Magnesiochromite Quebec, Canada
Thermal conductivity* [m cal cm^{-1} (°C^{-1})]	22·65	10·26	6·06
Bulk density* (g cm^{-3})	3·633	4·163	4·231
X-ray density† (g cm^{-3})	3·771	4·349	4·500

* Horai & Simmons (1969).
† Calculated with our lattice parameters at 20°C.

(Simmons, 1970; Pearson, 1967) were used as internal standards for low and high temperatures respectively since they mixed with the samples uniformly and gave a uniform smooth thin coating. The temperature of the heating stage was controlled to ± 2°C with the MRC temperature controller. The sample was annealed and scanned from 90 to 140° 2θ in both the up and down directions. The peaks corresponding to the reflexions 731, 751, 931, and 844 were used in the calculation of the lattice parameters. The wavelengths of Cu $K\alpha_1 = 1{\cdot}540562$ Å and Cu $K\alpha_2 = 1{\cdot}544390$ Å (Bearden, 1967) were used in the calculation.

The lattice constants were calculated by Cohen's (1935) analytical method using the $\cos\theta\cot\theta$ extrapolation function. The variation of lattice parameter is expressed in analytical form using a least-squares method:

$$a_t = a_0 + bt + ct^2 + \cdots \quad (1)$$

where a_t is the lattice parameter in Å at t°C and $a_0, b, c, \cdots$ are constants. The linear thermal expansion is

$$\alpha_t = \alpha_0 + \beta t + \cdots . \quad (2)$$

where α_t the thermal expansion coefficient at temperature t°C and $\alpha_0, \beta \cdots$ are constants. The mean thermal expansion coefficient is also presented in the given range of temperatures for each sample.

Results and discussion

The measured lattice parameters are adequately expressed by equation (1) and the thermal expansion by equation (2). The appropriate constants, determined by a least-squares fit of data, for natural spinel, ferroan gahnite, magnesiochromite, and synthetic spinel are given in Table 3. A parabolic equation for the lattice parameters fits the data better than a cubic equation. The maximum difference between the observed and the calculated lattice parameters is 0·0009 Å which may be taken as the precision of the measurements for the temperature range covered.

Table 3. *Constants for lattice parameter and thermal expansion for the expressions* $a_t = a_0 + bt + ct^2$ *and* $\alpha_t = \alpha_0 + \beta t$

The temperature range is 22° to 840°C.

Mineral	a_0	$b \times 10^6$	$c \times 10^9$	$\alpha \times 10^6$	$\beta \times 10^9$
Spinel, natural	8·0870	35·24	45·73	4·358	11·31
Spinel, synthetic	8·0821	45·79	35·69	5·666	8·83
Ferroan gahnite	8·1050	54·35	10·53	6·705	2·60
Magnesiochromite	8·2965	56·82	8·08	6·849	1·95

The lattice parameters and thermal expansion coefficients for natural $Mg_{0\cdot93}Fe_{0\cdot07}Al_2O_4$ and synthetic $MgAl_2O_4$ spinels are calculated with the above equations and are shown in Tables 4 and 5 respectively, along with the measured lattice parameters at various temperatures. The lattice constant for the natural spinel is 8·0878 Å at 22°C, whereas that of synthetic spinel is 8·0833 Å at 26°C. These data show that a small amount of iron replacing magnesium ions increases the lattice parameter. Other thermal expansion data determined by various authors along with our results are summarized in Table 6. Our studies on the thermal expansion of synthetic ($MgAl_2O_4$) and natural ($Mg_{0\cdot93}Fe_{0\cdot07}Al_2O_4$) spinel under the same conditions show that the mean thermal expansion for synthetic spinel is higher than that of natural spinel. This reveals that the replacement of Mg^{2+} by Fe^{2+} in spinel decreases the mean thermal expansion in the temperature range covered. A similiar conclusion can be drawn from the work of Rigby *et al.* (1946) on spinel and hercynite.

Table 4. *Lattice parameters and thermal expansion coefficients of natural spinel*

Temperature (°C)	Lattice parameter observed (Å)	Lattice parameter calculated (Å)	Thermal expansion $\alpha \times 10^6$ (°C^{-1})
22	8·0877	8·0878	4·61
285	8·1010	8·1007	7·58
375	8·1074	8·1066	8·60
463	8·1133	8·1131	9·59
495	8·1147	8·1156	9·95
558	8·1210	8·1209	10·67
628	8·1264	8·1272	11·46
715	8·1360	8·1356	12·44
771	8·1410	8·1413	13·08
830	8·1477	8·1477	13·75
840	8·1494	8·1489	13·86

Table 5. *Lattice parameters and thermal expansion coefficients of synthetic spinel*

Temperature (°C)	Lattice parameter observed (Å)	Lattice parameter calculated (Å)	Thermal expansion $\alpha \times 10^6$ (°C^{-1})
26	8·0832	8·0833	5·90
80	8·0860	8·0860	6·37
208	8·0931	8·0931	7·50
335	8·1017	8·1014	8·62
462	8·1114	8·1108	9·75
536	8·1162	8·1169	10·40
648	8·1268	8·1267	11·39
718	8·1327	8·1333	12·01
800	8·1421	8·1415	12·73

The lattice parameters and thermal expansion coefficients of ferroan gahnite $Mg_{0\cdot13}Zn_{0\cdot49}Fe_{0\cdot38}Al_2O_4$ at different temperatures are listed in Table 7. Swanson & Fuyat (1953) observed 8·0848 Å for the lattice parameter of synthetic gahnite at 26°C. Hutton (1957) determined the lattice parameter of a natural dark green ferroan gahnite having 14·53% FeO and reported its value 8·104 Å. Our value is 8·1062 Å at 22°C. Comparison of this value with that of Swanson & Fuyat (1953) for the synthetic gahnite suggests that larger Fe^{2+} ions replacing smaller Zn^{2+} ions in the gahnite structure increases the lattice parameter at room temperature. The mean thermal expansion is found to be $7{\cdot}82 \times 10^{-6}$ °C^{-1} from 22 to 845°C. A similar value was reported by Beals & Cook (1957).

Table 6. *Mean thermal expansion coefficients of spinel*

Authors	Method used	Temperature range (°C)	Mean thermal expansion $\alpha_m \times 10^6$ (°C^{-1})
Rigby *et al.* (1946)	Dilatometer	100–900	8·9
Beals & Cook (1957)	X-ray camera	20–1200	8·83
Nielsen & Leipold (1963)	Dilatometer	25–800	8·94
Present work	Diffractometer		
(*a*) Natural spinel		22–845	9·24
(*b*) Synthetic spinel		26–800	9·30

Table 7. *Lattice parameters and thermal expansion coefficients of ferroan gahnite*

Temperature (°C)	Lattice parameter observed (Å)	Lattice parameter calculated (Å)	Thermal expansion $\alpha \times 10^6$ (°C^{-1})
22	8·1065	8·1062	6·76
195	8·1157	8·1160	7·21
225	8·1172	8·1177	7·29
282	8·1214	8·1211	7·44
342	8·1243	8·1248	7·59
385	8·1281	8·1274	7·71
422	8·1297	8·1298	7·80
620	8·1431	8·1427	8·32
712	8·1485	8·1490	8·56
782	8·1543	8·1539	8·74
805	8·1553	8·1555	8·80
835	8·1576	8·1577	8·88
845	8·1585	8·1584	8·90

The calculated lattice parameters and thermal expansion as well as the measured values of magnesiochromite $Mg_{0 \cdot 34}Fe_{0 \cdot 42}(Cr_2O_4)_{0 \cdot 76}(MgAl_2O_4)_{0 \cdot 24}$ are given in Table 8. Swanson, Cook, Isaacs & Evans (1960) reported the lattice parameter of synthetic magnesiochromite as 8·333 Å at 26°C. Our value is 8·2977 Å at 22°C. This also shows that in our natural mineral there is appreciable replacement of chromium by aluminum thereby decreasing the lattice parameter. The our mean thermal expansion value from 22 to 823°C is $7 \cdot 67 \times 10^{-6}$ °C^{-1}. A slightly smaller value was reported by Beals & Cook (1957).

Table 8. *Lattice parameters and thermal expansion coefficients of magnesiochromite*

Temperature (°C)	Lattice parameter observed (Å)	Lattice parameter calculated (Å)	Thermal expansion $\alpha \times 10^6$ (°C^{-1})
22	8·2978	8·2977	6·89
190	8·3081	8·3076	7·22
270	8·3120	8·3124	7·37
345	8·3165	8·3170	7·52
405	8·3213	8·3208	7·64
425	8·3224	8·3221	7·68
500	8·3264	8·3269	7·82
570	8·3315	8·3315	7·96
623	8·3352	8·3350	8·06
660	8·3373	8·3375	8·13
718	8·3415	8·3414	8·25
766	8·3450	8·3447	8·34
785	8·3458	8·3461	8·38
823	8·3489	8·3487	8·45

Conclusion

Detailed determination of the lattice parameters shows that thermal expansion increases linearly. No anomaly or inversion of the thermal-expansion curve exists in the observed temperature range. It is also observed that the thermal expansion of the spinel is higher than that of the ferroan gahnite. This shows that the substitution of zinc and iron cations in the place of magnesium decreases the thermal expansion. The thermal expansion of the magnesiochromite is lower than that of spinel. This leads to conclusion that the replacement of Al_2O_3 in spinel by Cr_2O_3 decreases the thermal expansion.

We are thankful to Professor L. E. Murr for providing computer facilities for some of our calculations, to Dr H. R. Shell for supplying the synthetic spinel, and to Dr A. Reid for making the microprobe analyses. The work was supported by the national Aeronautics and Space Administration under Contract #NAS9-8102.

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