Thermal Expansion of Spinels $MgCr_2O_4$, $MgAl_2O_4$ and $MgFe_2O_4$

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The lattice constants of the cubic spinels $MgCr_2O_4$, $MgAl_2O_4$ and $MgFe_2O_4$ have been measured by high-temperature powder X-ray diffraction method in the temperature range from 20 to 1300°C. The dependence of the lattice constants on the temperature has been expressed by polynoms of second order, the respective coefficients being found by the least-squares method. The coefficients of the true thermal expansion $\alpha = a_1 + a_2t$ have been determined. The expansion of the above spinels are reversible.

The thermal expansion of $MgFe_2O_4$ includes a contribution Δa_{st} which is a function of the degree of inversion.

The properties of a polycomponent refractory material are determined by properties of all its crystalline phases. One of them is the thermal expansion. The data in the literature [1—5] concerning the cubic spinels $MgCr_2O_4$, $MgAl_2O_4$ and $MgFe_2O_4$ however, differ considerably from each other and do not yield informations about the true thermal expansion of these compounds. Their thermal expansion was, therefore, redetermined by means of a high-temperature powder X-ray diffraction method.

Barth and *Posnjak* [6] studied the distribution of cations in some spinel structures and found that there exist following spinel types: 1. normal spinel structure AB_2O_4 with tetrahedral positions occupied by A^{2+} cations and octahedral positions occupied by B^{3+} cations, 2. inverse spinel structure $B^{IV}(AB)^{VI}O_4$ in which the tetrahedral positions are occupied by B^{3+} cations whereas all the A^{2+} cations plus the remaining B^{3+} cations are statistically distributed over the octahedral positions, 3. mixed spinel structure $(A_{1-x}B_x)^{IV}(A_xB_{2-x})^{VI}O_4$, where $0 \leq x \leq 1$ is a degree of inversion. Both normal and inverse spinel can be looked upon as limiting cases of the mixed structure.

Some authors [7—10] investigated quenched spinel phases from different equilibrium temperatures and found out that the degree of inversion of the mixed and inverse spinels depends on the temperature. Such a dependence was not observed in the case of normal spinels. *Datta* and *Roy* [7] found experimentally a quantitative relationship between temperature and the degree of inversion of some spinels. They showed that such structural changes are reversible and are to be considered as „reconstruction changes of the disordered state“ of the second order with unchanged space group.

The lattice constants of $MgCr_2O_4$, $MgAl_2O_4$ and $MgFe_2O_4$ were, therefore, measured at elevated temperatures as well as after quenching from those temperatures in order to investigate the contribution of the degree of inversion to the observed thermal expansion.

Experimental

The compounds $MgCr_2O_4$, $MgAl_2O_4$ and $MgFe_2O_4$ were synthesized from Al_2O_3, Cr_2O_3, Fe_2O_3 and $MgCO_3$ (commercially available reagents). All the oxides were heated 12 hours at 1200°C, the $MgCO_3$ was heated 12 hours at 1350°C. The oxides with grain size less than 60 mμ in stoichiometric proportions, were homogenized and heated for 12 hours at 1200°C. After grinding in an agate mortar the specimens were heated again at 1300°C for 12 hours. Third heating was carried out at 1400°C for 18 hours [11].

Phillips et al. [12], later *Speidel* [13] found out that in the system $MgO-Fe_2O_3$, if heated in air, the thermal dissociation of Fe_2O_3 occurs. At 1300°C the specimens contain both Fe^{3+} and Fe^{2+} ions. In order to obtain a pure $MgFe_2O_4$ phase, the heating of the magnesium ferrite specimen at 1400°C for 6 hours in the oxygen atmosphere, was carried out, followed by slow cooling for obtaining the equilibrium distribution of cations in the $MgFe_2O_4$ structure [1].

The identity of all the synthesized compounds was confirmed by microscopical, chemical and X-ray analyses.

The lattice constants of the three above spinels were then measured in the temperature interval from 20 to 1300°C by the high-temperature X-ray powder method [2, 14]. At the beginning of these measurements, the lattice constants at normal temperature were determined, using silicon as an external standard, with following results

$$\begin{aligned} a_{MgCr_2O_4} &= 8.2375(5)\ \text{Å}, \\ a_{MgAl_2O_4} &= 8.0812(7)\ \text{Å}, \\ a_{MgFe_2O_4} &= 8.3716(9)\ \text{Å}. \end{aligned}$$

The specimens were then heated in the high-temperature X-ray powder camera (Rigaku Denki, Japan) coupled with the GON 03 (Chirana, Czechoslovakia) diffractometer. The temperature in this powder camera, that can reach 1400°C, is controlled by $Pt-Pt_{87}Rh_{13}$ thermocouple, connected with an electronic programming system that enables us to raise linearly the temperature. The junction of the thermocouple is located at very close distance from the specimen, held in a $Pt-Rh$ specimen holder so that the temperature measurement with accuracy of $\pm$ 2°C in the entire temperature range is possible.

Because of isotropical character of the thermal expansion of cubic structures, the thermal expansion coefficients of all individual interplanar spacings d_{hkl} are dependent on the thermal expansion coefficient of the lattice constant a only. Using a set of selected diffractions d_{hkl}, the lattice constant a of all three spinels under investigation at different temperatures was then calculated and its dependence on the temperature was expressed by a polynom of second order

$$a_t = a_0(1 + a_1 t + a_2 t^2), \tag{1}$$

where a_0 — lattice constant at 0°C,
a_1, a_2 — characteristic constants for a given spinel,
t — temperature in °C.

The constants a_1 and a_2 for each of the investigated spinels were determined by the least-squares method. The standard deviation in the whole temperature range from 0 to 1300°C does not exceed 0.001 Å.

With respect to the definition of the coefficient of the true thermal expansion

$$\alpha = \frac{1}{a_0}\frac{\mathrm{d}a}{\mathrm{d}t} \tag{2}$$

we obtain from (*1*)

$$\alpha = a_1 + a_2 t \tag{3}$$

that enables us to evaluate the coefficients of the true thermal expansion of the investigated spinels.

Results and Discussion

The thermal expansion of the spinels $MgCr_2O_4$, $MgAl_2O_4$ and $MgFe_2O_4$ was determined by measurements of their lattice constants at elevated temperatures (20, 300, 600, 900, 1100 and 1300°C) at atmospheric pressure. Obviously, the molar volume V_m and the density ϱ_0 will be also temperature-dependent. Thus, the measured values of the lattice constants were used for the evaluation of the characteristic coefficients

Table 1

Dependence of the lattice constant a_t on the temperature

Spinel	Constants of the equation $a_t = a_0(1 + a_1t + a_2t^2)$			σ(Å · 10⁴)	Temperature range
	a_0	$a_1 \cdot 10^6$	$a_2 \cdot 10^9$		[°C]
$MgCr_2O_4$	8.3266	5.38327	1.24497	3.99	0—1300
$MgAl_2O_4$	8.0802	6.20623	1.91771	3.81	0—1300
$MgFe_2O_4$	8.3699	9.69993	2.18669	9.83	0—1300

Table 2

Dependence of the molar volume of some spinels V_{m_t} on the temperature

Spinel	Constants of the equation $V_{m_t} = V_{m_0}(1 + a_1t + a_2t^2)$			σ [cm³ mol⁻¹ × × 10³]	Temperature range
	V_{m_0}	$a_1 \cdot 10^5$	$a_2 \cdot 10^9$		[°C]
$MgCr_2O_4$	43.55216	1.60446	3.88247	1.49	0—1300
$MgAl_2O_4$	39.72130	1.84990	6.03774	1.07	0—1300
$MgFe_2O_4$	44.14995	2.88892	7.13097	6.96	0—1300

Table 3

Dependence of the density ϱ_t some spinels on the temperature

Spinel	Constants of the equation $V_{m_t} = V_{m_0}(1 + a_1t + a_2t^2)$			σ [g cm⁻³ × × 10⁴]	Temperature range
	ϱ_0	$a_1 \cdot 10^5$	$a_2 \cdot 10^9$		[°C]
$MgCr_2O_4$	4.41498	—1.63234	—3.43792	1.91	0—1300
$MgAl_2O_4$	3.58140	—1.88439	—5.20230	1.25	0—1300
$MgFe_2O_4$	4.52964	—2.81195	—6.25671	6.86	0—1300

that may be comfortably used for the calculation of the lattice constant a_t, molar volume V_m, and density ϱ_t at any given temperature in the above temperature range. All these coefficients are given in Tables 1—3. The measured values of the lattice constants at the above temperatures are plotted in Figs. 1 and 2.

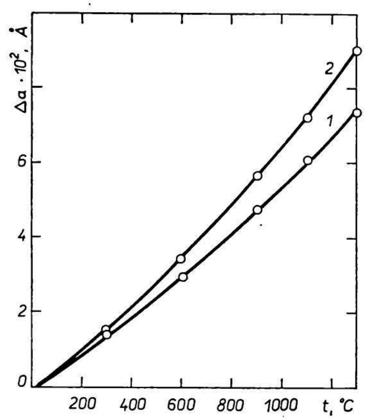

Fig. 1. Thermal expansion of $MgCr_2O_4$ (*1*) and $MgAl_2O_4$ (*2*) expressed in terms of the change of their lattice constants with temperature.

The mean coefficients of the thermal expansion in the temperature range from 20 to 1200°C for all three spinels investigated were then calculated. Their comparison with the data from the literature [1—5], obtained by the X-ray, interferometric and dilatometric method are given in Table 4. It can be seen that the results for the same compound, obtained by X-ray diffraction method, differ from each other much less than from the results obtained by other methods. This is easy to understand, since the specimens used for the dilatometric and interferometric method are in most cases massive blocks consisting of the aggregates of randomly oriented crystallites and containing pores of different sizes. Thus the thermal expansion data, obtained by these methods are inevitably influenced by the history of the specimens and cannot be directly compared with the results of the direct measurements of the structure expansion as determined by the X-ray diffraction method.

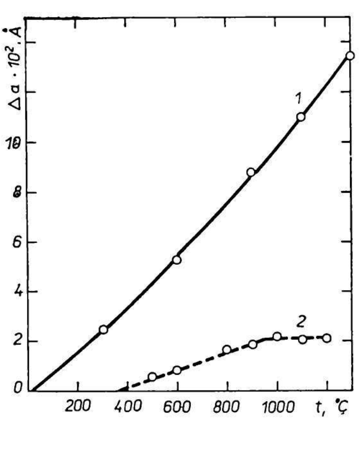

Fig. 2. Thermal expansion of $MgFe_2O_4$ expressed in terms of the change of its lattice constant with temperature.
1. the overall change of the lattice constant; *2.* the contribution to the change of the lattice constant Δa_{st} due to the change of the degree of inversion.

Table 4

Values of the mean coefficients of the linear thermal expansion of some spinels measured by different authors. The corresponding temperature range is given in the second line

Spinel		*1*	*2*	*3*	*4*	*5*	*6*
$MgCr_2O_4$	$\alpha \cdot 10^6$	—	7.00	6.91	8.2	—	9.3
	Δt [°C]	—	20—1200	20—1200	20—1200	—	25—900
$MgAl_2O_4$	$\alpha \cdot 10^6$	9.05	8.83	8.65	9.3	—	8.1
	Δt [°C]	20—1200	20—1200	20—1200	20—1200	—	25—900
$MgFe_2O_4$	$\alpha \cdot 10^6$	—	—	12.38	13.5	11.5	—
	Δt [°C]	—	—	20—1200	20—1200	20—1200	—

1. Zimmerman (X-rays) [3]; *2. Beals, Cook* (X-rays) [2]; *3.* this work (X-rays); *4. Rigby et al.* (dilat.) [5]; *5. Carter* (dilat.) [1]; *6. Parmelee* (interf.) [4].

The influence of the degree of inversion of all three spinels on their thermal expansion was also studied. The spinels $MgCr_2O_4$ and $MgAl_2O_4$ are normal [15, 16], whereas the $MgFe_2O_4$ is an inverse spinel [15, 17]. A measurement of the lattice constants of the first two spinels after quenching from different equilibrium temperatures to 20°C showed no detectable difference between the lattice constants obtained in this way and those at 20°C at the beginning of the experiment. In the case of $MgFe_2O_4$, however, a considerable difference was found at the temperatures between 350 and 1000°C. This can be assigned to the various degree of inversion at different temperatures, because the $MgFe_2O_4$ becomes more normal with increased temperature. These results are in good agreement with the observations of other authors [8, 10, 15] that the lattice constant of the low-temperature form of $MgFe_2O_4$ is about 0.06 Å lower than that of the high-temperature form. The overall thermal expansion Δa_t of the $MgFe_2O_4$ can be, therefore, considered as consisting of the contribution Δa_r due to the change of the equilibrium distance between ions, and of the contribution Δa_{st} due to the change of the degree of inversion with temperature.

The curve 2 on Fig. 2 that shows the contribution Δa_{st} to the overall thermal expansion of $MgFe_2O_4$ suggests the appearance of two breaking points at about 350 and 1000°C. It will, however, need further measurements, to decide with certainity about their existence.

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