Thermochimica Acta
Elsevier Publishing Company, Amsterdam
Printed in Belgium

THERMAL EXPANSION OF OXIDE COMPOUNDS WITH SPINEL STRUCTURE

G. BAYER
Institut für Kristallographie und Petrographie, Eidgen. Techn. Hochschule Zürich (Schweiz)

(Received September 13th, 1971)

ABSTRACT

A large number of oxide spinels, except ferrites, was prepared by solid state reactions. The thermal expansion behavior of these compounds in the temperature region 20–1020°C was investigated by means of a heating diffractometer. The results are discussed in relation to crystal chemistry.

INTRODUCTION

Compounds with a spinel structure have found many practical applications, especially the ferrites, semiconducting spinels, and $MgAl_2O_4$, which, as well as its hardness and high melting point, is also used as a substrate for integrated electronics. New methods of formation allow the preparation of polycristalline, transparent spinels for optical applications, or in the form of whiskers and fibers for composites. The crystal chemistry of spinels, mainly in relation to their magnetic properties, has been investigated in detail by Blasse[1]. The literature on spinel ferrites is quite comprehensive, however, only a few papers have been published which deal generally with the thermal expansion characteristics of spinels[2–4]. The probable reason is that the linear thermal expansion values of the investigated aluminate, ferrite and chromite spinels, were very similar, and not much change was expected when substituting other cations. The present paper is a first crystal chemical approach to evaluate the effects of cation size, valency and ionic distribution on thermal expansion. The thermal expansion is one of the important properties for many applications of materials.

The normal spinel structure shows cubic close packing of the oxygen ions, whereby 1/2 of the octahedral interstices and 1/8 of the tetrahedral interstices are occupied by the "B"- and by the "A"-cations, respectively. Fig. 1 shows the arrangement of the atoms in the cubic unit cell[5], which contains 8 formula units AB_2O_4. One AO_4-tetrahedron and one BO_6-octahedron are outlined in the figure, also the 3 B-ions and one A-ion surrounding each oxygen. This atomic arrangement certainly has some effect on the thermal expansion: not only are the B-ions closer to each other ($B–B = 1/4a\sqrt{2}$) than the A-ions ($A–A = 1/4a\sqrt{3}$), but the A-sites are also larger than the B-sites. Furthermore, the BO_6-octahedra are linked through edges, whereas the AO_4-tetrahedra are separated from each other. The lattice constants of the oxide spinels can show considerable differences (see Table I). Depending on the kind of ionic substitution, they vary from about 7.9 Å for $LiAl_5O_8$, to 9.16 Å for

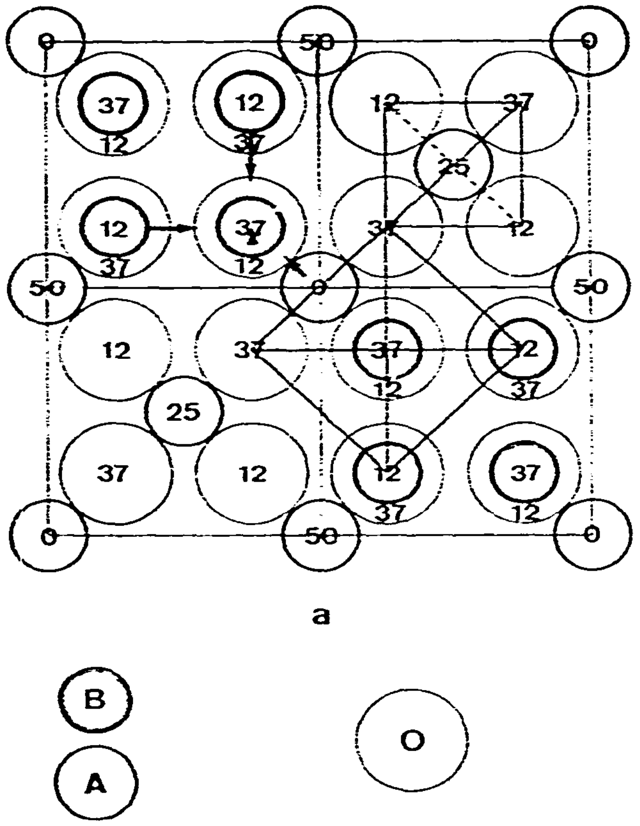

Fig. 1. Spinel structure, projection on the cube face of the atoms in the lower half of the unit cell.

$CdIn_2O_4$. Since the unit cell contains 32 oxygen ions, one can calculate the oxygen packing density for these two extremes as 74% and 48%, respectively. In spite of this difference both spinels have rather similar thermal expansion coefficients. Therefore, one cannot simply relate the thermal expansion to the packing density of the structure, but must take into account, first of all, the valency, size and distribution of the cations.

EXPERIMENTAL

The spinel compounds listed in Table I were prepared by solid state reaction of the corresponding oxides, carbonates or nitrates, in the temperature region from 600°C (*e.g.* Na_2WO_4), to 1250°C (*e.g.* $Co_7Sb_2O_{12}$). They were all checked for purity by X-ray powder photographs (Gunier camera, CuKα-radiation). Thermal expansion measurements were then carried out on finely powdered samples, up to 1020°C, using an X-ray diffractometer (CuKα-radiation), equipped with an MRC, high temperature, X-ray furnace (Pt/^{40}Rh heating strip). Since most of the compounds were well crystallized and gave sharp reflections, isothermal runs were possible in the high-angle region, *e.g.* values of 2θ from 85° to 100°, scanning the reflections

TABLE I

LINEAR THERMAL EXPANSION OF OXIDE COMPOUNDS WITH SPINEL STRUCTURE

Compound	*Cation valencies*	*Lattice constant* (Å)			β_a ($\times 10^{-6}$/°C)
		20°C	*520°C*	*1020°C*	
$LiAl_5O_8$	$1^+, 3^+$	7.9033	7.9298	7.9653	20–520°C = 6.7±0.3 20–1020°C = 7.8±0.3
Na_2WO_4	$1^+, 6^+$	9.1283	9.2407		20–520°C = 24.6±0.7
$LiZnAl_7O_{12}$	$1^+, 2^+, 3^+$	7.9750	7.9997	8.041	20–520°C = 6.2±0.5 20–1020°C = 8.0±0.5
$Li_2ZnGe_3O_8$ (superlattice)	$1^+, 2^+, 4^+$	8.200	8.250	8.271 (820°C)	20–520°C = 11.9±0.5 20–820°C = 11.2±0.6
$Li_2ZnTi_3O_8$ (superlattice)	$1^+, 2^+, 4^+$	8.358	8.409	8.470	20–520°C = 12.0±0.5 20–1020°C = 13.9±0.7
$LiGaTiO_4$ (superlattice)	$1^+, 3^+, 4^+$	8.2940	8.3317	8.3877	20–520°C = 9.1±0.5 20–1020°C = 11.3±0.6
$MgAl_2O_4$	$2^+, 3^+$	8.0783	8.1110	8.1495	20–520°C = 8.1±0.3 20–1020°C = 8.8±0.3
$CoAl_2O_4$	$2^+, 3^+$	8.0990	8.1292	8.1693	20–520°C = 7.5±0.4 20–1020°C = 8.7±0.4
$ZnAl_2O_4$	$2^+, 3^+$	8.0896	8.1238	8.1700	20–520°C = 8.4±0.3 20–1020°C = 9.9±0.4
$MgCr_2O_4$	$2^+, 3^+$	8.3287	8.3577	8.3914	20–520°C = 7.0±0.3 20–1020°C = 7.5±0.3
$CoCr_2O_4$	$2^+, 3^+$	8.3453	8.3728	8.4061	20–520°C = 6.6±0.3 20–1020°C = 7.3±0.3
$ZnCr_2O_4$	$2^+, 3^+$	8.3303	8.3586	8.3923	20–520°C = 6.8±0.3 20–1020°C = 7.5±0.3
$CdCr_2O_4$	$2^+, 3^+$	8.6028	8.6315	8.6566 (920°C)	20–520°C = 6.7±0.3 20–920°C = 7.0±0.4
$MgGa_2O_4$	$2^+, 3^+$	8.2943	8.3275	8.3784	20–520°C = 8.0±0.3 20–1020°C = 10.1±0.4
$ZnGa_2O_4$	$2^+, 3^+$	8.3381	8.3727	8.4193	20–520°C = 8.3±0.3 20–1020°C = 9.8±0.3
$CdIn_2O_4$	$2^+, 3^+$	9.1615	9.1948	9.2264	20–520°C = 7.3±0.3 20–1020°C = 7.8±0.3
Ni_2GeO_4	$2^+, 4^+$	8.2352	8.2637	8.2975	20–520°C = 6.9±0.4 20–1020°C = 7.6±0.4
Mg_2TiO_4	$2^+, 4^+$	8.4401	8.4809	8.5333	20–520°C = 9.7±0.3 20–1020°C = 11.0±0.4
Zn_2TiO_4	$2^+, 4^+$	8.4588	8.5032	8.5577	20–520°C = 10.5±0.4 20–1020°C = 11.7±0.4
Mg_2SnO_4	$2^+, 4^+$	8.6301	8.6673	8.7125	20–520°C = 8.6±0.3 20–1020°C = 9.5±0.4
Zn_2SnO_4	$2^+, 4^+$	8.6486	8.6862	8.7341	20–520°C = 8.7±0.4 20–1020°C = 9.9±0.5
$Co_7Sb_2O_{12}$	$2^+, 5^+$	8.5344	8.5806	8.6302	20–520°C = 10.8±0.6 20–1020°C = 11.3±0.6
$Zn_7Sb_2O_{12}$	$2^+, 5^+$	8.5816	8.6206	8.6665	20–520°C = 9.1±0.4 20–1020°C = 10.0±0.4
$Zn_2Co_3TeO_8$ (superlattice)	$2^+, 6^+$	8.5442	8.5810	8.6248 (820°C)	20–520°C = 8.6±0.3 20–820°C = 9.4±0.4
$Zn_3Ni_2TeO_8$	$2^+, 6^+$	8.5057	8.5420	8.5669 (820°C)	20–520°C = 8.5±0.3 20–820°C = 9.0±0.3

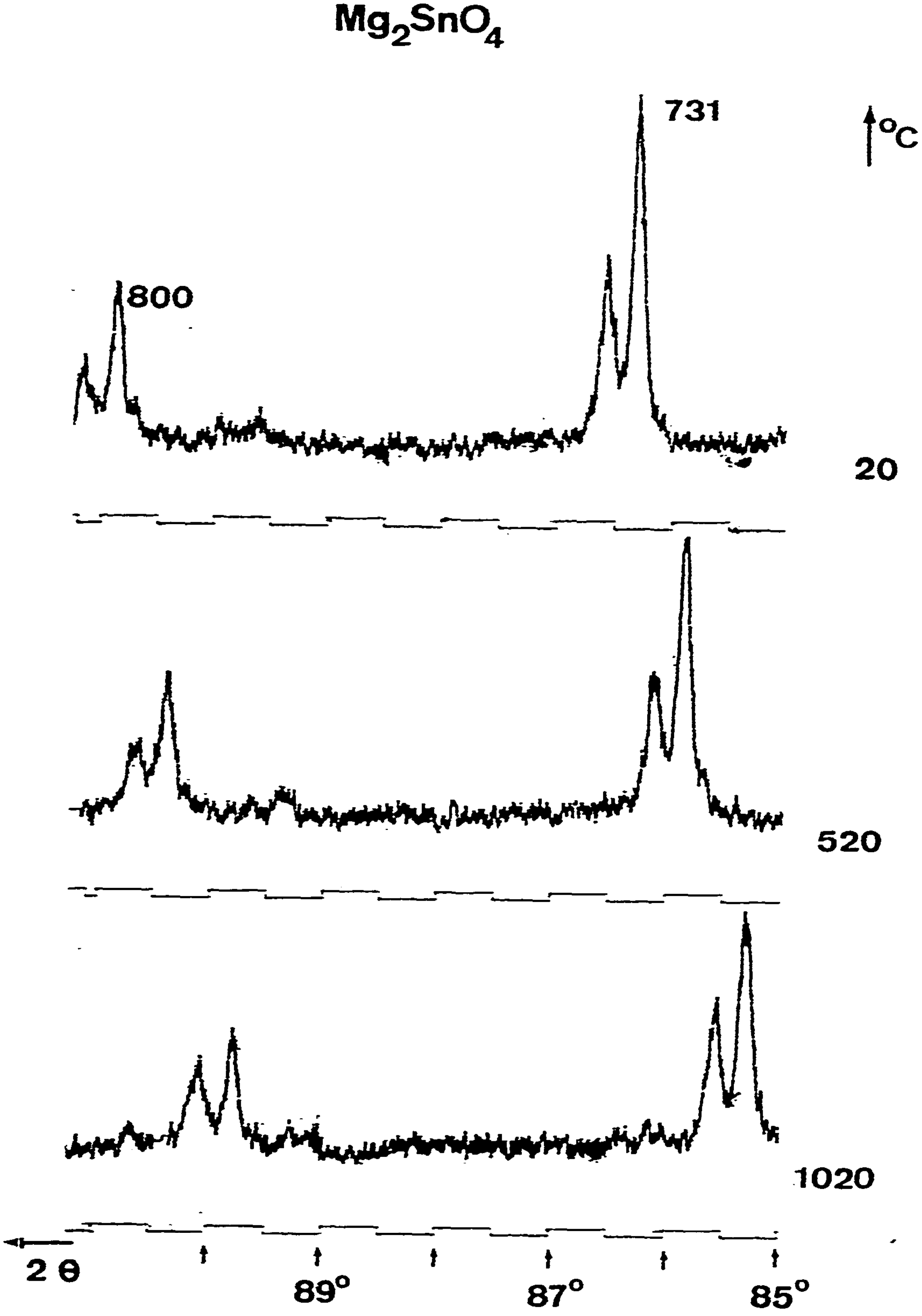

Fig. 2. Portions of the diffractometer tracing for Mg_2SnO_4 at 20°, 520°, and 1020°C.

(642), (731), (800) and (822). Fig. 2 shows a portion of the original diffractometer tracing for Mg_2SnO_4 at different temperatures. The high resolution is seen from the $\alpha_{1,2}$-splitting. The scanning speed for all samples was 1 degree $2\theta/4$ min, time constant 4, rate meter setting 8. The temperature was calibrated with melting standards to within ± 10°C at the highest temperature. Alignment of the diffractometer was checked frequently by measuring and comparing the precisely known[6] thermal expansion of α-Al_2O_3. The accuracy and reproducibility of the linear thermal expansion coefficients was usually better than ±5 relative %. The values listed in Table I correspond to the average of two or three independent runs, over at least 4 reflections.

RESULTS AND DISCUSSION

The results of thermal expansion measurements are summarized in Table I. The agreement with the data listed for some spinels in the literature[2,3] is good. An extremely high thermal expansion compared to that of the other spinels, was found for the salt-like compound Na_2WO_4. This is the spinel with the highest valency difference between the cations, the large sodium ions are arranged relatively close to each other on the octahedral sites. Among the $2^+/3^+$-oxides, the Cr-spinels generally had lower, and the Ga-spinels higher, thermal expansion than the corresponding aluminate spinels. An unexpected result was the low thermal expansion of Cd-spinels, especially of $CdIn_2O_4$, which has slightly larger cell dimensions than Na_2WO_4. All the Cd-spinels are unstable above 950°C due to volatilization of CdO. Ni_2GeO_4 had the lowest expansion of all $2^+/4^+$-spinels, and stannates had lower thermal expansion than the corresponding titanates. The antimonate spinels expand more on heating than the tellurate spinels. Li-spinels can show low thermal expansion, as in the case of $LiAl_5O_8$, or rather high expansion, like $Li_2ZnTi_3O_8$, where 1 Li^+ and 3 Ti^{4+} are distributed in ordered form over the octahedral sites. The cationic arrangement and formation of superlattices will certainly have some effect on thermal expansion. This needs further detailed studies at different temperatures.

The following qualitative conclusions for the thermal expansion behavior of spinel-type oxides can be derived from the results presented in Table I (values compared below are all $\times 10^6/°C$, and are for the temperature region 20–520°C).

(*1*) The greater the valency difference between the cations, the higher, generally, is the thermal expansion, *e.g.* $Na_2^{1+}W^{6+}O_4$ (24.6), $Co_7^{2+}Sb_2^{5+}O_{12}$ (10.8), $Zn_2^{2+}Ti^{4+}O_4$ (10.5), $Zn^{2+}Al_2^{3+}O_4$ (8.4), $Co^{2+}Cr_2^{3+}O_4$ (6.6).

(*2*) The valency difference among the octahedrally coordinated cations, their valency, size and distribution, also effects the thermal expansion. The expansion is mostly lower when the valency of these cations is identical: $Ge(Ni_2)O_4$ (6.9), $Zn(Al_2)O_4$ (8.4), as compared to $Zn_3(Zn_4Sb_2)O_{12}$ (9.1), $Zn(ZnTi)O_4$ (10.5), $LiZn(LiTi_3)O_8$ (12.0).

(*3*) $2^+/3^+$-spinels had the lowest expansion, especially those containing transition elements like Co^{2+} and Cr^{3+}, or B-group elements like Zn^{2+}, Cd^{2+}. $CdIn_2O_4$, which had the largest lattice constant from all investigated spinels, had rather low thermal expansion (7.3). Gallates had the highest expansion of all $2^+/3^+$-spinels.

(4) Li-containing spinels with superlattices have high thermal expansion: $LiZn(LiGe_3)O_8$ (11.9), $LiZn(LiTi_3)O_8$ (12.0). On the other hand low thermal expansion was found for $LiAl_5O_8$ (6.7), and for solid solutions of this spinel with $ZnAl_2O_4$ (6.2).

(5) The spinel structure shows a more or less dense packing of oxygen ions which is reflected by the medium to high thermal expansion coefficients. The lowest thermal expansion for spinel-type oxides is probably in the order of about 6.10^{-6}/°C, the highest one about 25.10^{-6}/°C. Intermediate values are found in accordance with the kind of ionic substitution. The occupancy of the octahedral sites is probably the main influence on the magnitude of thermal expansion.

ACKNOWLEDGMENT

The author is grateful to Owens-Illinois Inc. for financial support of this work.

REFERENCES

1 G. Blasse, *Philips Res. Repts. Suppl.*, 3 (1964) 1–139.
2 R. J. Beals and R. L. Cook, *J. Amer. Ceram. Soc.*, 40 (1957) 279.
3 A. Goldsmith, T. E. Waterman and H. J. Hiroschhorn, *Handbook of Thermophysical Properties of solid Materials, Vol. III, Ceramics*, McMillan, New York, 1961, pp. 599–671.
4 R. K. Kirby, *NBS Special Publication*, 303 (1969) 41–61.
5 R. W. G. Wyckoff, *Crystal Structures*, Vol. 3, 2nd edition, John Wiley and Sons, New York, 1965, p. 76.
6 W. J. Campbell and C. Grain, *Advances in X-ray analysis*, Vol. 5, Plenum Press, New York, 1962, p. 244.