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Single-crystal elastic constants of Co–Al and Co–Fe spinels

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The elastic stiffness moduli of single-crystals $CoAl_2O_4$, a normal spinel, and $CoFe_2O_4$, an inverse spinel, have been determined by an ultrasonic method. The measured values are: $C_{11} = 290.5$, $C_{12} = 170.3$ and $C_{44} = 138.6$ GPa for $CoAl_2O_4$, and $C_{11} = 257.1$, $C_{12} = 150.0$ and $C_{44} = 85.3$ GPa for $CoFe_2O_4$. The elastic constants are compared with previously published data of other spinel single crystals and the results show that the cation valence and cation distribution have little influence on the elastic properties of the spinel materials.

1. Introduction

Past interest in the elastic properties of cubic spinel structures [1–9] is derived from the close relationship of structural phase transitions to the structural stability conditions, as indicated by the variations of the elastic moduli with either hydrostatic pressure, temperature or chemical composition. As a result of this interest there has been a progressive accumulation of single crystal elastic moduli for certain spinel groups. Several different theories have been proposed regarding the dominant factors that contribute to the variations of elastic properties with chemistry. These data and theories were primarily published in the early 1970s and covered two stoichiometric aluminates $MgAl_2O_4$, $FeAl_2O_4$, one mixed aluminate $(MgFe)Al_2O_4$, and ferrites Fe_3O_4, $NiFe_2O_4$, $MnFe_2O_4$, $TiFe_2O_4$ and $ZnFe_2O_4$.

With respect to the single-crystal elastic moduli, C_{11}, C_{12}, C_{44}, $C' = (C_{11}-C_{12})/2$ and $K = (C_{11} + 2C_{12})/3$, there is one consistent principal observation: the ferrites have considerably smaller values for the shear modulus C_{44}. One possible explanation for this effect invokes a higher mass density for the ferrites and a consequent decrease in acoustic wave velocities, as observed by Birch [10] for oxides in general, regardless of crystal structure. A related explanation may be the relatively large differences between the lattice constant, a_0, for spinel aluminates and ferrites. The magnetic moment on the Fe ions in the ferrites may be a third factor.

A fourth factor may be the distribution of the cation among the tetrahedral and octahedral atomic sites in the spinel lattice. Grimes [9], for example, proposed that the values of the C_{44} shear modulus in normal spinels, where the divalent cation sits on the tetrahedral sites, is significantly larger than C_{44} of the inverse spinel structures, where the tetrahedral sites are occupied by trivalent ions, such as Fe^{3+} in the ferrites. This idea has, however, recently been shown to be inconsistent with accurate measurements of elastic moduli in single crystal $ZnFe_2O_4$ [11], which has a normal spinel cation distribution, but a C_{44} value at ambient temperatures similar to that of the inverse ferrite spinels.

The present measurements were carried out as a further investigation of the role of the cation valence distribution when the divalent ion is a transition metal, namely Co^{2+}. The mineral $CoAl_2O_4$ has the normal spinel structure, whereas $CoFe_2O_4$ has the inverse spinel structure. Our discussion of the results includes a summary of the published information on elastic moduli of single crystal spinels and on evaluation of the role of other physical properties on the individual elastic moduli.

2. Experimental procedure

Both $CoAl_2O_4$ and $CoFe_2O_4$ single crystals were grown from flux melt solutions. For $CoAl_2O_4$, a Bi_2O_3 flux was used. The melts were held at 1350 °C for 8 h and then slowly cooled to 900 °C at a rate of 2 °C h^{-1}. For $CoFe_2O_4$, a PbO/PbF_2 flux was used. The soaking temperature was 1250 °C and the cooling rate was also 2 °C h^{-1}. The crystals obtained were all in the form of intersecting ⟨1 1 1⟩ planes with face dimensions in the order of 2–3 mm. X-ray diffraction (XRD) and energy-dispersive spectrometry (EDS) were applied to confirm the crystal structures as well as the chemical compositions.

For ultrasonic measurement, the [1 1 0] direction of the single crystal was chosen as the acoustic wave vector, because the velocities of the three wave modes propagated in this direction provide direct measurement of the independent elastic stiffness moduli C_{11}, C_{12} and C_{44} of a cubic single crystal. The samples were oriented by an X-ray Laue method and two faces parallel to the (1 1 0) were carefully ground and polished, such that the bounding faces were parallel

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within 0.001 mm. The orientation error was a maximum of 1° as determined from Laue patterns. The final dimensions of the samples were about 2 mm × 2 mm and the thicknesses were about 1.2 mm. Because this short distance would allow only 0.3–0.4 μs between longitudinal wave echoes, it was conjectured that the resolution of the "in phase" frequency could be a difficult or prohibitive barrier to accurate measurement of the phase velocity. This, however, was not a problem and the relative ease in obtaining precise data indicates that the technique will be applicable to thickness as small as 0.7 mm. Such small samples may, in fact, be the best available for many crystals grown from flux melts or recovered from other sources.

The sound velocities through the samples were measured by the Fisher and McSkimin phase comparison method [12] in the 20–75 MHz frequency range. The one longitudinal and two transverse wave modes in the [1 1 0] direction provide the following equations for evaluating the stiffness moduli from the velocities, V

$$V_L^2 = (C_{11} + C_{12} + 2C_{44})/2\rho \qquad (1)$$

$$V_{T1}^2 = C_{44}/\rho \qquad (2)$$

$$V_{T2}^2 = (C_{11} - C_{12})/2\rho = C'/\rho \qquad (3)$$

where L denotes a longitudinal vibration mode, T1 and T2 denote transverse modes with polarization directions in [0 0 1] and [1 $\bar{1}$ 0], respectively, and ρ is the density of the crystal. For $CoAl_2O_4$, the sound velocities propagated parallel to the [1 0 0] direction were also measured to cross check the accuracy of the measurements. The measured sound velocities and the calculated elastic stiffness moduli are summarized in Table I.

The X-ray density values used for computing the C_{ij} of $CoAl_2O_4$ and $CoFe_2O_4$ are 4.416 and 5.304 g cm^{-3}, respectively. The measurements were carried out at room temperatures varying from 21–23 °C. "Nonaq" stopcock grease was used to produce longitudinal wave acoustic coupling between the sample crystal and the fused silica buffer rod, whereas solid salol was used for transverse wave coupling. The error of the velocity determinations was estimated, and confirmed by the cross check measurements of C_{11} and C_{44} given in Table I, to be less than 0.1%, with the largest uncertainty in the measurement of sample thickness.

TABLE I Sound velocities and elastic constants of $CoAl_2O_4$ and $CoFe_2O_4$ single crystals

	$CoAl_2O_4$	$CoAl_2O_4$	$CoFe_2O_4$
Direction of propagation	[1 1 0]	[1 0 0]	[1 1 0]
V_L (km s^{-1})	9.141	8.094	7.380
V_{T1} (km s^{-1})	5.602	5.599	4.010
V_{T2} (km s^{-1})	3.690	–	3.177
C_{11} (GPa)	290.5	289.3	257.1
C_{12} (GPa)	170.3	–	150.0
C_{44} (GPa)	138.6	138.4	85.3
C'^{a} (GPa)	60.2	–	53.5
$A = C_{44}/C'$	2.31	–	1.59

[a] $C' = (C_{11} - C_{12})/2$.

3. Results and discussion

The elastic constants of $CoAl_2O_4$ and $CoFe_2O_4$ are summarized in Table I. The elastic stiffness moduli of $CoFe_2O_4$ in all cases are smaller than those of $CoAl_2O_4$. The largest deviation is in C_{44} where the difference exceeds 30%. As previously indicated, several factors may contribute to this difference. The density, ρ, and the lattice parameter a_0 of $CoFe_2O_4$ are much higher than those of $CoAl_2O_4$. Moreover, the divalent cation Co^{2+} occupies different sites within the two spinel structures. It is known that the $CoAl_2O_4$ has a normal spinel structure and Co^{2+} ions are in the tetrahedral sites. In contrast, the $CoFe_2O_4$ is inverse spinel and Co^{2+} ions are in octahedral sites [13]. To clarify which factor may primarily affect the elastic moduli of those spinel materials, other published data for related aluminium and iron-based spinel single crystals are given in Table II.

Table II lists elastic constants of three aluminate normal spinel single crystals, $MgAl_2O_4$ [6], $CoAl_2O_4$ and $FeAl_2O_4$ [1], three inverse spinel ferrites, $NiFe_2O_4$ [5], $CoFe_2O_4$ and Fe_3O_4 [4], one normal spinel ferrite, $ZnFe_2O_4$ [11], and one mixed spinel ferrite, $MnFe_2O_4$ [8]. They are listed in the order of increasing lattice constant, a_0. The C_{11} values decrease gradually with a_0, whereas the C_{44} values of the ferrites are 30%–40% smaller than those of the aluminate spinels. It is of interest to note that although the $ZnFe_2O_4$ has the normal spinel structure, the C_{44} value, which has recently been accurately measured by Li and Fisher [11], is nearly the same as those inverse spinel ferrites. For $MnFe_2O_4$, it is known that 80% of the tetrahedral sites are occupied by Mn^{2+}, leaving only 20% of the Mn ions for octahedral sites [13]. The C_{44} of the $MnFe_2O_4$ [8] is also within the same range of those of inverse spinel ferrites. It, therefore, appears from Table II, that the elastic constants, especially C_{44}, of the spinel structures are not significantly influenced by the cation occupation of the sites.

Table II also lists the density, ρ, of the spinel single crystals. As can be seen, the correlation with a_0 is strong for C_{44}, moderate for C_{11} and weak to nonexistent for C_{12}, C' and A. As the a_0 of aluminate spinels is small, about 0.81 nm, the C_{44} values are significantly higher than those of ferrites which have large lattice parameters, ranging from about 0.835–0.85 nm. Because the smaller lattice parameter reflects the stronger attractive force between the atoms with the same spinel crystal structure, the stronger bond strength of Al–O is evidently responsible for the abrupt change in C_{44} and the gradual decrease in C_{11} with increasing a_0. However, there appears to be no strong correlation between the single crystal elastic moduli and the density for different spinel crystals. Within the ferrite group the effect of replacing the Fe^{2+} ion in magnetite with Co^{2+}, Ni^{2+}, Zn^{2+} or Mn^{2+} is to decrease the value of C' by more than 30%, with much smaller effects on C_{11} and C_{44}. The C' is a measure of resistance of the cubic lattice to an

TABLE II Elastic properties of spinel crystals

Formula	Type of spinel	a_0 (nm)	ρ g cm^{-3}	C_{11} (GPa)	C_{12} (GPa)	C_{44} (GPa)	C' (GPa)	A	K (GPa)	E (GPa)	G (GPa)	ν	V_p (km s^{-1})	V_s (km s^{-1})	Reference
$MgAl_2O_4$	Normal	0.8083	3.578	282.5	154.9	154.7	63.8	2.43	197.4	274.6	108.4	0.27	9.777	5.505	[6]
$CoAl_2O_4$	Normal	0.8103	4.416	290.5	170.3	138.6	60.2	2.31	210.4	256.8	99.1	0.30	8.807	4.738	Present work
$FeAl_2O_4$	Normal	0.8119	4.280	266.0	182.5	133.5	41.8	3.20	210.3	221.7	83.9	0.32	8.677	4.428	[1]
$NiFe_2O_4$	Inverse	0.8339	5.368	273.1	160.7	82.3	56.2	1.46	198.2	189.4	70.6	0.34	7.380	3.627	[5]
$CoFe_2O_4$	Inverse	0.8392	5.304	257.1	150.0	85.3	53.5	1.59	185.7	188.4	70.8	0.33	7.267	3.653	Present work
Fe_3O_4	Inverse	0.8396	5.163	267.6	105.6	95.3	80.1	1.18	159.6	225.8	89.3	0.26	7.347	4.159	[4]
$ZnFe_2O_4$	Normal	0.8441	5.324	250.5	148.4	96.2	51.1	1.89	182.4	196.9	74.6	0.32	7.276	3.743	[11]
$MnFe_2O_4$	Paramagnetic	0.8499	5.0	213.0	135.0	86.0	35.0	2.21	161.0	166.0	62.6	0.33	6.99	3.54	[8]

elastic tetragonal distortion. A significant softening of C' is often observed with decreasing temperature or increasing hydrostatic pressure and is generally a precursory phenomenon related to crystal structure transformation.

The polycrystalline elastic moduli of the spinel crystals are also calculated based on the Voigt–Reuss–Hill average method [14] and are listed in Table II. The K, E, G and ν in Table II are, respectively, the polycrystalline bulk modulus, Young's modulus, shear modulus and Poisson ratio. V_p and V_s are compressional wave velocity and shear wave velocity, respectively, for isotropic polycrystalline aggregates. They can be calculated from

$$V_p^2 = (K + 4G/3)/\rho \tag{4}$$

and

$$V_s^2 = G/\rho \tag{5}$$

From Table II, it is evident that there are no clear and consistent relations among the polycrystalline elastic moduli, density and lattice parameters. Although the elastic constants C_{44} of single-crystal spinels show a sharp and consistent difference between aluminates and ferrites, the polycrystalline E, K and G of those spinels are not consistently different. However, the V_p values do have a strong correlation with a_0. This is in agreement with previous literature reports [1, 10], which conclude that in studying the relationship between structures and elastic properties of polycrystalline materials, more details can be obtained by using compressional wave velocity than by using the polycrystalline elastic moduli.

4. Conclusion

The single-crystal elastic moduli of flux grown crystals with ultrasonic path lengths of the order of 1 mm can be readily measured by the phase comparison method using fused silica buffer rods. A comparison of the measured results for $CoAl_2O_4$ and $CoFe_2O_4$ with other elastic modulus data for aluminates and ferrites shows that the single-crystal elastic moduli, as well as the polycrystalline compressional velocity, V_p, are mainly affected by the lattice parameter, a_0, and are generally insensitive to the cation valences and cation occupied sites. The C_{44} shear modulus of spinel ferrites are significantly lower than those of spinel aluminates. Among spinel ferrites, the substitution of other divalence ions for Fe^{2+} effectively decreases the C' elastic shear moduli.

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