Synthetic spinels in the $(Mg,Fe^{2+},Zn)(Al,Fe^{3+})_2O_4$ system: I. Flux growth of single crystals

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ABSTRACT. — The flux growth method, with $Na_2B_4O_7$ as flux, was successfully used to produce high-quality single crystals of spinel with compositions corresponding to solid solutions of spinel *s.s.* $(MgAl_2O_4)$ - magnesioferrite $(MgFe^{3+}_2O_4)$ and spinel *s.s.* - hercynite $(Fe^{2+}Al_2O_4)$. Some intermediate terms of spinel *s.s.* - gahnite $(ZnAl_2O_4)$ and spinel *s.s.* - franklinite $(ZnFe^{3+}_2O_4)$ solid solutions were also produced. Low cooling rates (1-4°C/h) and linear temperature profiles were applied in the thermal interval 1200-800 °C. Thermal runs were performed in air or in an H_2/CO_2 reducing atmosphere. The resulting crystals underwent microchemical, structural and spectroscopic characterisation for later thermodynamic and kinetic studies of spinel order-disorder with temperature. Both the miscibility gap between spinel *s.s.* and magnesioferrite and the complete solid solution between spinel *s.s.* and hercynite were experimentally confirmed. The constant presence of minor ferric iron was found in hercynite, in spite of the highly reducing conditions imposed during crystal growth.

RIASSUNTO. — Monocristalli di spinello con composizione corrispondente alle soluzioni solide spinello *s.s.* $(MgAl_2O_4)$ - magnesioferrite $(MgFe^{3+}_2O_4)$ e spinello *s.s.* - ercinite $(Fe^{2+}Al_2O_4)$ sono stati prodotti mediante "crescita da flussante", con $Na_2B_4O_7$ usato come flussante. Sono stati prodotti inoltre anche alcuni termini intermedi delle serie spinello *s.s.* - gahnite $(ZnAl_2O_4)$ e spinello *s.s.* - franklinite $(ZnFe^{3+}_2O_4)$. L'intervallo termico utilizzato per la crescita è stato 1200-800 °C, con tasso di raffreddamento lento (1-4 °C/h) ed un profilo di temperatura lineare. I cicli termici sono stati effettuati in aria o in atmosfera riducente (flusso di H_2/CO_2). I cristalli prodotti sono stati caratterizzati mediante analisi microchimica, diffrazione dei raggi X da cristallo singolo e diverse tecniche spettroscopiche, per essere successivamente impiegati nello studio termodinamico e cinetico dei processi di ordinamento cationico intracristallino dovuti alla temperatura ed al tempo. Sono stati verificati sperimentalmente sia la lacuna di miscibilità esistente fra spinello *s.s.* e magnesioferrite, sia la completa soluzione allo stato solido fra spinello *s.s.* ed ercinite. Nonostante le condizioni di crescita in atmosfera controllata fossero molto riducenti, piccoli contenuti di ferro trivalente sono stati rilevati costantemente nei cristalli di ercinite.

INTRODUCTION

Multiple oxides with spinel structure AB_2O_4 occur as main or accessory minerals in many

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different rocks of the Earth, from the upper mantle to the crust. The wide ranges of composition and mineral assemblages of spinels allow them to be employed as petrogenetic indicators. Being sensitive to temperature, pressure, oxygen fugacity, and bulk rock and fluid composition, intra- and inter-crystalline equilibria in spinel are extremely useful for constructing mineral geothermometers, geobarometers and oxygen fugacity sensors. In addition, due to their magnetic properties, they are of great interest in geophysical research and in the ceramic industry. The wide range of physical properties (such as thermal and electrical conductivity, dielectric and magnetic properties) also make them very important in the metallurgic and electronic industries.

Spinel structure, based on a nearly ideal cubic close-packed array of oxygen atoms, has two non-equivalent cation sites, the tetrahedrally co-ordinated T site and the octahedrally co-ordinated M site. 2-3 spinels have divalent A cations (Mg, Fe^{2+}, Zn, etc.) and trivalent B cations (Al, Fe^{3+}, Cr, etc.), whereas 4-2 spinels have tetravalent A cations (Ti, Si, etc.) and the B cations are divalent (Fe^{2+}, Mg, etc.). In general, spinels do not adhere absolutely to the idealised configuration, with A cations in T site and B cations in M sites, as there is octahedral-tetrahedral disorder of A and B cations due to their thermal history. The parameter x (degree of inversion), defined as the fraction of B-type cations in the tetrahedral site, is conveniently adopted for spinels as a measure of "non-convergent" cation ordering (Sack and Ghiorso, 1991). Several thermodynamic models explain the crystal chemical constraints acting on the energetics of the solid solutions covering the compositional space of natural spinels (e.g., Nell et al., 1991, and references therein). The most important factors are: cation distribution, electron exchange reactions, and size mismatch. Disordering enthalpy is considered to depend linearly on the degree of order (O'Neill and Navrotsky, 1984) and the inversion parameter at intra-crystalline

equilibrium is related to temperature via thermometric functions (Della Giusta et al., 1996; Harrison et al., 1998; Redfern et al., 1999).

Because of the chemical complexity frequently observed in natural spinels and the difficulties in precise site assignment of the major cations, synthetic materials of well-defined compositions are generally studied to minimise system complexity. In the literature, most investigations have been performed on synthetic powders and, despite the large number of studies, results are often not in agreement with regard to cation distribution and energy parameterisation (e.g., Redfern et al., 1999, and references therein). Synthetic powder materials are generally difficult to characterise accurately in terms of chemical composition, since, due to synthesis conditions, they may be affected by variable ratios between A and B cations and structural vacancies. Small deviations from stoichiometry, especially when transition elements with more than one oxidation state are present, are easy to produce but difficult to reveal, as pointed out by O'Neill et al. (1992). An alternative approach is based on synthetic single crystals, exploiting the high accuracy provided by single-crystal structural, microchemical and spectroscopic methods. In fact, with synthetic crystals instead of powders, electron microprobe chemical analyses, X-ray diffraction structure refinement and spectroscopic characterisations can be performed on the same small crystal, with the advantage of greatly constraining the uncertainty of chemical composition and cation site populations. This coupled chemical-structural method has already been successfully applied to ordering configuration (and its relationships with temperature) of both natural and synthetic spinels (Della Giusta et al., 1987; Lucchesi and Della Giusta, 1994; Della Giusta et al., 1996; Lucchesi and Della Giusta, 1997; Lucchesi et al., 1998).

In the present case, a flux growth method was used to obtain high-quality spinel crystals with compositions corresponding to spinel s.s. ($MgAl_2O_4$), magnesioferrite ($MgFe^{3+}_2O_4$) and

hercynite ($Fe^{2+}Al_2O_4$) end members, as well as their solid solutions. Some experiments towards gahnite ($ZnAl_2O_4$) and franklinite ($ZnFe^{3+}_2O_4$) compositions were also carried out.

CRYSTAL GROWTH

The process of crystal growth from molten salt solvents at high temperatures is commonly known as «flux growth». A high-temperature solvent is called a flux because it permits growth to proceed at temperatures well below the melting point of the growing phase. This is one of the main advantages of this technique compared with growth from the pure melt, because relatively lower temperatures are involved in flux growth and better quality crystals can be grown. In fact, crystals grown from melts may be non-stoichiometric due to the high vapour pressure of one or more of the constituents (Elwell and Scheel, 1975).

In the present case, the starting materials consisted of analytical grade MgO, ZnO, Fe_2O_3 and $Al(OH)_3$ powders, which were dehydrated and dried at 1000 °C for 12 h before being mixed with $Na_2B_4O_7$, used as flux compound. $Na_2B_4O_7$ was chosen because of its low melting point (742.5 °C), the low-energy barriers to crystal growth in the borate flux (Berkes and White, 1969), and its absence of interaction with spinel compositions. About 5 g of starting material were thoroughly ground and mixed under acetone in an agate mortar, and then transferred to a 10-cc platinum crucible. The crucible was covered with a platinum lid and placed in a furnace with programmable temperature. For thermal runs in air, pure Pt crucibles were used, whereas runs in reducing atmosphere required yttria-stabilised Pt/Au(5%) crucibles, due to their good resistance to chemicals at high temperatures in reducing conditions (Okaj *et al.*, 1996).

For each run, the best ratio (N) between flux amount and sum of starting oxides was determined by trial and error, as no detailed literature regarding spinel flux growth could be found. It was observed that N must be decreased in order to grow spinels with increasing contents of transition element oxides. In particular, together with increasing Fe_2O_3 and decreasing Al_2O_3 (which is a refractory oxide), N may change from 1.5 to less than one (Table 1).

For thermal runs, ENTECH muffle and vertical furnaces were used, the former in air and the latter with controlled atmosphere. Crystals in the $(Mg,Zn)(Al,Fe^{3+}_2)O_4$ system were grown in air and a gas-controlled atmosphere, for iron reduction to the ferrous state, was required for crystals in the $(Mg,Fe^{2+})Al_2O_4$ system. The reducing atmosphere was created by a continuous flow of high-purity CO_2 and H_2 gases into the furnace. The CO_2:H_2 ratio was maintained by TYLAN flow controllers and was kept constant at 1:1 or 2:1 (Table 2). Oxygen fugacity ranged from 10^{-11} to 10^{-18} bars at 1200 and 800 °C, respectively. During thermal runs, both T and fO_2 were monitored by sensors close to the crucible and were recorded by computer.

The thermal runs were started with a rather steep increment up to 1200 °C, after which the temperature was kept constant for 24 hours, for complete dissolution and homogenisation of the oxide mixture. Slow cooling was applied down to 900 or 800 °C, after which temperature was decreased rapidly by turning off the power to the heating elements. Various cooling rates in the range from 1 to 4 °C/h were applied between 1200 and 800 °C. Both linear and saw-tooth temperature profiles were examined with the aim of improving crystal quality and size, and linear cooling was chosen as a result. It was observed that, in these experimental conditions, the influence of cooling path was very low when the appropriate N ratio was achieved. Instead, crystals improved in both size and quality when some MgO excess over the stoichiometric ratio was added to the starting mixture. A large MgO excess was necessary to obtain $MgFe^{3+}_2O_4$, as already observed by O'Neill *et al.* (1992).

Table 1

Flux grown spinels. Runs in air: molar proportions of starting oxide mixture, experimental conditions, results.

Run	SP3	MgF1aa	MgF1a	MgF1b	MgF1c	MgF2d	MgF2e	MgF1d	MgF1e	MgF2c	MgF100f	Gah1a	Frk1a	Frk1d
MgO	1.10	1.20	1.20	1.20	1.20	1.20	1.20	1.20	1.20	1.20	2.17	0.80	1.10	1.20
ZnO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.30	0.05	0.10
FeO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Fe_2O_3	0.00	0.05	0.10	0.12	0.15	0.15	0.17	0.18	0.18	0.20	0.92	0.00	0.10	0.10
Al_2O_3	0.90	1.00	1.00	0.90	1.00	0.90	0.90	0.90	0.90	0.90	0.00	0.90	1.00	0.90
N	1.500	1.450	1.425	1.350	1.350	1.300	1.300	1.300	1.300	1.300	0.800	1.500	1.400	1.300
T range (°C)	1200-800	1200-950	1200-976	1200-1050	1200-1050	1200-900	1200-950	1200-950	1164-950	1200-800	1200-900	1200-800	1200-900	1200-900
Cool. rate (°C/h)	2	4	1	2	2	4	4	4	4	2	4	2	2	4
Colour	colourless	yellow	red-brown	red-brown	brown	brown	brown	brown	brown	brown	black	colourless	yellow	orange
Quantity (mg)	100	50	100	50	50	100	50	50	50	50	200	50	150	50

TABLE 2

Flux grown spinels. Runs in controlled atmosphere: molar proportions of starting oxide mixture, experimental conditions, results

Run	He2d	He2f	He3a	He4a	He4b	He5a	He6a	He7a	He8a	He9a	He100a	He100b	He100c
MgO	1.10	1.00	0.90	0.80	0.60	0.50	0.40	0.30	0.20	0.10	0.00	0.00	0.00
ZnO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
FeO	0.20	0.20	0.30	0.40	0.40	0.50	0.60	0.70	0.80	0.90	1.00	1.00	1.00
Fe_2O_3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Al_2O_3	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.10	1.10
N	1.400	1.400	1.400	1.350	1.350	1.350	1.350	1.350	1.300	1.300	1.300	1.300	1.300
T range (°C)	1200-800	1200-900	1200-900	1200-900	1200-900	1200-900	1200-900	1200-900	1200-900	1200-900	1200-930	1200-900	1200-900
Cool. rate (°C/h)	2	4	2	4	4	4	4	4	4	4	4	4	4
CO_2:H_2 (cm^3/min)	30:30	40:20	40:20	40:20	40:20	40:20	40:20	40:20	40:20	40:20	40:20	30:30	40:20
Colour	pale lilac	pale lilac	sky-blue	green	green	dark green	dark green	dark green	dark green	dark green	black	black	black

The resulting run products consisted of an inter-grown network of octahedral spinels and elongated, prismatic iron-magnesium borate crystals embedded in minor glass. The spinel crystals nucleate not only on the walls of the crucible and the surface of the melt, but also in the bulk of material. Run products were immersed in hot, dilute hydrochloric acid for a few days in order to dissolve glass and borates. The spinel crystals were then easily hand-picked under a binocular microscope. The amount of spinel recovered from each run ranged from 50 to 300 mg, corresponding to some hundred single crystals.

These spinel crystals were transparent, regular or truncated octahedra, up to 2 mm in diameter and variable in colour according to chemical composition. Medium-sized to small crystals generally appeared gem-quality, homogeneous, and inclusion-free, whereas the largest sometimes contained imperfections, cracks or inclusions. In particular, crystals with high iron content sometimes showed a growth structure known as "hopper", which results from too rapid growth after the initial dendritic stage, in conditions where convection is limited and diffusion is a controlling factor (Elwell and Scheel, 1975).

RESULTS

$MgAl_2O_4$

Spinel *sensu stricto* (*s.s.*) crystals are colourless, perfectly transparent and inclusion-free octahedra, sized up to 1 mm. Various values for experimental parameters (i.e., oxide proportions, flux/oxide ratio N, temperature range, cooling rate, temperature profiles) and various combinations among them were tried. The best results were achieved with the conditions reported in Table 1 for the SP3 run. The chemical composition of several SP3 crystals was measured by electron microprobe, and average and standard deviations of Mg = 1.006(7) and Al = 1.996(4) atoms per formula unit were obtained for more than one hundred

spots (S. Carbonin, *personal communication*, 1999). The cell parameter of some of the SP3 crystals was measured by means of three different X-ray single-crystal automated diffractometers in the Universities of Rome "La Sapienza", Padova and Trieste (by courtesy of S. Lucchesi, A. Della Giusta and F. Princivalle, respectively) which gave as a mean $a = 8.0854(3)$ Å. This value perfectly corresponds to the cell parameter of vacancy-free $MgAl_2O_4$ spinel (Lucchesi and Della Giusta, 1994, and references therein; Maekawa *et al.*, 1997).

$MgAl_2O_4 - MgFe^{3+}_2O_4$

The compositions obtained along the solid solution spinel *s.s.* - magnesioferrite and the experimental conditions of synthesis runs are listed in Table 1. Crystals showed variable hues from perfectly colourless to honey-yellow, red-brown and dark-brown. Ferric iron distribution between T and M sites and the absence of ferrous iron were evidenced by both Optical Absorption Spectroscopy (OAS) and Mössbauer spectroscopy (work in progress). The ferric iron in tetrahedral co-ordination was identified by OAS to be responsible for colour changes. Samples SP3 and MgF 100f corresponded to end-members $MgAl_2O_4$ and $MgFe^{3+}_2O_4$, respectively. The other samples with MgF label corresponded to intermediate compositions with a magnesioferrite component up to 30%, as determined by electron microprobe. The magnesioferrite component of these crystals showed no strictly linear relationship with the iron content of the starting oxide mixture. For example, the iron content of the MgF 2c oxide mixture was double than that of MgF 1a, whereas the Fe_2O_3 contents in the corresponding crystals, measured by electron microprobe, were 27.6 wt% and 10.2 wt%, respectively. A possible explanation is that the partition coefficient of iron between crystals and melt increases as a function of the iron content of the system. Furthermore, both chemical and thermal gradients may exist in different regions of the

melt during crystal growth. Working between 1200 and 900 °C, crystals with magnesioferrite contents higher than 30% were not obtained, and the quality of products decreased progressively when this limit was approached. This experimental observation is in excellent agreement with the miscibility gap between the two end-members expected below 1000 °C, as proposed by Turnock and Eugster (1962) and modelled on a thermodynamic basis by Lehmann and Roux (1986). The latter authors described increasing immiscibility with decreasing temperature, and obtained up to 20% magnesioferrite in spinel at 800 °C. A structural explanation for the observed miscibility gap is that spinel *s.s.* and magnesioferrite are normal and inverse spinels, respectively. This means that the complete solid solution between them may only be stable at higher temperatures, where cation disorder of A and B species between T and M sites may occur.

$MgAl_2O_4$ - $Fe^{2+}Al_2O_4$

The compositions obtained along the solid solution spinel *s.s.* - hercynite and the experimental conditions of synthesis runs are reported in Table 2. Crystals show various hues regularly varying from almost colourless to pale lilac, sky-blue, green and black. Samples He 2d to He 9a correspond to stepwise increasing (~ 10% step) hercynite content, and samples labelled He100 correspond to end-member hercynite. Spectroscopic studies by OAS revealed increasing ferrous content in tetrahedral co-ordination, which indirectly causes the colour change. In hercynite-rich compositions, iron content in the crystals increases more than that in the starting oxide mixture, confirming that iron partitioning from melt to crystals tends to increase with increasing iron content, as already observed for magnesioferrite.

The isomorphic series between $MgAl_2O_4$ and $Fe^{2+}Al_2O_4$ was completely reproduced, in agreement with the complete solid solution expected at temperatures as low as 800 °C

(Lehmann and Roux, 1986). Since both spinel *s.s.* and hercynite are normal spinels, this means that cation substitution of Fe^{2+} for Mg in T site probably occur without temperature constraints.

The presence of minor Fe^{3+} was observed in hercynite, even though $f(O_2)$ in the furnace was suitable for stabilising ferrous iron only. Repeated experiments (He100a, b, and c) were performed in a strongly reducing atmosphere (with $f(O_2)$ decreasing from 10^{-11} to 10^{-16} bars between 1200 and 900 °C, respectively) with variable Al_2O_3 from stoichiometry to small excess, but ferric iron content up to 6% with respect to total iron was always revealed by Mössbauer spectroscopy. This may suggest the active role of spinel structure in stabilising small amounts of ferric iron, even in $f(O_2)$ conditions in which only ferrous iron is expected. To constrain this possibility, which has important implications, further experiments with different $f(O_2)$ and starting compositions are needed.

$ZnAl_2O$, and $ZnFe^{3+}_2O_4$

A few intermediate compositions along the isomorphic series spinel *s.s.* - gahnite (sample Gah 1a) and spinel *s.s.* - franklinite (samples Frk 1a and 1d) were grown in order to test the experimental conditions in the presence of Zn. Attempts were successful and the crystals obtained were very similar to those previously described (Table 1), being colourless, in the case of a gahnite component, or orange-yellow with franklinite. However, the crystallisation process appeared to be very different than that of magnesioferrite and hercynite. For example, although the starting oxide mixture for the Gah 1a run contained about Zn 25% and Mg 75% in molar proportion, a gahnite crystal analysed by electron microprobe showed Zn 0.66 and Mg 0.33 atoms per formula unit. Moreover, the same crystal was zoned, with the Zn-rich core described above and a Mg-rich, Zn-depleted rim. For borate fluxes at temperatures between 1200 and 800 °C, strong partitioning for zinc is therefore indicated towards the spinel structure,

together with the temperature dependence of its partitioning coefficient. The behaviour of zinc was also different from that of iron, as Zn shows a much greater tendency towards evaporation at high temperatures. This means that more precautions must be taken when Zn is present, in order to avoid contamination in the furnace and then in following experiments.

CONCLUSIONS

Flux growth is an excellent method for producing single crystals of spinel with variable compositions in the $(Mg,Fe^{2+},Zn)(Al,Fe^{3+})_2O_4$ system. The relatively low temperatures involved, comparable with growth from natural melts, do not induce deviations from stoichiometry or the formation of structural vacancies. The composition of products does not exactly correspond to the composition of the starting oxide mixture, because at the melt stage every element enters the growing spinel phase according to its melt/crystal partition coefficient. The sizes of the resulting crystals are suitable for electron microprobe analysis, single-crystal X-ray diffraction, and microscopic optical absorption spectroscopy in the UV-VIS-NIR fields. Furthermore, the quantity produced in a single run is enough for additional studies, like Mössbauer spectroscopy. Therefore, the possibility of accurate characterisation of these crystals makes them perfect materials for subsequent study of intracrystalline cation disorder dependency on temperature and time.

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