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Sol–Gel Synthesis of Ternary Metal Oxides. 1. Synthesis and Characterization of MAl_2O_4 (M = Mg, Ni, Co, Cu, Fe, Zn, Mn, Cd, Ca, Hg, Sr, and Ba) and $Pb_2Al_2O_5$

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Several ternary metal oxides having the formula MAl_2O_4 where M = Mg, Ni, Co, Cu, Fe, Zn, Mn, Cd, Cu, Hg, Sr, and Ba and the compound $Pb_2Al_2O_5$ have been synthesized with sol–gel methods and compared to materials produced by traditional high-temperature solid-state procedures. These transparent sol–gel materials are crystalline as shown by powder X-ray diffraction methods. The size and charge of M ions and their corresponding resultant structures are found to be related to crystal field and octahedral stabilization energies. Particle sizes range from 20 to 200 μm as determined by scanning electron microscopy experiments. Thermal stability of the $NiAl_2O_4$ material has been studied by differential scanning calorimetry methods. Small metal (M) ions form different structures such as the cubic $Pb_2Al_2O_5$ phase, the hexagonal phase of $BaAl_2O_4$, the monoclinic phase of $CaAl_2O_4$, and the hexagonal $CdAl_2O_4$ and $HgAl_{12}O_{13}$ phases.

Introduction

In 1846, Ebelmen[1] first reported the use of the sol–gel technique as a synthetic method to form silicate glass. Since that time and particularly in the past decade the interest in sol–gel has considerably grown.[2–7] The applications have included preparing glasses, coatings on high modulus fibers to control the bonding in composites[8] and also to form complex glasslike ceramics for use in glass ceramic matrix composites.[9] Some of the principle advantages of sol–gel over the conventional methods of synthesizing metal aluminates and aluminum oxides is that the synthesis is done at the molecular level producing very pure products, the heating times can be less and the temperatures can be lower.[7,10]

Many transition-metal aluminates with the general formula AB_2X_4 form spinels.[11] In our studies the A ion is varied and the B ion is aluminum, and the X ion is oxygen. In the spinel structure the anions are arranged in a cubic closest packed array with the cations packed into the holes in this array. There are eight tetrahedral holes and four octahedral holes per molecule. Normally the A cations are in tetrahedrally coordinated sites, and the B cations are in the octahedrally coordinated sites. However, in the inverse spinel structure one-half of the B cations are in tetrahedral sites and the remainder of the B cations and all of the A cations are in octahedral sites. When the aluminum atoms are in tetrahedral sites the metal aluminates have been shown to have high surface acidity.[12] As part of our systematic investigation of the use of sol–gel as a general synthetic tool, we have begun to investigate the possibility of forming a wide variety of aluminates by this technique. This paper details the synthesis and structural characterization of MAl_2O_4 (M = Mg, Ni, Co, Cu, Fe, Zn, Mn, Cd, Ca, Hg, Sr, and Ba) and $Pb_2Al_2O_5$.

Experimental Section

Aluminum isopropoxide (98%), barium nitrate (99+%), cadmium nitrate tetrahydrate (98%), iron(II) acetate (95%), lead acetate hydrate (99+%), magnesium oxide (99.99%), mercuric acetate (98%), nickel acetate tetrahydrate (98%), nickel nitrate hexahydrate (99.999%), nickel oxide (99.99%), and zinc oxide (99.999%) were purchased from Aldrich Chemical Co. of Milwaukee, WI.

Cobalt(II) nitrate hexahydrate (Baker Analyzed A.C.S.), copper acetate hydrate (Baker Analyzed A.C.S.), magnesium nitrate hexahydrate (Baker Analyzed A.C.S.) and zinc nitrate hexahydrate (Baker Analyzed) were purchased from J. T. Baker of Phillipsburg, NJ.

Manganese acetate tetrahydrate (purum p.a) was purchased from Fluka of Ronkonkoma, NY. Calcium acetate hydrate (Fischer Certified) was purchased from Fischer of Springfield, NJ. Cobalt(II) acetate tetrahydrate (Reagent) was purchased from Merck Inc. of Rahway, NJ.

The crystallinity of the materials prepared was confirmed by X-ray powder diffraction patterns obtained on a Scintag XDS 2000 X-ray powder diffractometer and data were compared to standard patterns from the JCPDS International Center for Diffraction Data, Inorganic Materials. Particle sizes were measured using an Amray Model 1810D scanning electron microscope with an EDAX Model PV9800 energy-dispersive X-ray analyzer. Thermal analysis were done on a du Pont Model DSC-910 differential scanning calorimeter at a scan rate of 4 °C/min.

General procedures for the synthesis of ternary metal aluminates are detailed as follows:

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Synthesis of $BaAl_2O_4$. Step 1: In a 250-mL round-bottom flask, 2.32 g of $Al(OC_3H_7)_3$ in 140 mL of deionized distilled water (DDW) was refluxed at 85–90 °C with stirring for 1 h. Step 2: A solution of 1.47 g of $Ba(NO_3)_2$ in 40 mL of hot DDW was slowly added to the aluminum sol. The resultant solution was further refluxed with stirring for an additional hour. The aluminum–barium sol was slowly concentrated until a gel formed. The gel was heated to 900 °C for 20 h in a quartz boat.

Synthesis of $CaAl_2O_4$. The same procedure in the synthesis of $BaAl_2O_4$ was used except in step 2 a solution of 0.995 g of $Ca(OOC_2H_3)_2\cdot H_2O$ in 40 mL of DDW was slowly added to the $Al(OC_3H_7)_3$ solution.

Synthesis of $CdAl_2O_4$. The same procedure as in the synthesis of Ba_2AlO_4 of was used, except that a solution of 1.743 g of $Cd(NO_3)_2\cdot 4H_2O$ in 40 mL of DDW was slowly added to the $Al(OC_3H_7)_3$ solution.

Synthesis of $CoAl_2O_4$. The same procedure as in the synthesis of Ba_2AlO_4 was used, except that a solution of either 1.407 g of $Co(O_2C_2H_3)_2\cdot 4H_2O$ or 1.644 g of $Co(NO_3)_2\cdot 6H_2O$ in 40 mL of DDW was slowly added to the $Al(OC_3H_7)3$ solution.

Synthesis of $CuAl_2O_4$. The same procedure as in the synthesis of Ba_2AlO_4 was used, except that a solution of 2.26 g of $Cu(O_2C_2H_3)_2\cdot H_2O$ in 40 mL of DDW was slowly added to the $Al(OC_3H_7)_3$ solution.

Synthesis of $FeAl_2O_4$. The same procedure as in the synthesis of Ba_2AlO_4 was used, except that a solution of 1.432 g of $Fe(O_2C_2H_3)_2$ in 40 mL of DDW was slowly added to the $Al(OC_3H_7)_3$ solution.

Synthesis of $HgAl_2O_4$. The same procedure as in the synthesis of Ba_2AlO_4 was used, except that a solution of 1.800 g of $Hg(O_2C_2H_3)_2$ in 40 mL of DDW was slowly added to the $Al(OC_3H_7)_3$ solution.

Synthesis of $MgAl_2O_4$. The same procedure as in the synthesis of Ba_2AlO_4 was used, except that a solution of 1.440 g of $Mg(NO_3)_2\cdot 6H_2O$ in 40 mL of DDW was slowly added to the $Al(OC_3H_7)_3$ solution.

Synthesis of $MnAl_2O_4$. The same procedure as in the synthesis of Ba_2AlO_4 was used, except that a solution of 1.320 g of $Mn(O_2C_2H_3)_2\cdot 4H_2O$ in 40 mL of DDW was slowly added to the $Al(OC_3H_7)_3$ solution.

Synthesis of $NiAl_2O_4$. The same procedure as in the synthesis of Ba_2AlO_4 was used, except that a solution of 2.812 g of $(CH_3CO_2)2Ni\cdot 4H_2O$ or 2.470 g of $Ni(NO_3)_2\cdot 6H_2O$ in 40 mL of DDW was slowly added to the $Al(OC_3H_7)_3$ solution.

Synthesis of $PbAl_2O_5$. The same procedure as in the synthesis of Ba_2AlO_4 was used, except that a solution of 2.140 g of $Pb(C_2H_3O_2)_2\cdot 3H_2O$ in 40 mL of DDW was slowly added to the $Al(OC_3H_7)_3$ solution.

Synthesis of $SrAl_2O_4$. The same procedure as in the synthesis of Ba_2AlO_4 was used, except that a solution of 1.190 g of $Sr(NO_3)_2\cdot 6H_2O$ in 40 mL of DDW was slowly added to the $Al(OC_3H_7)_3$ solution.

Synthesis of $ZnAl_2O_4$. The same procedure as in the synthesis of Ba_2AlO_4 was used, except that a solution of 1.68 g of $Zn(NO_3)_2\cdot 6H_2O$ in 40 mL of DDW was slowly added to the $Al(OC_3H_7)_3$ solution.

Results

The syntheses described above resulted in optically transparent homogeneous gels which on thermal treatment to temperatures between 800 and 900 °C led to crystalline materials.

Table I gives the X-ray powder diffraction results for the compounds that have spinel structures. The data of Table I show that *d* spacings for the Co, Cu, Fe, Mg, (Mg, Fe), Mn, Ni, and Zn derivatives have similar *d* spacings to that of spinel although not all *hkl* spacings are present. In Tables II–V the compounds that have the general formula MAl_2O_4 with structures different from spinel are reported.

Table I. *d* Spacings for MAl_2O_4 (M = Co, Fe, (Fe, Mg), Mg, Mn, Ni, Zn) with the Spinel Structure

	M				
spinel[a]	Co	Cu	Fe	Fe, Mg	*hkl*
2.858(40)	2.8566(55)	2.8421(45)	2.8732(45)	2.8982(40)	220
2.437(100)	2.4371(100)	2.4303(95)	2.4496(100)	2.4714(100)	311
2.020(65)	2.0231(19)	2.0122(55)	2.0244(68)	2.0551(32)	400
1.650(10)	1.6520(17)	1.6463(75)	1.6453(10)	1.6754(15)	422
1.5554(45)	1.5572(39)	1.5521(86)	1.5654(40)	1.5770(40)	511
1.4289(55)	1.4307(48)	1.4262(100)	1.4327(70)	1.4577(50)	440

M				
Mg	Mn	Ni	Zn	*hkl*
2.8414(32)	2.9234(36)	2.8451(18)	2.8548(71)	220
2.4265(100)	2.4887(100)	2.4257(100)	2.4356(100)	311
2.0138(79)	2.0792(35)	2.0126(60)	2.0192(9.2)	400
1.6457(10)	1.6933(18)	1.6452(10)	1.6498(25)	422
1.5519(53)	1.5991(53)	1.5474(28)	1.5556(40)	511
1.4259(70)	1.4611(16)	1.4222(62)	1.4287(48)	440

[a] Values in parentheses are relative intensities.

Table II. X-ray Diffraction Data for the Hexagonal Phase of $BaAl_2O_4$

D_{exptl}	D_{theor}[a]	I/I_0	*hkl*
4.5180	4.525	41	100
4.0619	4.022	7	101
3.153	3.153	100	102
2.6098	2.611	43	110
2.2583	2.2624	12	200
2.2442	2.2462	30	112
2.1979	2.1989	14	004
2.0102	2.0111	24	202
1.9770	1.9774	17	104
1.7100	1.7098	7	210
1.6821	1.6822	13	114
1.5936	1.5936	21	212
1.5764	1.5764	10	204
1.5072	1.5071	10	300

[a] JCPDS 17-306.

Table III. X-ray Diffraction Data for the Monoclinic Phase of $CaAl_2O_4$

D_{expt}	D_{theor}[a]	I/I_0	*hkl*
4.3931	4.38	12	103
3.0604	3.06	12	213
2.9658	2.966	100	220
2.5137	2.514	12	303
2.3987	2.399	45	313
2.1645	2.174	6	400
2.0041	2.005	8	040
1.9902	1.973	6	330
1.6975	1.698	20	312

[a] JCPDS 23-1037.

Table IV. X-ray Diffraction Data for the Hexagonal Phase of $CdAl_2O_4$

D_{expt}	D_{theor}[a]	I/I_0	*hkl*
2.7873	2.779	38	132
2.684	2.6840	90	410
2.4105	2.431	40	322
2.3786	2.372	100	600
1.9704	1.970	65	520
1.5906	1.594	63	006
1.4193	1.417	18	704

[a] JCPDS 22-119.

The X-ray results for $HgAl_{12}O_{13}$ and $Pb_2Al_2O_5$ are given in Tables VI and VII. These materials represent complex mixed metal oxides that have similar d spacings to the same phases prepared by other methods.[21] Table VIII reports the physical properties of the oxides prepared by sol–gel methods including density, color, and particle size, and Figures 1–3 show the morphology of the aluminates synthesized by sol–gel. The X-ray results of sol–gel

Table V. *d* Spacings for $SrAl_2O_4$

D_{exptl}	D_{theor}[a]	I/I_0	D_{exptl}	D_{theor}[a]	I/I_0
4.3930	4.41	32	2.4141	2.41	10
3.8853	3.91	25	2.2059	2.205	70
3.1273	3.14	100	1.9746	1.953	18
3.0445	3.05	25	1.8762	1.867	32
2.5493	2.55	40			

[a] JCPDS 9-39.

Table VI. X-ray Diffraction Data for the Hexagonal Phase of $HgAl_{12}O_{13}$

D_{exptl}	D_{theor}[a]	I/I_0	*hkl*
2.7993	2.791	57	110
2.6723	2.690	100	107
2.4300	2.403	67	201
2.2456	2.245	15	116
1.9790	1.967	31	207
1.5604	1.565	29	112
1.3995	1.401	71	308

[a] JCPDS 22-1170.

Table VII. X-ray Diffraction Data for the Cubic Phase of $Pb_2Al_2O_5$

D_{exptl}	D_{theor}[a]	I/I_0	*hkl*
4.6696	4.68	43	220
4.3863	4.42	40	300
3.9942	3.99	42	311
3.6579	3.68	10	320
3.2105	3.21	100	100
2.6316	2.65	60	500
2.2103	2.210	21	600
1.9542	1.954	25	631
1.8585	1.856	12	711
1.7234	1.726	18	731
1.6821	1.684	25	651
1.6066	1.608	28	820
1.5854	1.585	20	653
1.5413	1.541	44	831
1.4714	1.472	12	900
1.3981	1.398	56	831

[a] JCPDS 19-672.

Table VIII. Physical Properties of MAl_2O_4

M	density (g/mL)	color	particle size (μm)
Ca	1.57	white	50–100
Cd	2.74	white	50–100
Co	4.40	bright blue	20–50
Cu	4.48	chocolate	20–70
Fe	4.10	mahogany	200
Hg	2.52	light blue	100–120
Mg	3.79	white	70–100
Mn	4.10	brown	50
Ni	4.51	cerulean	70–100
Sr	3.48	white	50–100
Zn	4.68	white	50–70
Mg, Fe	3.61	brown	100–120

materials and conventional solid state prepared $MgAl_2O_4$, $NiAl_2O_4$, and $ZnAl_2O_4$ are shown in Figures 4–6. Thermal data for $NiAl_2O_4$ are shown in Figure 7.

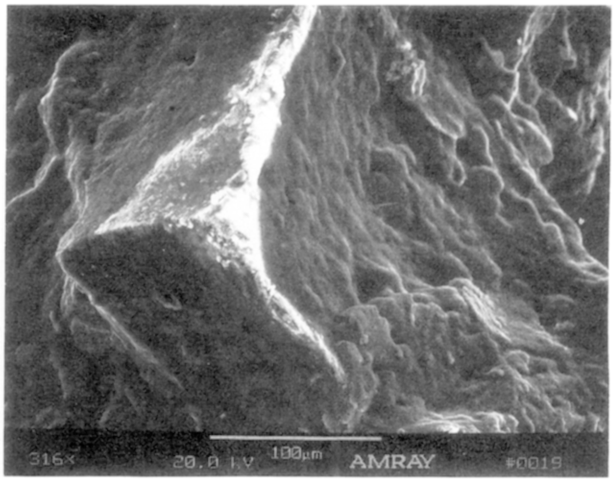

Figure 1. SEM micrograph of $FeAl_2O_4$.

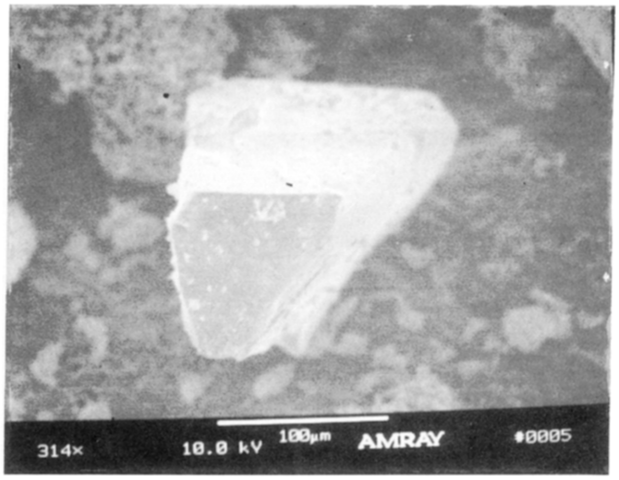

Figure 2. SEM micrograph of $CuAl_2O_4$.

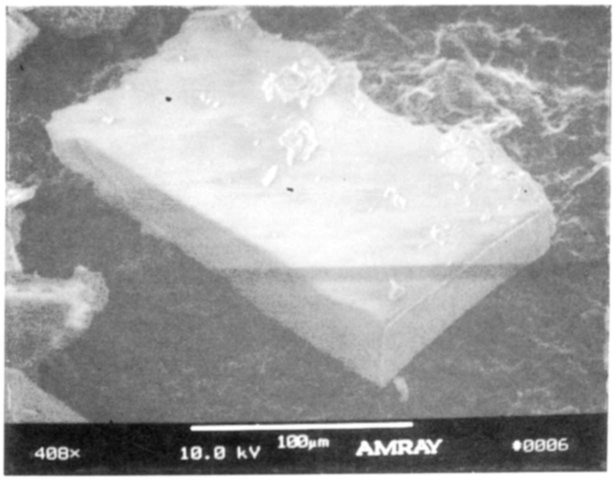

Figure 3. SEM micrograph of $NiAl_2O_4$.

Discussion

When the divalent cation is less than about 1.60-Å diameter (cobalt, iron, magnesium, manganese, and zinc) spinel structures were formed. When nickel or copper was the cation, an inverse spinel is formed with one-half of the aluminum atoms occupying tetrahedral sites. Another spinel which was prepared [$Mg(Al,Fe)_2O_4$] has both aluminum and iron occupying the octahedral sites. Crystal-field stabilization energies (CFSE, Table IX) have been used to predict whether a metal cation will prefer octahedral or tetrahedral sites.[13,14]

The probability of Fe^{2+}, Mn^{2+}, or Co^{2+} being in octahedral sites is very small; therefore, the normal spinel structure results. The stabilization for Ni^{2+} in an octahedral site is 8.45 D_q, which is enough energy to invert the structure. $MgAl_2O_4$ and $ZnAl_2O_4$ have the most stable

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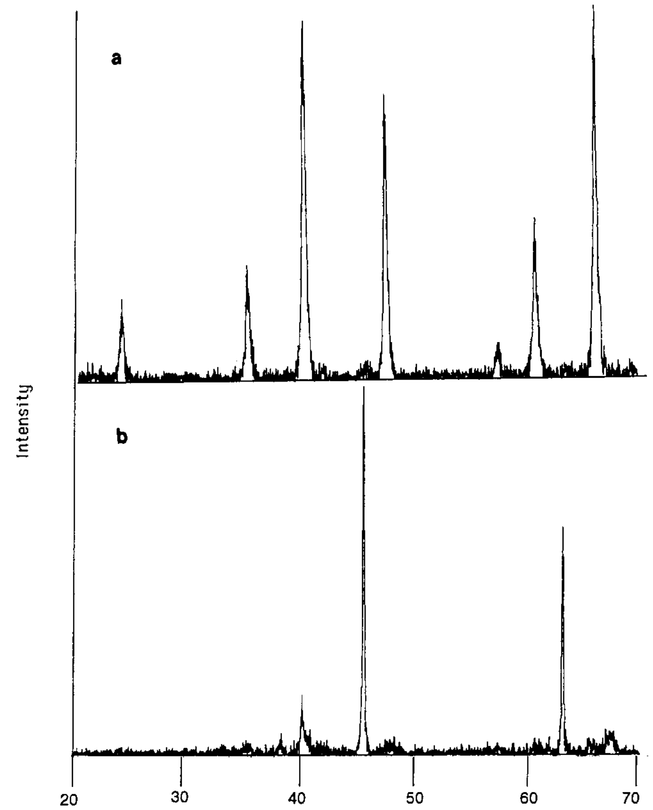

Figure 4. Comparison of XRD diagrams of (a) $MgAl_2O_4$ synthesized by the sol–gel method and (b) mixture of $MgAl_2O_4$ and reactant oxides prepared by the conventional solid-state method.

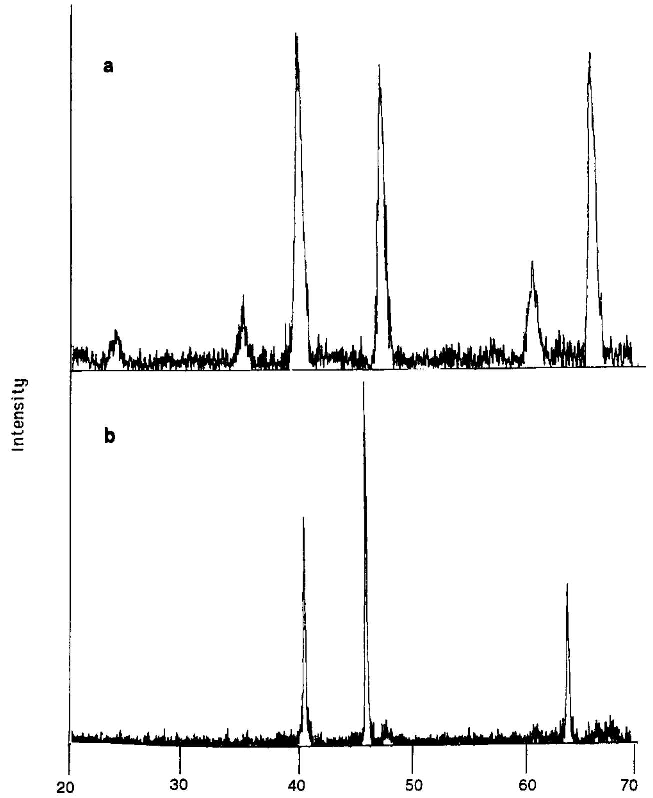

Figure 5. Comparison of XRD diagrams of (a) $NiAl_2O_4$ synthesized by the sol–gel method and (b) mixture of $NiAl_2O_4$ and reactant oxides prepared by conventional solid-state method.

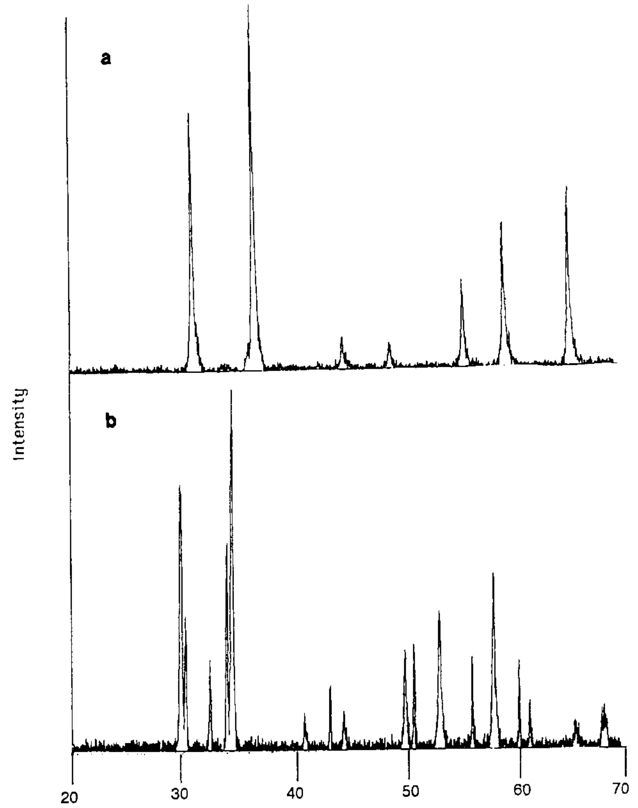

Figure 6. Comparison of XRD diagrams of (a) $ZnAl_2O_4$ synthesized by the sol–gel method and (b) mixture of $ZnAl_2O_4$ and reactant oxides prepared by the conventional solid-state method.

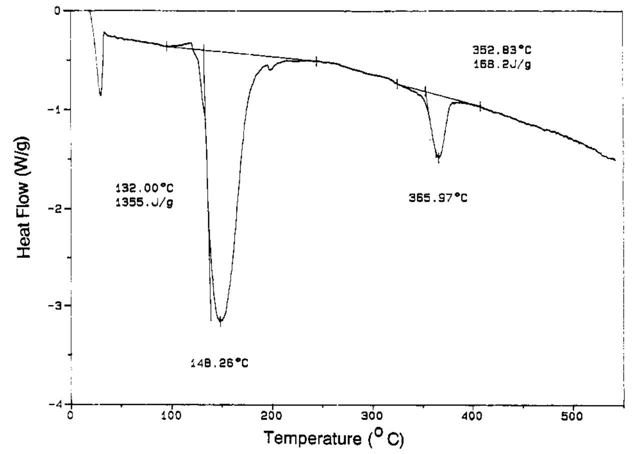

Figure 7. DSC curve for precursor gel of $NiAl_2O_4$.

Table IX. CFSE and Octahedral Site Stabilization Energies (OSSE) for M^{2+} (M = Co, Fe, Mn, Ni, Cu)[13,14]

M^{2+}	CFSE (tetrahedral) OSSE (units = D_{q0})	oct site D_{q0}	oct site preference (kJ mol^{-1})
Mn	0	0	0
Fe	2.67	1.33	16.3
Co	5.33	2.57	8.8
Ni	3.55	8.45	95.2
Cu	1.78	4.22	65.2

arrangement of divalent cations in tetrahedral geometries and trivalent cations in octahedral geometry resulting in the normal spinel structure. The compound $Mg(Al, Fe)_2O_4$ also has the spinel structure. In this case both Al^{3+} and Fe^{3+} occupy octahedral sites, the octahedral stabilization energy for Fe^{3+} being zero.

A different structure results when the divalent cation is greater than about 2.2-Å diameter (Ba, Ca, Sr, Cd, and

Table X. Ionic Radii of Divalent Ions

2+ ion	ionic radius[a]	2+ ion	ionic radius[a]
Ba	1.34	Hg	1.10
Ca	0.99	Mg	0.66
Cd	0.97	Mn	0.80
Co	0.72	Ni	0.69
Cu	0.72	Sr	1.12
Fe	0.74	Zn	0.74

[a] Ahrens, L. H. *Geochim. Cosmochim. Acta* **1952**, *2*, 155.

Hg). The size of these cations does not allow the cubic spinel structure to form. The ionic radii of the divalent cations studied is given in Table X. Both Ba, Cd, and Hg moieties form hexagonal phases. The monoclinic phase is formed when the divalent cation is calcium. When the divalent cation is Pb the $Pb_2Al_2O_5$ structure results. Again the size of the Pb^{2+} is too large to be incorporated into the spinel structure.

The position of the Al^{3+} in either an octahedral or tetrahedral site is of interest because of resultant Lewis acid properties. If the aluminum is in a tetrahedral site the activity of the aluminate as a catalyst is greater than corundum.[12,15,16] Figure 4 shows the X-ray data comparison of sol–gel synthesized and conventional solid state prepared $MgAl_2O_4$.[22] The conventional method involves mixing magnesium oxide with alumina and sintering the sample at 900 °C for 20 h. The X-ray pattern of sol–gel $MgAl_2O_4$ is shown in Figure 4a, and the conventional synthesized material is shown in Figure 4b. The diffractogram for the $MgAl_2O_4$ prepared by a conventional method shows peaks for magnesium oxide. The X-ray pattern of $MgAl_2O_4$ synthesized by sol–gel methods shows only the spinel phase present.

Hettig et al.[17] reported the synthesis of zinc aluminate. They report that the spinel phase begins to form at 850 °C and complete transformation to the spinel occurs at 1150 °C. Using sol–gel methods to synthesize zinc aluminate, we find that at 900 °C only the spinel is formed. The comparison of the X-ray patterns of synthesis of $NiAl_2O_4$ is shown in Figure 5. The pattern of the conventional synthesized material (Figure 5b) shows only nickel oxide lines and no transformation to the spinel. The X-ray pattern of the sol–gel synthesized material shows only the spinel phase present without nickel oxide being formed (Figure 5a). When zinc oxide and alumina are mixed and sintered at 900 °C some spinel formation is seen in the X-ray pattern (Figure 6b) but for the sol–gel synthesized material only the X-ray pattern of the spinel phase is present (Figure 6a).

The DSC curve for $NiAl_2O_4$ gel is shown in Figure 7. The DSC curve shows an endotherm at 148 °C. This curve corresponds to the loss of physisorbed water and the loss of ligands and solvents. There is also another weaker endotherm at 365 °C. This endotherm is presumably the result of the pseudo-boehmite to γ-Al_2O_3 transformation. This transformation can occur between 350 and 450 °C.[18-20] Tayaa et al.[18] report that in the modification of the processing of aluminas by sol–gel synthesis that if the additive participates in gel formation and is not a good complexing ligand toward aluminum that the DTA curve will show an intense and narrow endotherm at 140 °C, followed by a weak endotherm at 380 °C. They also attribute the endotherm at 380 °C to the alumina transformation. X-ray results before and after the endotherm show only nickel oxide lines.

A reviewer has suggested we comment on the use of precipitation methods[24-26] that have been used to prepare spinels at temperatures as low as 500–600 °C in contrast to the sol–gel methods described here. The precipitation method is useful for simple spinels; however, phase segregation of separate metal oxides often occurs with this method, especially for the more exotic mixed metal spinels and for the nonspinel oxide systems reported here (i.e., Pb, Ca, etc.). In addition, it is more difficult to control the stoichiometry of spinels formed by coprecipitation[24-26] than with sol–gel methods.

Conclusions

Sol–gel methods have been developed here to prepare normal and inverse spinel materials as well as other oxide phases. Transparent gels result from reactions of aluminum isopropoxide and nitrate or acetate transition metal salts. Thermal treatment of the amorphous gels to temperatures of 900 °C leads to single phase crystalline spinel and related materials in less time (20 h) and lower temperatures than traditional high-temperature solid-state materials. Particles sizes range from 20 to 200 μm with colors varying from white (Ca, Cd, Mg, Sr, Ba) to bright (Co, Hg, Ni, Fe) to dark (Cu, Mn, Mg–Fe). Cation radii for ions in the tetrahedral sites of resultant spinels need to be less than about 0.8 Å unless other phases are desired. Crystal field and octahedral site stabilization energies can be used to predict the preference for specific cations to occupy tetrahedral versus octahedral sites. Similar studies have shown that this general synthetic method can be used to prepare other solids such as ferrites, superconductors, films, foams and other materials.[23]

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