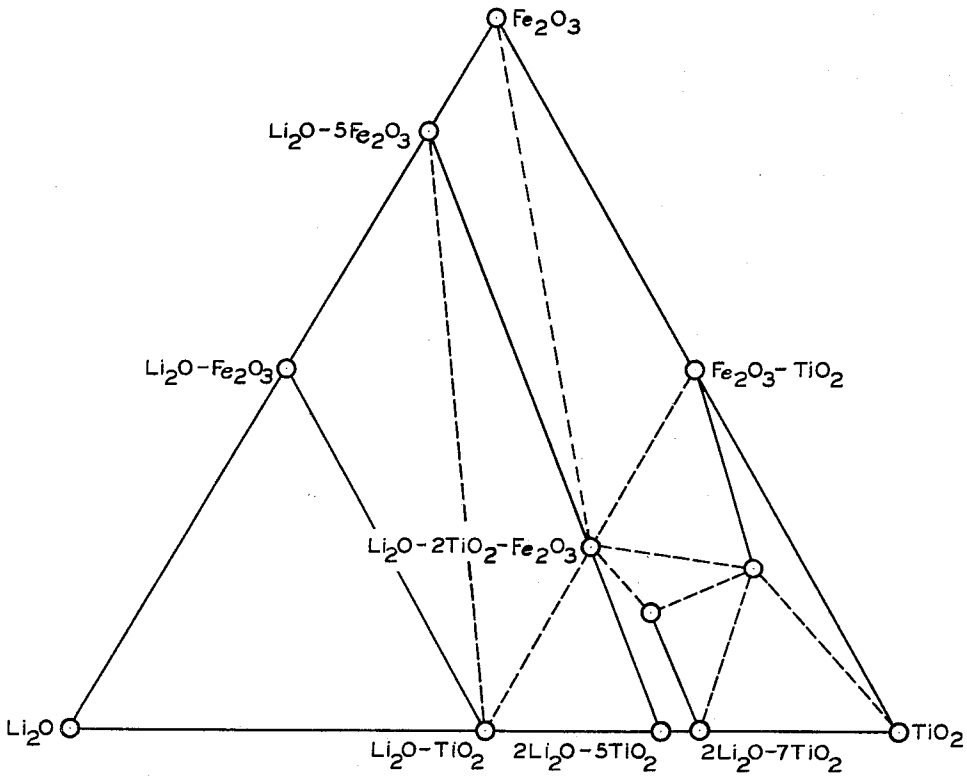
July 2, 1963 R. V. SARAKAUSKAS ET AL 3,096,288

FERRI-MAGNETIC SPINEL BODIES

Filed Dec. 23, 1957



——— SOLID SOLUTION
– – – – – – BINARY PHASE LINES
TEMP. RANGE: 1050 °C TO 1250 °C

INVENTORS
RAYMOND V. SARAKAUSKAS
MASON C. COX
NORMAN R. THIELKE

BY John F Hohmann

ATTORNEY

United States Patent Office 3,096,288 Patented July 2, 1963

3,096,288

FERRI-MAGNETIC SPINEL BODIES

Raymond V. Sarakauskas, North Olmsted, Mason C. Cox, Bay Village, and Norman R. Thielke, North Olmsted, Ohio, assignors to Union Carbide Corporation, a corporation of New York

Filed Dec. 23, 1957, Ser. No. 704,732
11 Claims. (Cl. 252—62.5)

This invention relates to a novel series of ferritic compounds possessing a variety of magnetic properties.

The present invention has for its main object the provision of novel ferritic compositions, certain properties of which may be maximized to render the same particularly useful in given applications.

Another object of the invention is to provide novel ferritic materials valuable for use as low loss cores in electric components operated at radio frequency.

The single FIGURE accompanying this disclosure is a triaxial composition diagram representing the oxide system Li_2O—TiO_2—Fe_2O_3 and shows the compatible phase areas demarcating the field of this invention.

Ferrites are ceramic materials which respond to applied magnetic fields at frequencies as high as the megacycle range, and which possess an electrical resistance far superior to any magnetizable metal. Most ferrites yield X-ray diffraction patterns identifying them structurally with the mineral, spinel, $MgOAl_2O_3$. The unit cell of this structure is a cubic arrangement of 32 anions (X), with 24 cations (A, B) distributed in certain interstices between the anions. In the so-called normal spinel unit cell, "A" type cations occupy lattice sides formed by four adjoining "X" anions, and, therefore, are said to be tetrahedrally coordinated; whereas "B" type cations occupy lattice sides formed by six adjoining "X" anions and are said to be octahedrally coordinated. The resulting formula for such an arrangement is AB_2X_4.

Also known are so-called "inverse" spinels, which correspond to the formula $BABX_4$. In such compounds, half the "B" type cations occupy tetrahedral sites, while the remaining "A" and "B" type cations share octahedral sites.

The magnetic behavior of ferrites or spinels arises from the existence and relative alignment of unpaired spins of electrons in their orbits. Partial spin alignment in the direction of an applied magnetic field results in paramagnetic response in direct proportion to the magnitude of the field. In addition, cooperative, reinforcing spin alignments by many unpaired electrons closely adjoining one another result in ferromagnetic response to an applied magnetic field, as evidenced by the typical hystersis loop pattern. Similar cooperative reinforcing spin alignment for ions on the "A" site opposes the cooperative reinforcing spin alignment for ions on the "B" sites yielding a net "A, B" response to a field which may equal or exceed zero. This response is direct ferrimagnetism, and is, therefore, a function of the identity, distribution and spacial relationship of ions in the crystal lattice.

To elaborate on the occurrence of the unpaired electrons previously discussed, it is helpful to consider the periodic classificaiton of elements. The fourth period thereof includes a transition series which comprises those elements having electrons in the 3d orbit of the "M" shell. Unpaired electrons occur periodically as a result of the incremental addition of 3d electrons in the series scandium through copper. Thus metallic potassium, calcium, scandium, titanium, chromium and manganese are increasingly paramagnetic in character; and iron, cobalt and nickel are decreasingly ferromagnetic. When ionization occurs in the atoms of this transition series,

the number of unpaired electrons is altered, and the magnetization changes accordingly.

It has been observed that ions of transition elements give rise to ferri-magnetic behavior when properly distributed on the alternative lattice sites available in a spinel structure. By contrast, other ions having no unpaired 3d electrons have been found in compounds which possess the spinel structure, but which do not exhibit ferrimagnetism. In common with the transition metal ions, such ions still conform to certain requirements for ion size and radius ratio, so that the spinel structure may be stated to require that tetrahedrally and octahedrally coordinated ions possess dimensions as follows:

	Radius Angstrom Units	Radius Ratio
Cations:		
A Type	0.34–1.12	A:B=0.6–1.0
B Type	0.62–1.10	A:X=0.4–0.8
Anions:		
X Type	1.32–1.95	B:X=0.4–0.7

Accordingly, a ferrite could be chemically described according to prior art by the formula $RO{\cdot}Fe_2O_3$ (or RFe_2O_4), where R was a doubly charged ion, or was fractionally composed of two or more ions, for example, 30 percent zinc, 70 percent nickel, with the result that the compound might be written $Zn_{0.3}Ni_{0.7}Fe_2O_4$. Every ferrite of this type has inherent properties such as initial permeability, maximum permeability, residual magnetism, coercive force, and Jordan loss constant. Simple combinations of ferrites containing different divalent ions allowed the researchers of the prior art to adjust given magnetic properties of ferrites, but only at the expense of other properties.

Another difficulty with the prior art ferritic materials of the $RO{\cdot}Fe_2O_3$ type was the necessity of employing temperatures of 1400° C. to 1600° C. At such high temperatures special furnaces and atmosphere controls were required, thereby increasing the cost of the end product.

The present invention is based upon the realization that one of the oxides present in the conventional ferrite formula may be replaced by two or more oxides, the cations of which have similar ionic bonding radius and cation to anion radius characteristics, or whose statistical parameters conform to these requirements. Thus it has been found that certain spinels tolerate this combinational replacement of ions, and that in a compound of the type $ROFe_2O_3$, both the doubly charged R ion and the triply charged Fe ion may be replaced by appropriate compositions of cations. In contrast to the prior art line of ferrite compositions, which may be expressed as $RO{\cdot}Fe_2O_3$ and analogs thereof, the present invention provides novel substitutional series represented by the formula:

$$a{Li_2O}{\cdot}b{RO_2}{\cdot}c{R_2'O_3}$$

wherein R stands for Ti, Mn; R′ stands for Fe, Cr; a ranges from 1 to 2; b ranges from 0 to 5; c ranges from 0 to 5; and the sum of $a+b+c$ ranges from 3 to 7.

Obviously the permutations of multiple oxide substitutions are very numerous, even if all the arrangements of oxides having no magnetically active cations present are excluded. In order that the magnetic spinel structure remain, it is necessary that the amount of $R_2'O_3$ not be less than a certain value unless other spinel forming materials such as $RO{\cdot}Fe_2O_3$ are present. This minimum value is approximately 10 mol percent of the final compound, which in the above formula is equivalent to a lower limit for c of about 0.1 $(a+b+c)$, or when a equals 1, of about 0.1 $(1+b+c)$. The present invention makes

available a continuum of fundamental composition which can be combined with any proportions of other $ROFe_2O_3$ ferrites to give greater variety in magnetic properties than are heretofore possible. With the novel compositions of this invention it is possible to optimize magnetic properties such as Curie temperature, permeability, loss factor and saturation magnetization.

With the ferrites of the invention it is also possible to obtain compositions which have such low iron content that they are almost unrecognizable as ferrites, but which nevertheless possess valuable magnetic properties.

The properties of the ferrites of the invention are a function of the constituents present therein, of their mode of combination and of the individual property contributions from each constituent. In general, the characteristics contributed by each constituent reactant are additive.

By increasing the density of these ferrites by varying the kind of reactant, the fabrication procedure or the conditions of heat treatment, the permeability of the ferrites increases and their resistivity falls.

Briefly stated, the ferrites of the invention are prepared by finely dividing oxides or carbonates containing the desired ions, mixing the same in the dry state, wet milling a slurry of the reactants, drying the slurry, pre-calcining the dried slurry to a temperature below the particular final sintering temperature for these reactants, to effect substantially complete transformation thereof to the ferrite form; cooling the calcined mass, repulverizing the resulting calcine; forming a compressed body therefrom, preferably with plasticizers and bonding agents; firing the formed body at a temperature range of 950° C. to 1350° C. and then cooling. To obtain a completely single phased product, an excess of about 0.1 percent of lithium compound should be used. Omitting this excess, however, in no way changes the properties of the products.

Instead of starting with oxides or carbonates containing the ions desired in the final ferrite formulation, such oxides may be precipitated in hydrated form from separate or mixed solutions of the desired salts. In a further variant of the invention, use is made of formates and oxalates which thermally decompose into extremely fine reactive crystals capable of accelerating ferrite formation and crystal growth.

In the case of certain ferrites, particularly those containing manganese oxides or amounts of Fe_2O_3 exceeding the stoichiometric value for the ferrite, atmosphere control may be resorted to for the stabilization of the oxidation rate of the cation. In practice, atmosphere control is employed only during the cooling cycle or alternatively during a second reheat cycle at a lower temperature.

The compositions of the invention include, in summary, the following systems:

(*a*) System Li_2O—TiO_2—Fe_2O_3

(1) Ferrospinel-type compositions along join $Li_2O\cdot 5Fe_2O_3$—$2Li_2O\cdot 5TiO_2$

(2) Two-phase bodies in the compositional areas defined by the compatibility triangles immediately adjacent to the spinel-type solid solution join,

$Li_2O\cdot 5Fe_2O_3$—$Li_2O\cdot 2TiO_2\cdot Fe_2O_3$:

(*a*) triangle $Li_2O\cdot 5Fe_2O_3$ —$Li_2O\cdot 2TiO_2\cdot Fe_2O_3$—$Li_2O\cdot TiO_2$,

(*b*) triangle $Li_2O\cdot 5Fe_2O_3$ —$Li_2O\cdot 2TiO_2\cdot Fe_2O_3$—$Fe_2O_3$, and

(*c*) triangle $Li_2O\cdot 2TiO_2\cdot Fe_2O_3$ —$Li_2O\cdot TiO_2$—$2Li_2O\cdot 5TiO_2$

(3) Multiphase bodies in the compositional areas defined by the compatibility triangles next most adjacent to the ferrospinel solid solution join:

(*a*) triangle $Li_2O\cdot 5Fe_2O_3$ —$Li_2O\cdot TiO_2$—$Li_2O\cdot Fe_2O_3$, and

(*b*) triangle $Li_2O\cdot 2TiO_2\cdot Fe_2O_3$ —Fe_2O_3—$Fe_2O_3\cdot TiO_2$

The utility of these compositions is indicated by the diminishing values of powder permeability of powder specimens of those compositions observed for compositions farther from the spinel solid solution join.

(4) The compositional area of marginal utility may be extended to include the compatibility triangles:

(*a*) $Li_2O\cdot 5Fe_2O_3$—$2Li_2O\cdot 5TiO_2$—$Li_2O\cdot TiO_2$, and the polygon

(*b*) $Li_2O\cdot 5Fe_2O_3$—$2Li_2O\cdot 5TiO_2$ —$2Li_2O\cdot 7TiO_2$—$Fe_2O_3\cdot TiO_2$—Fe_2O_3

(5) At even more elevated temperatures, the miscibility gaps disappear, and the polygonal areas indicated are of interest:

(*a*) $Li_2O\cdot 5Fe_2O_3$—$Li_2O\cdot Fe_2O_3$ —$Li_2O\cdot TiO_2$—$2Li_2O\cdot 5TiO_2$, and

(*b*) $Li_2O\cdot 5Fe_2O_3$—$2Li_2O\cdot 5TiO_2$ —$Fe_2O_3\cdot TiO_2$—Fe_2O_3

Further latitude becomes available when other ferrites are incorporated into compositions embraced within the system Li_2O—TiO_2—Fe_2O_3. A number of these variants are indicated:

(*aa*) System Li_2O—TiO_2—Fe_2O_3, with compositional ranges as described in

(*a*) above, but containing, in addition, a proportion of $ZnO\cdot Fe_2O_3$ in solid solution as single phase ferro-spinel compositions.

(*ab*) Related compositions employing $CdO\cdot Fe_2O_3$,

(*ac*) More distantly related compositions employing other ferrites of "normal" type or mixed types, such as $MgFe_2O_4$, $NiFe_2O_4$, $MnFe_2O_4$ and others of these types.

(*ad*) Complex systems, comprising a substituted ferrite, e.g., $Li_2O\cdot TiO_2\cdot 3Fe_2O_3$, plus a conventional "inverse" ferrite:

(1) $CuO\cdot Fe_2O_3$
(2) $MgO\cdot Fe_2O_3$
(3) $MnO\cdot Fe_2O_3$
(4) $NiO\cdot Fe_2O_3$
(5) $CoO\cdot Fe_2O_3$

(*ae*) Systems of further complexity, comprising a substituted ferrite, e.g., $Li_2O\cdot 2TiO_2\cdot Fe_2O_3$, plus a conventional "inverse" ferrite, as above, plus a conventional "normal" ferrite, such as zinc ferrite.

(*b*) System Li_2O—MnO_2—Fe_2O_3.

(*c*) Compositions in which aluminum or other trivalent ions replace part of the trivalent iron.

(*d*) Compositions based on the oxide formulations of the type $R_aO_b\cdot R_cO_d\cdot Fe_2O_3$.

(*e*) Compositions based on oxide formulations of the general formula $R_aO_b\cdot R_cO_d\cdot R_2O_3$, where R_2O_3 comprises a ferromagnetically active oxide such as Cr_2O_3, Mn_2O_3, V_2O_3, rare-earth sesquioxides, etc.

(*f*) Compositions based on spinel-type formulations other than those derived from the $RO\cdot R_2O_3$ prototype. These include:

(1) Derivatives of the formulation $R_2O\cdot RO_3$,

(2) Derivatives of the formulation $2RO\cdot RO_2$, etc.

(*g*) Compositions of the spinel structure and formulation in which a portion or all of the oxygen ions are replaced by divalent sulfur, selenium or tellurium ions or monovalent fluorine or hydroxyl ions, in appropriate stoichiometric proportion. Derivatives of these types predicted from the known degrees of similarity in ion size, bond character and electronic structure among these elements, evidenced by their mutually neighboring position in the periodic system and by their frequent appearance in closely related structures.

It should be noted that the solid solution series between $Li_2O\cdot Fe_2O_3$ and $Li_2O\cdot TiO_2$ is cubic, NaCl type. The central solid solution series between $Li_2O\cdot 5Fe_2O_3$ and $2Li_2O\cdot 5TiO_2$ shows the spinel structure or a close deriva-

tive of it. The third solid solution series originating at $Fe_2O_3 \cdot TiO_2$ is found to be orthorhombic. The series of primary interest comprises the cubic, ferrospinel type compositions between $Li_2O \cdot 5Fe_2O_3$ and $2Li_2O \cdot 5TiO_2$. Reacted compositions along this join showed only a single phase solid solution of the ferrite type, whereas those to either side of this join contained, in addition, a proportion of the phase identified at the respective apex of the adjoining composition triangle. The relative amounts of the phases present are determinable by the usual lever-arm relationship applied in phase equilibrium problems.

Preliminary observations of magnetic activity were obtained by measurements of inductance on solenoidal coils with and without a core comprising powdered compositions of these ferrospinels. These were extended to many other compositions along the ferrospinel join and in adjacent areas. The degree of magnetic activity to be expected in the sintered compacts may be inferred roughly, at least, from the trends in effective magnetic permeability of the powder core.

The systems of the present invention are especially suitable as low loss cores in a variety of electronic components used at radio frequency. Generally the materials of the invention have initial permeability values of 24 to 52 on toroids, and 20 to 40 on rods at a test frequency of about one megacycle per second with associated resistivities of 10^3 to 10^6 ohm-centimeters.

The magnetic and electric properties of typical novel ferrite compositions are summarized in Table I.

TABLE I

Properties of Novel Ferrite Compositions

Code Number	Rods or Bars (Test Frequency—0.9 mc./s.)					Toroids (Test Frequency—1.2 mc./s.)			
	Sintering Temperature ° C.	Percentage Theoretical Density	Effective Relative Initial Permeability	Quality Ratio Q_e/Q_0	Log Resistivity Ohm-cm.	Sintering Temperature ° C.	Percentage Theoretical Density	Effective Absolute Initial Permeability	Quality Ratio Q_e/Q_0
5025	1,295	80.0	[1] 31	[2] 0.3	[4] 6.3	1,280	85.3	[3] 52	[2] 1.6
5123	1,300	77.2	34	0.5	3.3	1,280	83.5	38	0.7
5221	1,315	76.4	34	0.5	3.1	1,280	79.5	40	2.4
5319	1,290	83.0	30	0.3	4.0	1,280	79.5	36	2.4
5417	1,325	82.8	31	0.2	3.9	1,280	80.0	39	2.2
5515	1,250	85.3	31	0.4	3.8	1,285	87.5	34	1.6
2010-A	1,285	87.8	32	0.4	4.8	1,285	88.0	39	2.2
218-A	1,285	90.5	28	0.7	2.0	1,285	90.6	32	2.0
226-A	1,285	87.5	39	0.2	3.8	1,285	88.3	42	1.4
234-A	1,285	82.9	20	0.7	4.9	1,285	78.5	24	1.9
242-A	1,285		2	0.5	5.0	1,285			

[1] Solenoidal coil and Q-meter; permeability of core calculated on basis of 100% coil occupancy.
[2] Ratio of Q values of circuit element with and without core respectively.
[3] National Electronics Permeameter and Q-meter.
[4] Resistivity at 60 c./s.

The compositions corresponding to the code numbers used are:

Mol percent			Code Number
Li_2O	TiO_2	Fe_2O_3	
16.67	0.00	83.33	5025
17.34	4.00	78.66	5123
18.00	8.00	74.00	5221
18.67	12.00	64.33	5319
19.33	16.00	64.67	5417
20.00	20.00	60.00	5515

Code Number	Molar Composition
2010-A	$Li_2O \cdot 5Fe_2O_3$
218-A	$Li_2O \cdot 0.5TiO_2 \cdot 4Fe_2O_3$
226-A	$Li_2O \cdot 1.0TiO_2 \cdot 3Fe_2O_3$
234-A	$Li_2O \cdot 1.5TiO_2 \cdot 2Fe_2O_3$
242-A	$Li_2O \cdot 2.0TiO_2 \cdot 1Fe_2O_3$

For a clearer understanding of the invention, the following example is given. A ferrite having the formulation—$Li_{0.23}Ti_{0.06}Zn_{0.60}Fe_{2.11}O_4$, was prepared from 9.25 gms. Li_2CO_3, 5.00 gms. TiO_2, 54.00 gms. ZnO and 187.00 gms. Fe_2O_3. These oxides and carbonates were mixed as a slurry with alcohol for approximately one hour, with a Hobart N–50 mixer. The well mixed powders were placed in fire clay crucibles and calcined at 1050° C. for two hours in an air atmosphere. The ferrite powder which consisted only of a spinel phase was milled with 100 cc. of alcohol in a porcelain mill with Alundum balls for five hours. The slurry was discharged and then permitted to dry in an oven at 55° C. The fine-ground ferrite (250 gms.) was mixed thoroughly with a 2 percent solution of methocel (30 cc. of above-mentioned solution to 50 gms. of ferrite powder). The slurry was permitted to dry at 55° C. to a hard cake which then was pulverized to pass 20 mesh sieve. Five percent water was added to this powder containing the binder; the mixture was sealed in a jar and permitted to stand overnight. The powder then was pressed as toroids under a load of 5000 p.s.i.

Toroids were fired on setters lined with platinum and fired to a peak temperature of 1200 to 1225° C. for periods of time ranging from 4 to 16 hours. Heating rate to this temperature was 200° C. per hour in an air atmosphere, and cooling was at the normal free kiln cooling rate.

Toroidal specimens of the above composition exhibited initial permeability values of 715 when fired at 1225° C. for four hours and of 815 when fired at 1200° C. for ten hours.

What is claimed is:

1. A substituted ferrite material of spinel structure suitable for use as low loss cores in electric components, said material having the formula:

$$Li_2O \cdot bRO_2 \cdot cF_2O_3$$

wherein b ranges from 0 to 5 and c ranges from about 0.1 $(1+b+c)$ to 5; R stands for a cation selected from the group consisting of titanium and manganese, the sum of $(1+b+c)$ being from 3 to 7.

2. The substituted ferrite defined in claim 1 wherein R represents titanium.

3. A ferrite material comprising a composition which when represented on a molar three-phase diagram of Li_2O, Fe_2O_3, and TiO_2 as shown in the drawing, and when crystallized at a temperature in the range of 1050° C. to 1250° C. lies on a straight line connecting the points $Li_2O \cdot 5Fe_2O_3$ and $2Li_2O \cdot 5TiO_2$ and which contains at least about 10 mole percent Fe_2O_3.

4. A ferritic composition consisting essentially of a material having the composition $Li_2O \cdot 0.5TiO_2 \cdot 4Fe_2O_3$.

5. A ferritic composition consisting essentially of a material having the composition $Li_2O \cdot TiO_2 \cdot 3Fe_2O_3$.

6. A ferritic composition consisting essentially of a material having the composition $Li_2O \cdot TiO_2 \cdot 2Fe_2O_3$.

7. A ferritic composition consisting essentially of a material having the composition $Li_2O \cdot 2TiO_2 \cdot Fe_2O_3$.

8. A ferritic composition consisting essentially of a material having composition

$$17.34Li_2O \cdot 4.00TiO_2 \cdot 78.66Fe_2O_3$$

9. A ferritic composition consisting essentially of a material having the composition

$$18.00Li_2O \cdot 8.00TiO_2 \cdot 74.00Fe_2O_3$$

10. A ferritic composition consisting essentially of a material having the composition

$$18.67Li_2O \cdot 12.00TiO_2 \cdot 64.33Fe_2O_3$$

11. A ferritic composition consisting essentially of a material having the composition

$$19.33Li_2O \cdot 16.00TiO_2 \cdot 64.67Fe_2O_3$$

References Cited in the file of this patent

UNITED STATES PATENTS

2,549,089	Hegyi	Apr. 17, 1951
2,584,324	Bousky	Feb. 5, 1952
2,640,813	Berge	June 2, 1953
2,736,708	Crowley	Feb. 28, 1956
2,770,523	Toole	Nov. 13, 1956
2,851,419	Gorter et al.	Sept. 9, 1958

FOREIGN PATENTS

713,370	Great Britain	Aug. 11, 1954
735,375	Great Britain	Aug. 17, 1955
752,659	Great Britain	July 11, 1956
76,660	Netherlands	Nov. 16, 1954
1,100,865	France	Apr. 13, 1955
1,707,654	France	Aug. 10, 1955
514,251	Canada	June 28, 1955

OTHER REFERENCES

J. Institute of Electrical Engineers, Japan, November 1937, pp. 4, 5, 7.

Kordes et al.: Chem. Abs., vol. 46, column 4411, May 25, 1952.

Gorter: Proceedings of the IRE, December 1955, p. 1933.

Gorter: Philips Research Reports, vol. 9, No. 6, pp. 403–418.

Weisz: Ceramic Ind., vol. 58, pp. 130–134, April 1952.