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Preparation and properties of active submicronic solids and new metastable phases obtained via a metal–organic precursor method

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The mixing of constituent ions on an atomic scale accomplished in single phase metal–organic precursors facilitates the occurrence and completion of the reactions such as decomposition, oxidation and reduction at reduced temperatures and in shorter times. This has been particularly shown for the first series of transition metals and for the lanthanide elements for which simple, and mixed oxides or their oxide solid-solutions have been prepared via decomposition and treatment of their respective organic salt precursors. The method gives compounds with increased homogeneity, purity and reactivity and allows isolation of submicronic solids and sometimes of new metastable phases, which could not have been obtained by high-temperature reactions. The morphological and other application properties of these submicronic solids and of new metastable phases can be widely modified and regulated by varying the composition and treatment given to the metal–organic precursors.

1. Introduction

For many years, inorganic and organic precursors of metals have been utilized for preparation of simple and complex metal oxides and other related systems. These efforts have uniquely contributed towards forging ahead the practice of soft chemical methods in inorganic syntheses thus providing new and effective means for production of active solids. As early as 1951, Robin and Benard [1, 2] carried out the decomposition of the mixed oxalates of iron and cobalt in order to study the iron–cobalt oxygen system. This initial work was followed by that of Wickham and co-workers [3, 4] who extended this work for the preparation of a number of mixed oxide compounds. Side by side, use of various inorganic precursors such as those of metal nitrates, sulphates, carbonates, and oxide hydrates continued for the preparation of various mixed metal oxides. For over two decades we have been interested in the problems of inorganic syntheses using metal–organic salt methods. This has resulted in studies aimed at extending the range of the metal–organic precursors [5, 6] and have enabled us to obtain effective means for isolating submicronic solids and new metastable phases with original application properties [7, 8].

This paper presents a brief outline of the current practice of metal–organic precursors giving examples of preparation of simple and mixed oxides and oxide solid-solutions for the elements of the first transition metals series and the lanthanides. The aspects of preparation and characterization of already known compounds, of submicronic solids and of new metastable phases have been addressed with a view to exemplify the proper and rational utilization of the metal–organic precursor method in regulating and modifying the original application properties of the products.

2. Metal–organic precursors and their rational utilization in syntheses of inorganic solids

According to Yoldas [9] the term "metal–organic" includes the compounds having organic groups along with a metal (or metals) and in which organic groups are bound to a metal via oxygen, etc. In these solids which are generally the salts constituted of simple or complex ions, one or more metals are associated to the organic anions susceptible of having a "coordinating" effect in certain cases.

From the viewpoint of the synthetic strategies more interesting compounds that we have distinguished can be grouped into two series. The first group of the salts is formed by the anions with less carbon and includes salts such as formates $HCOO^-$, acetates CH_3COO^- and oxalates $C_2O_4^{2-}$ etc., of metal ions. The second group comprises the complex salt-forming anions which are richer in carbon. This includes the salts of lactates $C_3H_5O_3^-$, tartrates $C_4H_4O_2^{2-}$ and citrates $C_6H_5O_7^{3-}$. Though a complete set of such salts does not exist for every metal in the periodic table of the elements, in general, it is possible to isolate at least one salt for each metal, in solid form. This equally applies either for the simple salts like oxalates of bivalent metals $M^{II}C_2O_4 \cdot 2H_2O$ (M^{II} = iron, cobalt, nickel, zinc, copper, . . .) or for the complex salts like the trivalent metal oxalates $(NH_4)_3|M^{III}(C_2O_4)_3| \cdot 3H_2O$, ($M^{III}$ = iron, chromium, aluminium, vanadium, gallium). Several substitutions suitably carried out on bivalent cations in the first case and on trivalent cations and on ammonium ions in the second case, result in a mixing of many metallic elements on an atomic level and permit preparation of mixed compounds and solid solutions. Combination of transition metal ions and rare earth ions to give their mixed oxides was realized by Szabo [6], using the mixed citrates of the type $(NH_4)_3|Ln^{III}M^{III}(OH)(C_6H_4O_7)_2| \cdot nH_2O$, where Ln represents rare earth or yttrium and M^{III} represents iron, manganese, vanadium, chromium, ... Szabo [6] prepared a very wide range of mixed oxide compounds taking advantage of the substitutions suitably carried out on the rare earth sites and on the transition metal atoms and of incorporation of aluminium and gallium ions as well. In a single phase metal–organic precursor, incorporation of two or more metal ions in a controlled manner have permitted preparation of mixed compounds or solid solutions of metal oxides [1, 8, 10, 11] metal carbides [12], metal nitrides [13], and metal chalcogenides [14, 15]. One simple decomposition in air of the metal–organic precursors may directly lead to the formation of mixed oxides or solid solutions only in a certain number of cases. However, more often, rigorous conditions are required to be maintained for obtaining the desired products. In fact, initial oxidation states of the transition metal ions are rarely conserved during the pyrolysis of their organic salts in air atmosphere. At the moment of decomposition of the metal–organic salt precursor in a strongly reducing atmosphere (e.g. $CO-CO_2$), a diminution of the oxidation state takes place followed by an increase, when oxygen reappears over the extremely reactive solid phase [7, 16, 17].

These fluctuations are often cause for demixing and appearance of polyphase systems. In view of this, a deeper analysis of the salt decomposition mechanism and also of the oxide formation, at the same time must be made for attaining the maximum efficacy of the process. These analyses show generally the necessity to control the oxygen pressures and thus to use a specific schedule of heat treatment for the precursors.

As an example, let us consider the case of the preparation of solid solutions $\alpha(Al_{1-x}Cr_x)_2O_3$ starting from the precursor $(NH_4)_3|Al_{1-x}Cr_x(C_2O_4)_3|3H_2O$, its decomposition in air systematically yields a mixture of rhombohedral solid solutions: one based on corundum α-Al_2O_3 and the other based on the escolaite α-Cr_2O_3. Many hours of heating at high temperatures (1300° C) are then necessary to attain monophase solids. Contrarily, the decomposition of the same salt precursors in an oxidation–reduction atmosphere (H_2/H_2O) (during the course of which the chromium maintains its oxidation state as +3), at relatively low rate of temperature increase ($150° C h^{-1}$) enables one to obtain directly the phases α-$(Al_{1-x}Cr_x)_2O_3$. Accordingly, the composition of the solid solutions appearing between 600 and 1000° C by the same procedure rules out the necessity of processing the precursors at high temperatures [17].

3. Preparation and properties of materials obtained via organic precursor methods: some representative examples

3.1. Soft synthesis of already known mixed inorganic compounds

In the beginning, the organic precursors had been essentially used with the purpose of facilitating the synthesis of mixed phases or solid-solutions of oxids, carbides, nitrides and sulphides. In fact, these compounds are generally prepared by ceramic methods, which necessitate some "hard" conditions: high-temperatures and long-duration processing, the grinding-operations and sometimes even the use of high pressures.

Organic precursors permit the use of a lower preparation temperature in particular, and reduce treatment time. The grinding and sometimes even the application of high pressures may be largely dropped or avoided while using the organic precursors. The purity, stoichiometry and compositional homogeneity of the products are equally improved. For example, the rare earth aluminates, $LnAlO_3$, have been obtained by Szabo [6] at 900° C by simple decomposition of the citrates $(NH_4)_3|Ln(OH)Al(C_6H_4O_7)_2| \cdot nH_2O$ in air. Ceramic preparation methods of the same require many hours of heating at temperatures of the order of 1500° C. The perovskite manganites $HoMnO_3$ and $YMnO_3$, earlier prepared in particularly difficult conditions, which necessitate in addition to a temperature of 900° C, a pressure of 80 kbar [18, 19], have been obtained by Szabo by simple decomposition of the corresponding mixed citrates [6, 20]. Finally, to illustrate the advantages obtained with respect to purity we consider the case of $FeAlO_3$, the orthorhombic phase, whose stability domain is situated between 1320 and 1420° C and which cannot be prepared in a pure state by the ceramic method [21, 22]. It is by employing the precursor $(NH_4)_3|Fe_{0.5}Al_{0.5}(C_2O_4)_3|3H_2O$ that we could synthesize this compound without a trace of unreacted alumina [7].

A considerable decrease in preparation temperature is not without effect on the morphology, which in certain cases can be regulated (in terms of size, form and elementary grain texture of the particles produced by the precursor method); and on structure particularly with respect to the distribution of cations in the crystal network. The example of the ferrites obtained by these methods below 500° C are well known [23, 24] in this context.

3.2. Effect on the establishment of equilibria between different phases

Most of the phase diagrams have been constructed with the help of solid–solid reactions equilibria. In the present case, this occurs very often when the kinetics of the reaction is slow such that the state of the equilibrium may not be attained in reasonable time. This then results in errors when the domain of miscibility is on the low temperature side, in particular. Thus for the Fe–Cr–Al–O system, studied starting with the solids emerging initially from the precursors $(NH_4)_3|Fe_{1-x-y}Al_xCr_y(C_2O_4)_3|3H_2O$, we have obtained *prima facie* evidence of total miscibility of the oxides Fe_3O_4–$FeAl_2O_4$ and $FeCr_2O_4$ starting at 700° C [8].

Previously, in this very system, existence of a very large miscibility gap had been inferred [25] below 1000° C. It is of obvious interest that our results have been observed to be in accord with the recently reported theoretical work of Petric and Jacob [26].

3.3. Observation and elucidation of new metastable phases

This is one of the more interesting areas of the processes involving organic precursors. Often, in fact, these metastable phases have not been recorded earlier. These very phases present original properties (see Section 3.5) but, at the same time as they transform to the stable phases, these metastable phases permit study of the mechanisms of reactions in solids [27].

The metastable phases appear either directly, after decomposition of the precursors, or indirectly, via subjecting the solids which emerge from pyrolysis to the gas–solid reactions at low temperatures.

Szabo [6] and Sallavuard [15] have directly obtained hexagonal $SmAlO_3$, and hexagonal gallates $LnGaO_3$, of the first five lanthanides, utilizing the decomposition of the corresponding citrates. By employing one similar method involving the pyrolysis of corresponding metal nitrates, Bertaut and Mareschal [28] earlier obtained hexagonal aluminates $LnAlO_3$ (Ln = europium, gadolinium, terbium, dysprosium, holmium, erbium and yttrium). The domain of existence of these systems being lower than 1000° C rules out their preparation by typical ceramic methods. The decomposition of the mixed oxalates of chromium and aluminium in oxidation–reduction atmosphere directly leads to the formation of cubic γ-$(Al_{1-x}Cr_x)_2O_3$ solid solutions of the spinel type, identifiable by electron diffraction [29]. By an indirect way, but again starting with very reactive oxides that result from the decomposition of iron-based mixed oxalates in air atmosphere, we have been able to illustrate the formation of a number of cubic lacunar spinel phases. These consist of metastable solid solutions derived by the substitution of ferric sesquioxide γ-Fe_2O_3. On one side, Fe^{3+} ions are substituted by trivalent ions, e.g. Al^{3+}, Cr^{3+} [30–32], and on the other, Fe^{3+} ions and vacancies are substituted with the divalent ions, e.g. Co^{2+}, Zn^{2+}, Mn^{2+}, Ni^{2+} [33–36]. These phases which have their domain of existence below 700° C could not have been synthesized by ceramic procedures. With the advent of these phases, intensive studies on their physicochemical properties resulted, aimed at investigating correlations with their compositions and position of vacancies in the spinel lattice [31, 34, 37–40].

3.4. Preparation of submicronic solids

The decomposition of the organic precursors that terminates generally at low temperature (say 200 to 500° C) always gives very finely divided phases comprising the crystallites of several nanometres (specific surfaces being higher than $100\,m^2\,g^{-1}$) and non-identifiable with X-rays (see Fig. 1). At this stage and in the case of polymetallic organic precursors, the oxides formed are already mixed phases or solid solutions like those we have shown several times in studying their specific reactivity *vis-à-vis* intimate mixing of the simple oxides in them.

The annealing schedule that follows the thermal decomposition of the precursors permits improvement and regulation of the average dimensions of the crystallites to the desired values. This can be interesting, for example, in tailoring and modifying ceramics. Also contrary to what happens in the solid–solid reactions, the size of the crystallites is little "frozen" by the temperature. Rather, it has an evolutive character and thus can be better controlled and regulated. The chemical reactivity of a solid is very strongly linked with its state of division. Our studies, with all the interest attached to obtain very divided phases for realizing the gas–solid reactions at very low temperatures for which no similar reactions exist for massive solids, have amply testified this. An illustrative example for this is the preparation of rate-earth sulphides and oxysulphides [15] or that of the magnetites substituted by manganese [36], achieved at temperatures lower than 500 to 600° C, against that of earlier preparations which resulted in large crystallites of size of several tens of nanometres.

These possibilities of controlling the state of division of solids permit new investigations in the area of chemical reactivity. The kinetic studies initiated in collaboration with Gillot *et al.* have produced some original results concerning the relations between the positions of the ions in the spinel lattice and their aptitude towards oxidation [36, 41].

3.5. Original and application properties of new metastable phases

In general, these properties are linked either to the state of division of solids or to their original structure, characteristic of their preparation at low temperature. One of the first experimental verifications of the theories of Neel [42], on the superparamagnetism of fine antiferromagnetic particles was made in collaboration with Mollard [43] utilizing the solid solutions α-$(Fe_{0.24}\cdot Cr_{0.76})_2O_3$ obtained at 400° C starting with the oxalate precursor $(NH_4)_3|Fe_{0.24}Cr_{0.76}(C_2O_4)_3|3H_2O$. The control of the size of the crystallites permitted us to give for the first time evidence of the evolution of the blocking temperature, T_B, as proposed theoretically (Fig. 2).

In the area of the materials for high density magnetic recording purposes, the utilization of the precursors $(Fe_{1-x-y}M_xM'_y)C_2O_4\cdot 2H_2O$, where M and M′ represent cobalt, zinc, nickel and manganese, have permitted us to prepare new lacunar ferrites [44] of the type:

$$Fe^{3+}_{3-3x}Zn^{2+}_{3x}|Fe^{3+}_{5+x-2y}Co^{2+}_{3y}\square_{1-(x+y)}|O^{2-}_{12},$$

$$(0 < x + y < 1).$$

The interest in these phases has considerably increased since we determined their preparation in the form

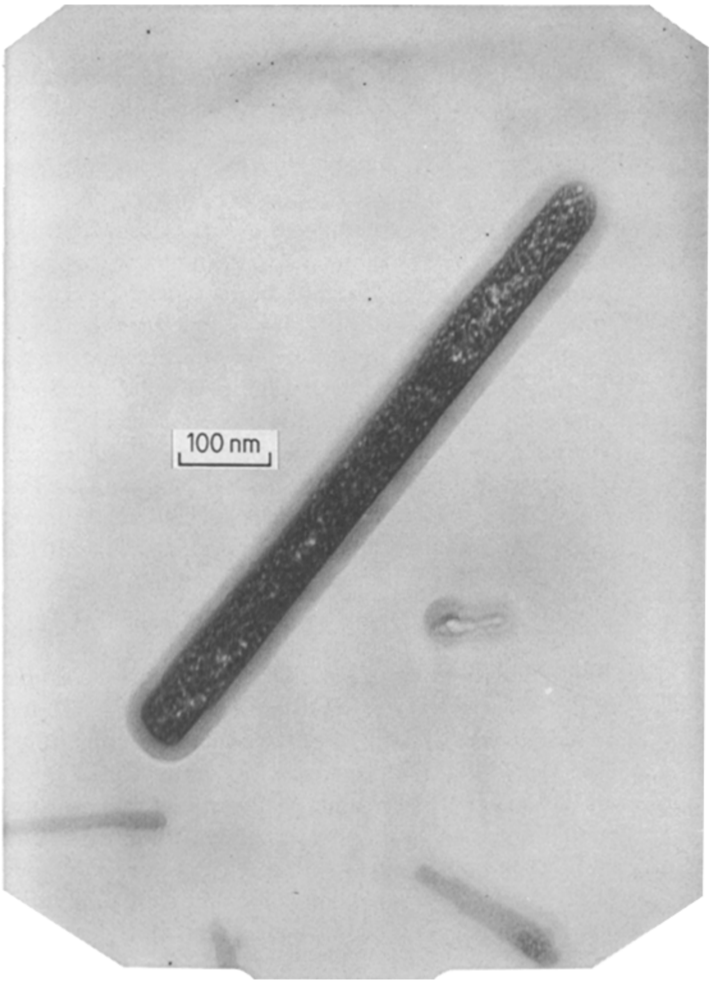

Figure 1 Electron micrograph of iron oxide obtained by pyrolysis of iron oxalate below 300° C.

of acicular particles with very reduced dimensions ($0.35\,\mu$m × $0.05\,\mu$m) (see Fig. 3). Control of the size of the crystallites in the interior of these acicules permits us to obtain higher values of the coercive field, $He(\simeq 1000\,\mathrm{Oe}$ or more), of the saturation magnetization, $\sigma_S(80\,\mathrm{emu\,g^{-1}})$, and of remanence magnetization, $\sigma_R(45\,\mathrm{emu\,g^{-1}})$.

The possibility of producing in the same compound, evolution from a very finely divided state, to a bulk massive form is of great interest in the study of the thermodynamic properties and, in particular, to the study of surface energies. In this connection we have shown a difference of $8\,\mathrm{kJ\,mol^{-1}}$ for enthalpy of transformation of γ-Fe_2O_3 involving a change of the specific surface from 90 to $20\,\mathrm{m^2\,g^{-1}}$ [45].

Again it is the exceptional chemical reactivity of the very finely divided phases that has permitted us to obtain the oxygen spinels possessing tetrahedrally ordered vacancies, as is the case with the compound $Fe^{3+}\square|Cr_6^{3+}|O_{12}^{2-}$ [40]. Also, in collaboration with Gillot we have observed for the first time the phenomenon of conductivity by hopping on the tetrahedral sites in a spinel lattice [46].

4. Conclusion

The overview summarizing the possibilities offered by the use of organic precursors gives an idea about the motivations attached to these procedures.

Of course, this metal–organic precursor method, like all other methods, is not a universal one and has

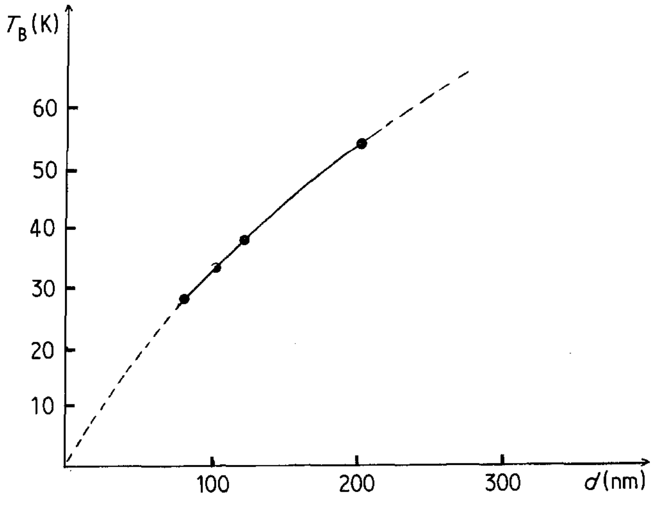

Figure 2 Evolution of the blocking temperature (T_B) as a function of the crystalline size (d).

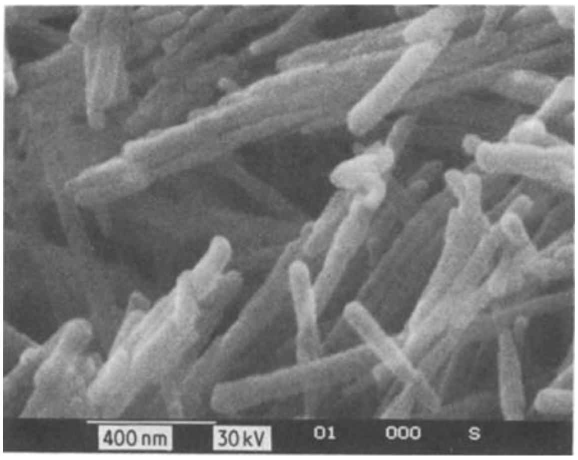

Figure 3 Electron micrograph of acicular ferrites.

some weaknesses notably at the level of yield since one large part of the initial starting material is lost. Moreover, traces of carbon can exist in some phases obtained in reducing atmospheres. It is clear, after numerous examples that we have cited, that this method presents good advantages over the ceramic method on the level of efficacy in preparation of pure and homogeneous phases and also in controlling their morphology. Like many other techniques of the "soft chemistry" (such as sol–gel, lyophilization, etc.) the principle of the method is based on achieving a dispersion of metallic elements on an atomic scale in the organic precursors in the desired proportions to give, after combination, the requisite inorganic solids.

To utilize all the advantages of these methods based on organic precursors, it is important that the synthesis of the precursor must be such as to give a very homogeneous distribution. Furthermore, this homogeneity must not be disrupted during the course of decomposition and with different subsequent treatment of the precursor. In view of this, detailed studies on the decomposition mechanism of metal–organic precursors and on the characterization of the liquid–solid equilibria that establishes just at the moment of preparation of the precursor itself, are all the more justified.

In conclusion, the metal–organic precursor method has continued to play a strong contributory role in the arsenal of soft chemical methods of preparative solid state chemistry. The studies on preparation and characterization of submicronic solids and of new metastable phases obtained via the organic precursor method have helped in identifying and modifying the original properties of these active solids and in linking and explaining the structural and mechanistic aspects associated with the more involved processing of metal–organic precursors.

References

1. J. ROBIN and J. BENARD, *C. R. Acad. Sci. Paris* **232** (1951) 1830.
2. J. ROBIN, PhD thesis, Paris (1953).
3. D. G. WICKHAM, E. R. WHIPPLE and E. G. LARSON, *J. Inorg. Nucl. Chem.* **14** (1960) 217.
4. D. G. WICKHAM and W. J. GROFT, *J. Phys. Chem. Solids* **7** (1958) 351.
5. J. PARIS, PhD thesis, Lyon (1963).
6. G. SZABO, PhD thesis, Lyon (1967).
7. A. ROUSSET, PhD thesis, Lyon (1969).
8. F. CHASSAGNEUX, PhD theses, Lyon (1974) and (1981).
9. B. E. YOLDAS, *J. Mater. Sci.* **12** (1977) 1203.
10. J. SAIKALI, PhD thesis, Lyon (1970).
11. G. PARIS, PhD thesis, Lyon (1967).
12. E. CLAR, PhD thesis, Lyon (1964).
13. M. ROUBIN, PhD thesis, Lyon (1967).
14. E. VALLET, PhD thesis, Lyon (1967).
15. G. SALLAVUARD, PdD thesis, Lyon (1971).
16. A. ROUSSET and J. PARIS, *Bull. Soc. Chem.* (1967) 3888.
17. *Idem, ibid.* (1968) 4009.
18. A. WAINTAL, J. J. CAPPONI and F. BERTAUT, *Solid State Commun.* **4** (1966) 125.
19. A. WAINTAL and J. CHENAVAS, *C. R. Acad. Sci. Paris* **264 B** (1967) 168.
20. R. PARIS, J. PARIS, G. SZABO, G. PARIS and B. VULLIERMET, "Les Elements Terres Rares", Colloque International du CNRS – Paris, Grenoble (1969) (Centre National de la Recherche Scientifique, France 1970) p. 257.
21. A. MUAN, *Amer. J. Sci.* **256** (1958) 413.
22. R. R. DAYAL, J. A. GARD and F. P. GLASSER, *Acta Crystallogr.* **18** (1965) 574.
23. G. A. SAWARTZKY, F. VAN DER WOOD and A. H. MORRISH, *Phys. Rev.* **187** (1969) 747.
24. G. DUPRE, thesis, Lyon (1976).
25. V. CREMER, *N. Jb. Miner. Abh.* **111** (1969) 184.
26. A. PETRIC and K. T. JACOB, *Solid State Ionics* **6** (1982) 67.
27. B. GILLOT, F. BOUTON, F. CHASSAGNEUX and A. ROUSSET, *J. Solid State Chem.* **33** (1980) 245.
28. E. F. BERTAUT and J. MARESCHAL, *C. R. Acad. Sci. Paris* **257** (1963) 867.
29. J. PARIS, A. ROUSSET and P. GERMI, *Mat. Res. Bull.* **4** (1969) 681.
30. A. ROUSSET, P. MOLLARD and J. PARIS, *Ann. Chem.* **7** (1972) 119.
31. A. ROUSSET, F. CHASSAGNEUX and P. MOLLARD, *C. R. Acad. Sci. Paris* **279** (1974) 1129.
32. B. GILLOT, J. TYRANOWICZ and A. ROUSSET, *Mat. Res. Bull.* **10** (1975) 775.
33. A. ROUSSET, P. MOLLARD and A. GIRAUD, *C. R. Acad. Sci. Paris* **275** (1972) 709.
34. P. MOLLARD, A. COLLOMB, J. DEVENYI, A. ROUSSET and J. PARIS, *IEEE Trans. Mag.* **11** (1975) 894.
35. G. DUPRE, A. ROUSSET and P. MOLLARD, *Mat. Res. Bull.* **11** (1976) 473.
36. P. TAILHADES, M. EL GUENDOUZI, A. ROUSSET and B. GILLOT, *C. R. Acad. Sci. Paris* **299** (1984) 13.
37. P. MOLLARD, P. GERMI and A. ROUSSET, *Physica* **86** (88b) (1977) 1393.
38. B. GILLOT, R. M. BENLOUCIF, J. C. MUTIN and A. ROUSSET, *C. R. Acad. Sci. Paris* **296** (1983) 1505.
39. B. GILLOT, F. CHASSAGNEUX and A. ROUSSET, *J. Solid. State Chem.* **38** (1981) 2284.
40. F. CHASSAGNEUX, A. ROUSSET and J. P. REDOULES, *ibid.* **56** (1985) 74.
41. B. GILLOT, F. JEMMALI, F. CHASSAGNEUX, C. SALVAING and A. ROUSSET, *ibid.* **95** (1982) 317.
42. L. NEEL, *C. R. Acad. Sci. Paris* **254** (1962) 598.
43. J. COHEN, P. MOLLARD, J. PARIS and A. ROUSSET, *ibid.* **268** (1969) 1001.
44. P. MOLLARD, J. PARIS and A. ROUSSET, US Pat. 3 873 461 (1975).
45. A. ROUSSET, G. BOISSIER, J. P. CAFFIN and F. CHASSAGNEUX, *C. R. Acad. Sci. Paris* **299** (1984) 781.
46. B. GILLOT, F. BOUTON, F. CHASSAGNEUX and A. ROUSSET, *Phys. Status Solidi* **50** (1978) 109.

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