



HAL
open science

Influence of the annealing temperature on the site preference of cations, structural and magnetic properties in RE₃Fe_{4.5}Al_{0.5}O₁₂ (RE = Y, Gd) synthesized by citrate route

Fabien Grasset, Stéphane Mornet, Alain Demourgues, Josik Portier, Etienne Duguet

► **To cite this version:**

Fabien Grasset, Stéphane Mornet, Alain Demourgues, Josik Portier, Etienne Duguet. Influence of the annealing temperature on the site preference of cations, structural and magnetic properties in RE₃Fe_{4.5}Al_{0.5}O₁₂ (RE = Y, Gd) synthesized by citrate route. Key Engineering Materials, 2002, 214-215, pp.241-246. 10.4028/www.scientific.net/KEM.214-215.241 . hal-00707390

HAL Id: hal-00707390

<https://hal.science/hal-00707390>

Submitted on 13 May 2022

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Influence of the Annealing Temperature on the Site Preference of Cations, Structural and Magnetic Properties in $\text{RE}_3\text{Fe}_{4.5}\text{Al}_{0.5}\text{O}_{12}$ (RE = Y, Gd) Synthesized by Citrate Route

Fabien Grasset¹, Stéphane Mornet², Alain Demourgues^{2,3}, Etienne Duguet², Josik Portier²

¹ National Institute for Research in Inorganic Materials, NIRIM-STA, Namiki 1-1, Tsukuba, Ibaraki, 305-0044, Japan

² Institut de Chimie de la Matière Condensée de Bordeaux, ICMCB-CNRS, Université Bordeaux-1, 87 avenue du Dr Albert Schweitzer, F-33608 Pessac, France

³ Rhodia Recherches, 52 rue de la Haie Coq, F-93300 Aubervilliers, France

Keywords: Citrate Route, Garnet, Magnetism, Rietveld Method.

ABSTRACT

The compounds $\text{Y}_3\text{Fe}_{4.5}\text{Al}_{0.5}\text{O}_{12}$ and $\text{Gd}_3\text{Fe}_{4.5}\text{Al}_{0.5}\text{O}_{12}$ have been first time synthesized by the citrate route at 800°C. The influence of the annealing temperature on the site preference of cations has been investigated. The crystal structure of the compounds annealed at 800°C and 1150°C has been refined from X-ray powder data. It appears clearly that the Al^{3+} is always located in the 24d position for the Gd or Y compound annealed at 800°C. Nevertheless, in the case of Y compound, the site preference of aluminum is very sensitive to the annealing temperature, whereas for Gd compound no change was observed. The magnetic properties of $\text{Y}_3\text{Fe}_{4.5}\text{Al}_{0.5}\text{O}_{12}$ and $\text{Gd}_3\text{Fe}_{4.5}\text{Al}_{0.5}\text{O}_{12}$ annealed at different temperatures have been compared which confirm the structural inferences.

INTRODUCTION

Garnets are a group of technologically important magnetic materials of current interest, in particular, in the conception of microwave equipment (insulators, circulators, dephasers) [1,2]. Rare earth iron garnet (REIG) and its substituted derivatives are of primary importance for use in these range of technological applications. Recently, the potential use of REIG and aluminum substituted derivatives in medicine and biology have been reported [3]. The usual method for preparing polycrystalline REIG and substituted REIG [4, 5] requires a long annealing time at high temperatures (1400°C) followed by a grinding operation. However, this process is long and costly. So new methods have been developed to be alternative to the classical process. Few studies have been carried out on the synthesis of YIG and substituted YIG submicron diameter particles like hydroxide coprecipitation [5], coprecipitation in microemulsion [6], metal alkoxides hydrolysis [7], glycothermal synthesis [8], glass-crystallization method [9] or citrate route [3, 10, 11]. The magnetic properties of substituted garnet compounds (coercive field, magnetization,...) are highly correlated to the cationic distribution, but to our knowledge only the chemical and morphological aspects were investigated in the garnets synthesized at low temperature. This paper is devoted to the crystal structure and magnetic properties of $\text{RE}_3\text{Fe}_{4.5}\text{Al}_{0.5}\text{O}_{12}$ (RE = Y, Gd). The correlation between structural variation and magnetic properties was studied for the compounds synthesized at 800°C, and compared to the results obtained for higher synthesis temperature. The first synthesis of $\text{Gd}_3\text{Fe}_{4.5}\text{Al}_{0.5}\text{O}_{12}$ by the citrate route is reported. Results obtained by transmission electron microscopy and specific surface area measurements are also presented

EXPERIMENTAL SECTION

The preparation of the polycrystalline aluminum substituted yttrium iron garnet by the citrate route has been described previously in some detail [3]. The protocol employed in the present study for aluminum substituted gadolinium iron garnet was based on these earlier procedure. Typically, polycrystalline sample $\text{Gd}_3\text{Fe}_{4.5}\text{Al}_{0.5}\text{O}_{12}$ were initially prepared from a solution of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Gd}(\text{NO}_3)_3$ and citric acid in appropriate stoichiometric ratios at 65°C during 3 h until gelation. Gels were dried at 110°C for 1 h, cooled, heated in air with a heating rate of 5°C/min up to 800°C and aged at this temperature for 2 h.

Powder X-ray diffraction data were recorded at room temperature on Rigaku Rint2200HF using Bragg-Brentano geometry with CuK α radiation (40kV, 50mA, mask = 10mm, Soller slit = 0.02mm, divergence slit = 1°, receiving slit = 0.1mm and scatter slit = 1°). Step scans were performed over the angular range $10 < 2\theta/^\circ < 100$, a 2θ step size of 0.02 was used in all cases, with integration times of 20s. Rietveld refinements [12] were performed using the WinPLOTR program package included FULLPROF program [13]. The peak shape was described by a pseudo-Voigt function and the background level was defined by a polynomial function with six refinable coefficients. For each diffraction pattern, a scale factor, a count zero point, asymmetric parameters and the unit cell parameters were refined in addition to the atomic parameters. The estimated standard deviation of the parameters and the R values are not exactly comparable with a single-crystal work [14]. The estimated standard deviation σ_i concerns the precision of the parameters. According to Berar J.F. et P. Lelann [15], a better estimate of the accuracy of structural parameters is obtained in multiplying σ_i by the parameter SCOR (Berar's factor) given by the FULLPROF program. Also, the standard deviations, which are mentioned in parenthesis in Tables 3 and 4, are corrected by Berar's factor. The profil R_p and R_{wp} values given in this paper are the R values calculated from pure Bragg scattering, i.e. from background-cleaned step intensities [14].

JEOL-2000 FX electron microscope operating at 200 kV coupled with a Noran spectrometer (voyager 4 system) was used to perform the EDX analysis.

Specific surface area of the samples was measured by nitrogen adsorption using Micromeritics ASAP 2010.

Magnetic susceptibilities were measured using a Quantum Design Superconducting QUantum Interference Device (SQUID) magnetometer equipped of the oven option for high temperature measurements. The temperature dependence of the Zero field-cooled magnetization (ZFCM), the field-cooled magnetization (FCM) and the remnant magnetization (REM) were measured in the range $5K < T/K < 550K$. Magnetization versus field were measured at 5 K. No correction was made for the diamagnetic contributions of the different cations.

RESULTS AND DISCUSSION

Structural Characterization

Analysis of our X-ray powder diffraction data indicates that aluminum substituted iron yttrium or gadolinium garnet sample, obtained by heating at 800°C for only 2 h, appear as a single phase. In the previous work, it was already observed that crystallized garnet nanoparticles were obtained at 800°C [3, 10]. The thermal decomposition of citrate molecules occurred around 300°C, but some carbonates remained in the powder up to 700°C [10, 11]. The EDX analysis corroborates the presence of O, Fe, Al and RE and the homogeneity of the samples. No other element was detected. Atomic ratios RE/(Fe,Al) reported in Table 1 are close to the theoretical value (0.6), taking into account the method accuracy. Nevertheless, we can notice that after sintering at 1150°C, the Gd compound, show small diffraction peaks of the perovskite-type compound GdFeO₃.

Table 1. Results of EDX analysis and BET measurements for compounds annealed at 800°C

Composition	Atomic ratio RE/(Fe,Al) (1)	Specific surface area (m ² /g) (2)	Curie Temperature (°C)
Y ₃ Fe _{4.5} Al _{0.5} O ₁₂	0.64	13.1	210(2)
Gd ₃ Fe _{4.5} Al _{0.5} O ₁₂	0.63	9.1	221(2)

(1) as determined by Energy Dispersive X-Ray analysis

(2) by the BET method

The lattice parameters refined from the X-ray powder patterns are given in Table 2 and are in agreement with values previously found [7, 16].

Table 2. Crystal and refinement data for compounds annealed at 800°C and 1150°C

Composition	Y ₃ Fe _{4.5} Al _{0.5} O ₁₂	Y ₃ Fe _{4.5} Al _{0.5} O ₁₂	Gd ₃ Fe _{4.5} Al _{0.5} O ₁₂	Gd ₃ Fe _{4.5} Al _{0.5} O ₁₂
a ₀ (nm)	1.235(1)	1.235(1)	1.245 (1)	1.244 (1)
Temperature (°C)	800	1150	800	1150
Space group	Ia $\bar{3}$ d			
No. of total refined parameters	21	22	21	21
R ₁ (%)	2.7	4.7	2.6	3.8
R _w (%)	8.0	11.9	8.5	9.6
R _{wp} (%)	9.3	16.3	9.8	12.2

Substituted yttrium or gadolinium iron garnet have the general composition A₃B₂B'₃O₁₂ and crystallize in a cubic space group, Ia $\bar{3}$ d, with eight formula units per cell [17]. The A = Y³⁺ or Gd³⁺ site is eight-coordinated site, the B = Al³⁺, Fe³⁺ site six-fold octahedral, and the B' = Al³⁺, Fe³⁺ site four-fold tetrahedral considering the effective ionic radii [18]. A view of the garnet structure in terms of the polyhedral network is shown in Figure 1.

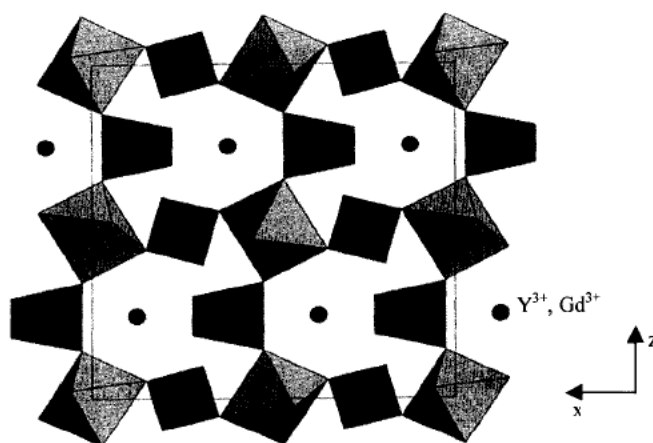


Fig. 1 Polyhedral connections in the garnet structure showing the octahedral (○) and tetrahedral (■) sites

Tetrahedral and octahedral sites share corners with each other and edges with the dodecahedral sites. The atomic position of Y₃Fe₄Ga₁O₁₂ as well as the space group (Ia $\bar{3}$ d) has been used as a trial model [19]. So the Rare earth atoms are placed in the 24c position which are in a dodecahedral sites. Iron and aluminum atoms are located in the 16a and 24d positions. The crystal data and final R values for compounds annealed at 800°C and 1150°C are given in Table 2. The refined atomic positions and isotropic displacement parameters are listed in Table 3. The principal interatomic distances are given in Table 4. The observed, calculated and difference X-ray diffraction profiles for Y₃Fe_{4.5}Al_{0.5}O₁₂ annealed at 1150°C are shown in Figure 2. Owing to the high correlations between occupancy and the isotropic displacement parameter, simultaneous refinements were difficult and, therefore, first the occupancy parameters of Fe³⁺ and Al³⁺ were refined step by step before final refinement with all parameters. The isotropic displacement parameter of oxygen atoms are fixed to realistic values, and for Al³⁺ and Fe³⁺ located in the same site, the same value of isotropic displacement parameter was refined. Different positions have been tested for the aluminum and iron cations and it appears clearly that Al³⁺ is always located in the 24d position in the both compounds annealed at 800°C.

Table 3. Atomic coordinates and atomic displacement parameters for compounds annealed at 800°C and 1150°C

Composition	Position	x	y	z	B (\AA^2)
$\text{Y}_3\text{Fe}_{4.5}\text{Al}_{0.5}\text{O}_{12}$ (800°C)	24c	0.125	0	0.25	0.20(8)
	16a	0	0	0	0.38(16)
	24d	0.375	0	0.25	0.07(15)
	96d	-0.0291(8)	0.0566(9)	0.1499(12)	0.5
$\text{Y}_3\text{Fe}_{4.5}\text{Al}_{0.5}\text{O}_{12}$ (1150°C)	24c	0.125	0	0.25	0.32(9)
	16a	0	0	0	0.23(14)
	24d	0.375	0	0.25	0.42(15)
	96d	-0.0271(7)	0.0558(9)	0.1514(11)	0.5
$\text{Gd}_3\text{Fe}_{4.5}\text{Al}_{0.5}\text{O}_{12}$ (800°C)	24c	0.125	0	0.25	0.28 (7)
	16a	0	0	0	0.26 (12)
	24d	0.375	0	0.25	-0.11 (12)
	96d	-0.0323 (7)	0.0538 (9)	0.1485(8)	0.5
$\text{Gd}_3\text{Fe}_{4.5}\text{Al}_{0.5}\text{O}_{12}$ (1150°C)	24c	0.125	0	0.25	-0.02 (6)
	16a	0	0	0	-0.05 (11)
	24d	0.375	0	0.25	0.05 (10)
	96d	-0.0324 (10)	0.0531 (12)	0.1505 (12)	0.5

Table 4. Main interatomic distances (\AA) for compounds annealed at 800°C and 1150°C

Composition	TR-O	B'-O	B-O	TR-B' (or B)	B'-B
$\text{Y}_3\text{Fe}_{4.5}\text{Al}_{0.5}\text{O}_{12}$ (800°C)	4 x 2.364(12)	4 x 1.840(14)	6 x 2.026(13)	Y-B' 3.088(1)	3.452(1)
	4 x 2.437(15)			Y-B 3.452(1)	
$\text{Y}_3\text{Fe}_{4.5}\text{Al}_{0.5}\text{O}_{12}$ (1150°C)	4 x 2.342(10)	4 x 1.849(11)	6 x 2.020(12)	Y-B' 3.086(1)	3.451(1)
	4 x 2.442(12)			Y-B 3.451(1)	
$\text{Gd}_3\text{Fe}_{4.5}\text{Al}_{0.5}\text{O}_{12}$ (800°C)	4 x 2.425(12)	4 x 1.837(10)	6 x 2.007(10)	Gd-B' 3.112(1)	3.480(1)
	4 x 2.493(10)			Gd-B 3.480(1)	
$\text{Gd}_3\text{Fe}_{4.5}\text{Al}_{0.5}\text{O}_{12}$ (1150°C)	4 x 2.409(12)	4 x 1.815(14)	6 x 2.025(12)	Gd-B' 3.109(1)	3.476(1)
	4 x 2.501(14)			Gd-B 3.476(1)	

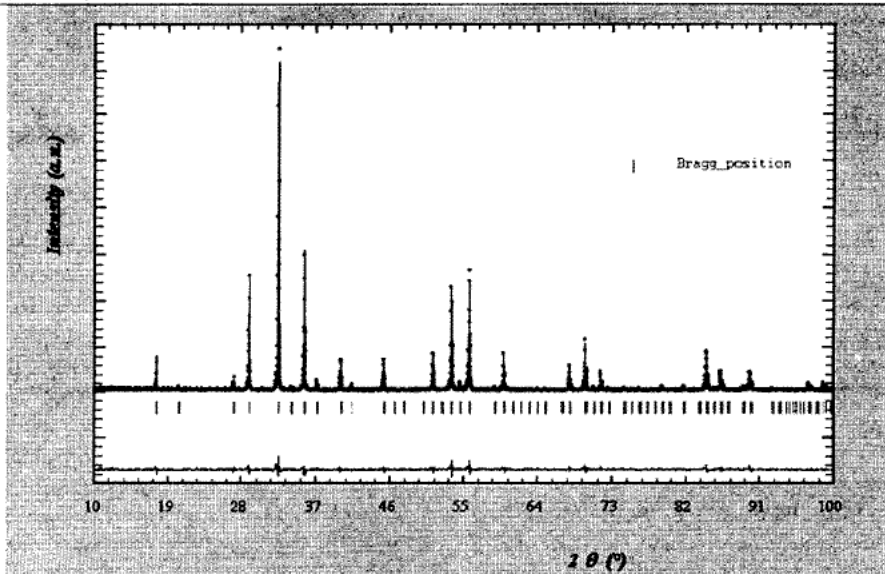


Fig. 2 Observed (dots), calculated (full) and difference (bottom) X-ray powder diffraction profiles of $\text{Y}_3\text{Fe}_{4.5}\text{Al}_{0.5}\text{O}_{12}$ annealed at 1150°C.

Gilleo *et al.* [20] have defined a f_t value like the fraction of Al ions found in the tetrahedral sites, i.e. $f_t = z/x$ with the composition $Y_3[Fe_{2-y}Al_y](Fe_{3-z}Al_z)O_{12}$ with 'y' represent the Al ion in the octahedral site, 'z' those in tetrahedral site and $x = y + z$. In the case of the Y compound annealed at 1150°C, it is seen that the f_t value 0.86, determined by Rietveld refinement, appears quite reasonable when compare to those of $x = 0.33$ ($f_t = 0.95$) and $x = 1$ ($f_t = 0.84$) compounds [20]. Moreover the weak increase of the average B'-O interatomic distance (Table 4) is in good agreement with an occupation of the tetrahedral site by Fe^{3+} (1.87Å) [21]. For the Gd compound, the average interatomic distance B'-O decreases and the distances TR-O are modified (Table 4). This indicates the shift of the O atoms to the four-coordinated site due to contraction of the tetrahedron and deformation of the dodecahedral site with annealing temperature. Also in Gd compound, smaller Al^{3+} is preferred to the 24d site at both temperatures. Nevertheless, the values of interatomic distance of B'-O found are slightly short when compared to the average values reported in the literature (1.87Å) [21].

Magnetic Properties

The magnetic properties of $Y_3Fe_{4.5}Al_{0.5}O_{12}$ and $Gd_3Fe_{4.5}Al_{0.5}O_{12}$ annealed at 800°C and 1150°C have been compared. Substitution of diamagnetic ions for iron changes the magnetic moment by altering the difference in the number of magnetic ions in tetrahedral and octahedral sites. In the same way, the magnetization is very sensitive to the site preference of cations. Figure 3 shows the hysteresis loops recorded at $T = 5$ K for the samples annealed at 800°C and 1150°C during 2 hours. In occurrence of yttrium compound, the increase of magnetization can be easily correlated to displacement of aluminum from 24d site to 16a site. The saturation magnetization of 17.4 μ_B per formula unit at 5 K is very close to the expected value [16]. In the case of Gd, the magnetic data confirm that Al^{3+} ions preferred the tetrahedral sites at both temperatures (Figure 3). The difference observed in the decrease of the coercive field (Figure 3) can be explained principally by the particle size dependence. The particle size increases with the increasing temperature.

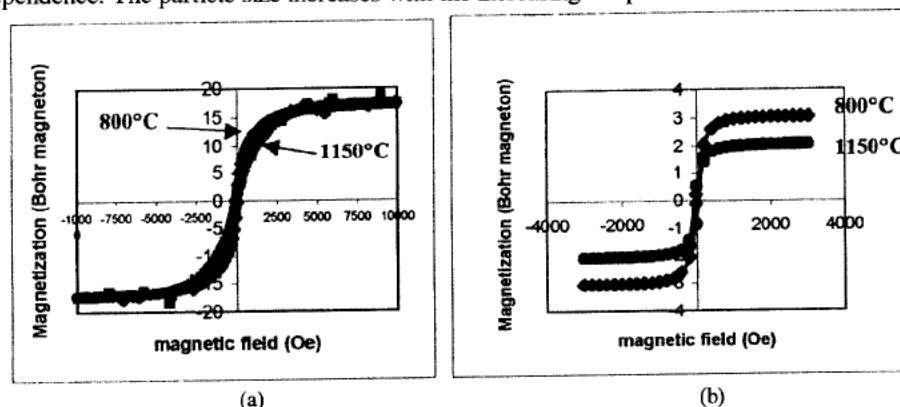


Fig 3. Hysteresis loops recorded at $T = 5$ K for $Gd_3Fe_{4.5}Al_{0.5}O_{12}$ (a) and $Y_3Fe_{4.5}Al_{0.5}O_{12}$ (b) samples annealed at 800°C and 1150°C

The complete study of the solid solution $Y_3Fe_{5-x}Al_xO_{12}$ ($0 \leq x \leq 2$) annealed at 800°C has demonstrated that Al cations preferred the tetrahedral site for $x < 0.7$ [3]. Previous studies showed that all Al^{3+} ions replace Fe^{3+} ions in the tetrahedral sites only for $x < 0.4$ and the aluminium concentration on octahedral site increases with increasing sintering temperature [22, 23, 24]. The preference to the tetrahedral site at low temperature for Al^{3+} in all cases can be explained qualitatively by the fact that the octahedral positions provide a larger volume than the tetrahedral sites (the Shannon-Prewitt radius are respectively 0.49 Å for Fe^{3+} and 0.39 Å for Al^{3+}). Nevertheless, this preference can not depend only on the ionic radius of the cations. Nakatsuka *et al.* [19] showed that the substitution of Fe^{3+} by Ga^{3+} in $Y_3Fe_{5-x}Ga_xO_{12}$ introduces structural instability like strong cation-cation interaction. They considered that the change for the site

preference is caused in order to relax the structural or energetic instabilities. Moreover, the studies of the cation distribution in $Y_3Al_{5-x}Ga_xO_{12}$ by M. Marezio *et al.* [25] showed that, even for higher x values, the gallium ion prefers the tetrahedral sites in the garnet structure more than the aluminium, although, the gallium ion is reported to have a larger ionic radius than the aluminium ion (the Shannon-Prewitt radii are respectively 0.47Å for Ga^{3+} and 0.39Å for Al^{3+}). Considering these results, the Ga^{3+} preference for the four-coordinated site in $Y_3Al_{5-x}Ga_xO_{12}$ seems to be due to the nature of Ga^{3+} itself and not to Al^{3+} preference site. The cationic distribution also appears to depend on the electronic configuration of the cation (the electronic configuration for Al^{3+} and Ga^{3+} are respectively [Ne] and [Ar] 3d¹⁰), the cation-anion distances, anion-anion distances and the cation-cation interaction. The effect of the substitution of Gd^{3+} by Y^{3+} ions changes drastically the site preference distribution, which reflects the differences in the contributions of Y^{3+} and Gd^{3+} ion to the local magnetic field.

CONCLUSION

To conclude the citrate route seems to allow an easy control of the magnetic moment values for aluminium substituted yttrium iron garnet ($x < 0.7$), with the annealing temperature by stabilization of aluminium in the tetrahedral site. This last point may be to bring closer to the study of the synthesis of α -alumina at low temperature by the same citrate process [26]: it was observed that γ -alumina is formed first (a defect spinel structure with 21.33 Al atoms arranged at random in the 16 octahedral and 8 tetrahedral positions of the structure) before to be transformed at 1050°C in α -alumina (hexagonal close packing of oxygen atoms with Al cations in octahedral sites).

ACKNOWLEDGEMENT

The authors thank S. Denaire, D. Denux, C. Hedouin, and T. Wada for great technical assistance. Dr. O. Cadour is greatly acknowledged for helpful discussions.

REFERENCES

- [1] G.F. Dionne, *J. Appl. Phys.*, **81**(8) (1997), p. 5064.
- [2] T. Abraham, *Am. Ceram. Soc. Bull.*, **73**(8) (1994), p. 62.
- [3] F. Grasset, S. Mornet, A. Demourgues, E. Duguet, J. Portier, J. Bonnet and A. Vekris, *Proceeding of the 8th International Conference on Ferrites ICF 8, Kyoto, Japan.*
- [4] C.E. Miller, *J. Phys. Chem. Solids*, **17** (1961), p. 229.
- [5] P. Grosseau, A. Bachiellini and B. Guilhot, *Powder Technology*, **93** (1997), p. 247.
- [6] P. Vaqueiro, M.A. Lopez-Quintela and J. Rivas, *J. Mater. Chem.*, **7** (1997), p. 501.
- [7] S. Taketomi, Y. Ozaki, K. Kawasaki, S. Yuasa and H. Miyajima, *J. Magn. Magn. Mater.*, **122** (1993), p. 6.
- [8] M. Inoue, T. Nishikawa and T. Inui, *J. Mater. Chem.*, **13** (1998), p. 856.
- [9] D. Bahadur, B. Sharma and D. Chakravorty, *J. Mater. Sci. Lett.*, **1** (1982), p. 106.
- [10] P. Vaqueiro, M.P. Crosnier-lopez and M.A. Lopez-Quintela, *J. Solid State Chem.*, **126** (1996), p. 161.
- [11] P. Vaqueiro and M.A. Lopez-Quintela, *Chem. Mater.*, **9** (1997), p. 2836.
- [12] H.M. Rietveld, *J. Appl. Crystallogr.*, **2** (1969), p. 65.
- [13] T. Roisnel and J. Rodriguez-Carvajal, WinPLOTR (June 2000) and FULLPROF (vers. 1.5 April 2000), LCSIM Rennes and LLB Saclay, France.
- [14] E. Jansen, W. Schafer and G. Will, *J. Appl. Cryst.*, **27** (1994), p. 492.
- [15] J.F. Berar and Lelann, *J. Appl. Cryst.*, **24** (1991), p. 1.
- [16] S. Geller, H.J. Williams, R.C. Sherwood and G.P. Espinosa, *J. Appl. Phys.*, **36**(1) (1965), p. 88.
- [17] F. Bertaud and F. Forrat, *Compt. Rend. Aca. Sci.*, **242** (1956), p. 382.
- [18] R. D. Shannon, *Acta Cryst.*, **A32** (1976), p. 751.
- [19] A. Nakatsuka, A. Yoshiasa and S. Takeno, *Acta Cryst.*, **B51** (1995), p. 737.
- [20] M.A. Gilleo and S. Geller, *Phys. Rev.*, **110**(1) (1958), p. 73.
- [21] S. Geller, *Zeit. Kryst.*, **125** (1967), p. 1.
- [22] P. Fisher, P. Hälg, P. Rogwiller and E.R. Czerlinsky, *Solid State Commun.*, **16** (1975), p. 987.
- [23] S. Geller, H.J. Williams, G.P. Espinosa and R.C. Sherwood, *Bell Syst. Tech. J.*, **43** (1964), p. 565.
- [24] D.C. Leo, D.A. Lepore and J.W. Nielsen, *J. Appl. Phys.*, **37** (1966), p. 1083.
- [25] M. Marezio, J.P. Remeika and P.D. Dernier, *Acta Cryst.*, **B24** (1968), p. 1670.
- [26] F.S. Shiau and T.T. Fang, *Mater. Chem. Phys.*, **60** (1999), p. 91.