

# Hyperfine Characterization of Pure and Doped Zircons

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The aim of this work has been to investigate the influence of two coloring dopant ions on the ZrSiO<sub>4</sub> host lattice. Pure, vanadium-doped and praseodymium-doped zircon powders have been synthesized by the ceramic method and analyzed using X-ray diffraction and the perturbed angular correlations (PAC) hyperfine technique, which probes the nearest environments of zirconium ions. XRD results indicated that vanadium and praseodymium incorporations in the host lattice result in crystalline solid solutions. In turn, PAC information allowed in both cases the determination of two contributions to the hyperfine interaction. In the case of vanadium-doped zircon, V<sup>4+</sup> substitutes mainly for Zr<sup>4+</sup> and in a minor fraction for Si<sup>4+</sup> or else it localizes at a tetrahedral interstitial site. In praseodymium-doped zircon, a low fraction of Pr<sup>4+</sup> cations locate at Zr<sup>4+</sup> sites. A slight modification of the zircon lattice is probably caused by the incorporation of the remaining cations at tetrahedral interstitial sites of the solid solution. © 2000 Academic Press

## I. INTRODUCTION

Coloring agents based on zircon are widely employed in the tile, tableware, and sanitary ware industries. Their use lies on their ability to withstand the extreme chemical and thermal conditions involved in glazing and enameling since they exhibit the most important requirements of any coloring materials: dissolution resistance and tinctorial strength. Vanadium-blue (1) and praseodymium-yellow colors based on zircon are two of the principal coloring agents.

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Zircon colors are produced when zirconia is combined with silica in the presence of coloring species, the coloring ion locating at one of the zircon lattice sites. A mineralizing agent like NaF can be added to catalyze the zircon formation and assist the incorporation of the coloring species at lower temperatures.

The easiness of color generation has been found to depend on the type of the coloring species. The high reactivity and volatility of vanadium makes it the easiest color to produce, being rapidly transported with the silicon to the reaction site. The V<sup>4+</sup> ions (ionic radius = 0.72 Å) are responsible for the blue color of zircon (2). Praseodymium is not so reactive but it also settles in the zircon lattice as a tetravalent ion Pr<sup>4+</sup> (ionic radius = 0.96 Å), developing a yellow coloration.

The principal structural unit of zircon is a chain of alternating edge-sharing SiO<sub>4</sub> tetrahedra and ZrO<sub>8</sub> triangular dodecahedra extending parallel to the *c*-axis (3). The chains are joined laterally by edge-sharing dodecahedra. The unit cell parameters are *a* = 6.6164 Å and *c* = 6.0150 Å (4). Zircon is a highly stable structure, which decomposes at about 1670°C to yield zirconia and silica.

V–ZrSiO<sub>4</sub> solid solutions have been repeatedly studied but the position that the V<sup>4+</sup> ion occupies is still controversial. Demiray *et al.* (2) suggested, from studies of optical-absorption spectra performed on vanadium-doped zircon powder, that the V<sup>4+</sup> is located in the distorted dodecahedral site of Zr<sup>4+</sup> (ionic radius = 0.84 Å). Also, Beltrán *et al.* (5) concluded that the substitution of V<sup>4+</sup> for Zr<sup>4+</sup> at the eight-fold-coordinated site is energetically fairly favorable. On the contrary, Di Gregorio *et al.* (6), based on analyses of electron spin resonance, reported that V<sup>4+</sup> substitutes for Si<sup>4+</sup> (ionic radius = 0.26 Å) at the four-fold-coordinated site. However, other authors revealed that vanadium incorporates into both the Zr<sup>4+</sup> and the Si<sup>4+</sup> sites of ZrSiO<sub>4</sub> (7–9). The principal problem that arises in electronic

spectral studies is that the distorted Si tetrahedral site and the distorted Zr dodecahedral one have the same symmetry ( $D_{2d}$ ). Thus, the selection rules and the polarization of electronic bands originating from  $V^{4+}$  ions at each one of the sites are identical. Moreover, it is difficult to assess both the extents of possible lattice distortion and symmetry modification on substitution and the mechanism by which the dopant ion enters the host lattice. Finally, Siggel *et al.* (10) from XRD investigations have proposed that vanadium occupies distorted interstitial tetrahedral positions in the zircon lattice.

Regarding praseodymium doping, the last mentioned authors (10) have determined that the coloring cation substitute for zirconium atoms. Also, Ocaña *et al.* (11) recently, through the use of XRD and XAS spectroscopy, have determined that the  $Pr^{4+}$  cations in doped zircon pigments form a solid solution with the zircon lattice, substituting for zirconium at its triangular dodecahedral positions.

It is known that the incorporation of the coloring ion to form a substitutional or interstitial solid solution or otherwise its insolubility in the host lattice are of relevant importance concerning the chromatic stability of the pigment when subjected to thermal treatments as well as to the chemical action of the ceramic matrix and molten glazes.

In this work the electric field gradients (EFGs) of the zircon lattice doped with vanadium and praseodymium have been determined by using the extremely localized perturbed angular correlations (PAC) technique. The aim was to elucidate the site of the dopant ions through the characterization of the nearest environments of zirconium ions. XRD was used as a complementary technique.

PAC spectroscopy (12, 13) is a highly localized technique which measures the hyperfine interaction between the quadrupole moment  $Q$  of the probe nucleus, a radioactive nucleus inside the solid, and the EFG acting on it, produced by the charge distribution in the lattice. If the nuclear quadrupole moment is known, the technique allows the determination of the EFG at zirconium sites, equivalent to the description of the lattice at a nanoscopic level. The technique is based on the fundamental principle of conservation of angular momentum. Considering that the angular momentum of a radiation is related to its angular distribution, one can easily realize that when a nucleus decays through a  $\gamma$ - $\gamma$  cascade, it is possible to obtain information about the intermediate nuclear state by measuring the angular distribution of the cascade, i.e., the distribution of the second  $\gamma$  ray with respect to the first one. During its life in the intermediate state the nucleus may be perturbed by the crystalline field which changes its orientation in space, therefore changing the above-mentioned angular distribution. Zirconium-containing materials such as zircon-based pigments involve 1–3% hafnium natural impurities, which due to chemical similarity, occupy zirconium sites. Upon neutron irradiation, radioactive  $^{181}\text{Hf}$  isotopes are ob-

tained. These, in turn, disintegrate by  $\beta^-$  to excited levels of  $^{181}\text{Ta}$  nuclei and then to its ground state through, among others, two  $\gamma$  rays in cascade ( $\gamma_1 = 133$  keV and  $\gamma_2 = 482$  keV) (14). It is the intermediate level of this cascade, with adequate values of quadrupole moment  $Q$  and half-life  $\tau_N$ , the “nuclear probe” which reflects in a very efficient way the effect of its interaction with the nearest neighborhood, thus giving information of the lattice EFGs at the sites of the probes. In fact, if an EFG exists at the site of the  $^{181}\text{Ta}$  nucleus, the angular correlation will be modified within the time that the intermediate level lives. The resulting central experimental function in a PAC experiment is the spin rotation curve  $A_2G_2(t)$  or PAC spectrum, where  $A_2$  is the anisotropy of the  $\gamma$ - $\gamma$  cascade of the isolated nucleus,  $G_2(t)$  is the perturbation factor which involves the characteristics of the extranuclear EFG, and  $t$  is the time during which the probe nucleus is acted by the EFG, i.e., the time separation between  $\gamma_1$  and  $\gamma_2$ . The PAC spectrum is drawn from the temporal distribution of  $\gamma_1$ - $\gamma_2$  coincident events obtained for different angular separations between both  $\gamma$  radiations. By fitting an appropriate theoretical function to the experimental curve, the quadrupole parameters describing the EFGs acting on the  $^{181}\text{Ta}$  probes of a zirconium-containing lattice can be derived. The EFG is conventionally described by  $\omega_Q$  (the quadrupole frequency, proportional to the major component  $V_{zz}$  of the EFG tensor) and the asymmetry parameter  $\eta = (V_{xx} - V_{yy})/V_{zz}$ , which measures the degree of departure of the EFG from the axial symmetry. A third parameter,  $\delta$ , known as the frequency distribution width, takes into account the spread of the EFG due to the existence of impurities or defects in the lattice and is also obtainable from the experiment. Besides, due to its short-sighted nature, the method allows distinguishing among different sites and the relative fraction or PAC population  $f_i$  of each nonequivalent zirconium neighborhood can be determined as well.

In addition, the method presents the advantage that measurements can be done at any temperature, thus providing information about the thermal evolution of the EFG of the crystalline lattice. In that respect it has been repeatedly observed that the expansion and contraction of the lattice as the temperature is varied is revealed at nanometric scale by the decrease and increase of the hyperfine quadrupole frequency, respectively.

## II. EXPERIMENTAL

Three zircon ceramic powders, i.e., pure zircon and vanadium-doped blue pigment  $\text{ZrSiO}_4(\text{V})$  and praseodymium-doped yellow pigment  $\text{ZrSiO}_4(\text{Pr})$  were synthesized and analyzed at microscopic and nanoscopic levels. The samples were obtained via the ceramic route (15–17). The two pigments  $\text{Pr}_6\text{O}_{11}$  (Carlo Erba RPE) and  $\text{NH}_4\text{VO}_3$  (Merck), in a concentration of 6 wt%, were separately added

to mixtures of  $\text{ZrO}_2$  and  $\text{SiO}_2$  in the stoichiometric 1:1 molar ratio. Both samples were wet homogenized for 40 min in a fast agate ball mill. After drying, the mixtures were further ground for 30 min to ensure a complete homogenization of the raw materials. The resulting precursors were fired in air in a platinum vessel in an electrical muffle kiln at  $1400^\circ\text{C}$  for 2 h to develop the desired phase and colors. A last grinding was then performed to homogenize the products and reduce the particle size. During the preparation, a flux of NaF was employed as the mineralizing agent. In the case of V- $\text{ZrSiO}_4$ , additional quartz was added at room temperature after zircon synthesis was performed. This was done to modify the color of the obtained pigment to resemble the color of the V- $\text{ZrSiO}_4$  industrially adopted and to control the particle size distribution that extremely affects the color development.

For the PAC experiment, the  $^{180}\text{Hf}$  isotopes (35% of the 2–5% Hf impurities naturally occurring in zirconium) are converted into the parent nuclei  $^{181}\text{Hf}$  via thermal neutron irradiation. These, in turn, disintegrate by  $\beta^-$  to excited levels of the probe nuclei  $^{181}\text{Ta}$  and these ones to the ground state through, among others, the 133–482 keV  $\gamma$ - $\gamma$  cascade which serves as the nuclear tool for the PAC experiment. Three-day long measurements were performed on each sample, using conventional high-revolution equipment of two  $\text{BaF}_2$  detectors in a planar arrangement.

PAC results were complemented with those obtained by XRD on unirradiated pure and doped zircons.

### III. RESULTS AND DISCUSSION

Figures 1 and 2 and Table 1 show, respectively, the X-ray diffractograms, the PAC spectra, and the hyperfine quadrupole parameters derived from the fits of the PAC spectra, as determined for pure and doped zircons.

#### (a) Pure Zircon $\text{ZrSiO}_4$

**XRD.** No evidence of any other compound but  $\text{ZrSiO}_4$  was observed, indicating that the substance had been properly synthesized.

**PAC.** The hyperfine study revealed the presence of a somewhat disordered interaction, denoted as I in Table 1, of very similar quadrupole parameters to those reported for a natural powder of zircon (18) and also for the isomorphous  $\text{HfSiO}_4$  compound (19). The non-zero value of the asymmetry parameter ( $\eta = 21\%$ ) reflects a certain departure from the axial symmetry expected at Zr sites within the tetragonal zircon lattice. However, this evidence matches Demiray *et al.*'s results (2), who reported that the oxygen ions in  $\text{ZrO}_8$  dodecahedra of zircon are positioned at the corners of a highly distorted cube.

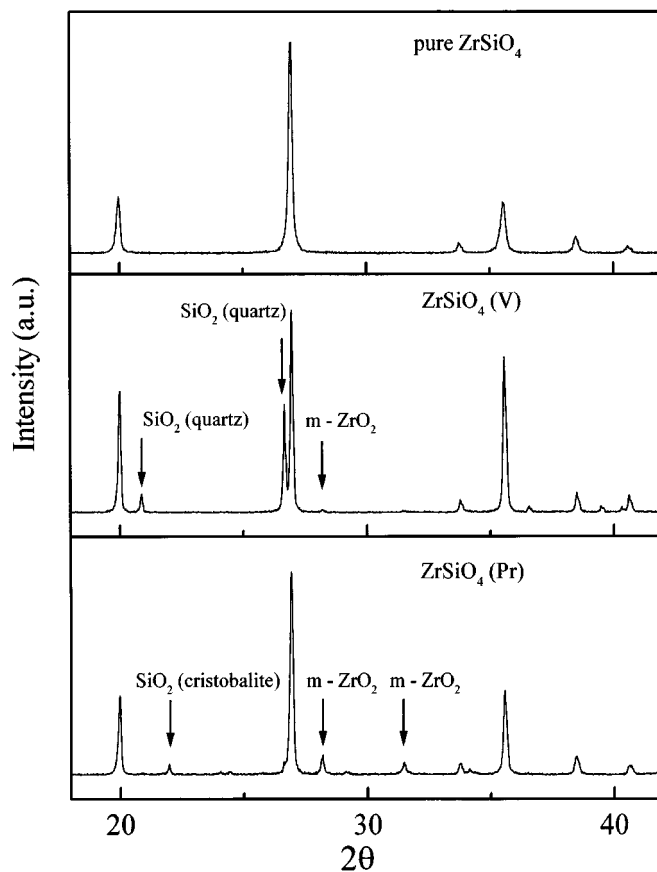


FIG 1. X-ray diffractograms ( $2\theta = 18\text{--}42^\circ$ ) of the samples investigated. Main diffraction lines of impurities are indicated.

#### (b) Vanadium-Doped Zircon $\text{ZrSiO}_4$ (V)

**XRD.** The diffraction pattern revealed the presence of  $\text{ZrSiO}_4$  and of some impurities, i.e., an important fraction of  $\text{SiO}_2$ -quartz and traces of monoclinic  $\text{ZrO}_2$ . While the first of the impurities was added on purpose for reasons mentioned before, the presence of zirconia is certainly due to an incomplete reaction during the ceramic synthesis. As compared with pure zircon, a shift of the diffraction zircon lines toward greater angles indicated a reduction of the interplanar spacings and thus of the dimensions of the lattice unit cell. Reminding the different ionic radii of  $\text{V}^{4+}$ ,  $\text{Zr}^{4+}$ , and  $\text{Si}^{4+}$ , it seems probable that the vanadium-zircon solid solution was formed predominantly with vanadium cations positioned at zirconium sites.

**PAC.** Three hyperfine interactions, hereinafter labeled  $I_1$ ,  $I_2$  and  $I_m$  (see Table 1), were derived from the best fits of the spin rotation curves. The last interaction  $I_m$ , with a very low intensity, is the well-known characteristic of monoclinic zirconia (20). According to XRD information, the other two

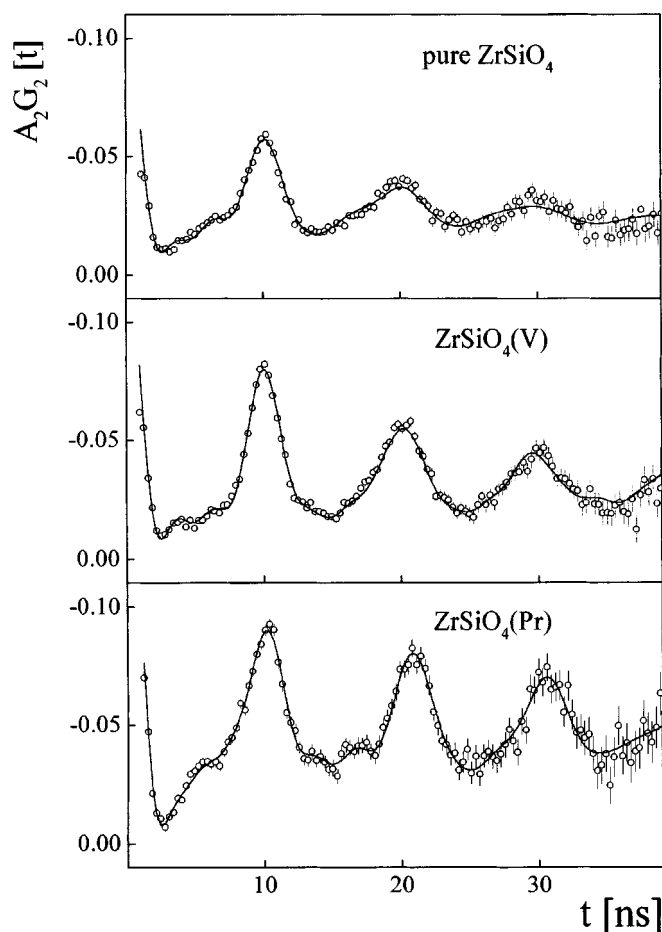


FIG 2. PAC spectra of the samples investigated. Full lines represent the theoretical curves that fit better the experimental data.

interactions must necessarily be connected to the solid solution of vanadium into zircon and, certainly, their quadrupole parameters are not very far from those of the I interaction characterizing the pure compound. However, as

TABLE 1  
Relative Fractions and Quadrupole Parameters of the Hyperfine Interactions Determined in the Samples Investigated

Sample	Hyperfine interaction	$f$ (%)	$\omega_Q$ (Mrad/s)	$\eta$ (%)	$\delta$ (%)
ZrSiO <sub>4</sub>	I	100	101 <sub>1</sub>	21 <sub>1</sub>	10 <sub>1</sub>
ZrSiO <sub>4</sub> (V)	I <sub>1</sub>	85 <sub>6</sub>	104 <sub>1</sub>	0*	6 <sub>1</sub>
	I <sub>2</sub>	12 <sub>3</sub>	96 <sub>1</sub>	34 <sub>6</sub>	4 <sub>2</sub>
	I <sub>m</sub>	3 <sub>1</sub>	127 <sub>1</sub>	41 <sub>3</sub>	0*
ZrSiO <sub>4</sub> (Pr)	I <sub>1</sub>	7 <sub>1</sub>	91 <sub>3</sub>	25 <sub>6</sub>	4 <sub>2</sub>
	I <sub>2</sub>	60 <sub>8</sub>	101 <sub>1</sub>	14 <sub>1</sub>	5 <sub>1</sub>
	I <sub>m</sub>	32 <sub>2</sub>	124 <sub>1</sub>	38 <sub>1</sub>	8 <sub>3</sub>

Note. Subscripts are quoted errors. The symbol (\*) indicates a fixed parameter during fitting.

compared with this latter hyperfine interaction, both I<sub>1</sub> and I<sub>2</sub> exhibit reduced EFGs spreads, indicating that vanadium incorporation to form the solid solution V<sub>x+y</sub>Zr<sub>1-x</sub>Si<sub>1-y</sub>O<sub>4</sub> causes an improvement of the lattice ordering. It has been reported that in iron zircon pigments, crystallization occurs at a much lower temperature than the 1400°C corresponding to pure zircon crystallization (21). If a similar situation were involved in this experiment, it is likely that the sintering temperature used here would lead to a more crystalline lattice in the case of doped zircon than in the case of pure zircon, as observed. Besides, the major interaction I<sub>1</sub> exhibits a somewhat higher quadrupole frequency than that determined for I. This evidence led the authors to consider the interaction I<sub>1</sub> (present in 85%) as the one reflecting the effect of the location of the smaller vanadium cations at the sites of the larger zirconium cations. The assumption, assisted by the XRD result concerning the reduction in the unit cell size, bears the idea of the predominance of the vanadium substitution for zirconium, in agreement with previous results (2, 5) and also with Chandley *et al.*'s simulation results (7). In fact, the latter authors reported that the effect of the incorporation of vanadium into the zirconium sites was to shorten the four equatorial bonds Zr–O and to lengthen the four axial bonds, which results in the net change of the equatorial oxygen atoms in 0.08 Å closer to the V<sup>4+</sup> ion and alters the lattice ion bond distances from 2.12 Å (Zr–O) to 2.04 Å (V–O). In turn, the reduction of the  $\eta$  parameter of I<sub>1</sub> as compared with that of I characterizing pure zircon reveals that vanadium doping causes the solid solution EFG to become quite symmetric.

Concerning I<sub>2</sub>, the magnitudes of the asymmetry parameter and of the quadrupole frequency relative to those of pure zircon indicate, respectively, a greater distortion of the lattice structure and probably an enlargement of the unit cell size. This experimental evidence might combine one or both of the two following hypotheses: (a) V<sup>4+</sup> larger cations substitution for Si<sup>4+</sup> smaller cations and (b) V<sup>4+</sup> localization into a tetrahedral interstitial position. The first idea is supported by Di Gregorio's results (6) and also by Chandley *et al.*'s simulations (7) who reported that the effect of the doping vanadium into the silicon site is that the four oxygen atoms bonded to the vanadium ion move away, altering the ion-to-oxygen bond lengths from 1.63 Å (Si–O) to 1.75 Å (V–O) and a great distortion of the lattice occurs. Regarding the second assumption, it is coherent with the proposal of Siggel *et al.* (10) who concluded that V<sup>4+</sup> occupies strongly distorted tetrahedral interstitial sites, though for these authors this localization is the unique one vanadium cations can achieve in the zircon lattice.

### (c) Praseodymium-Doped Zircon ZrSiO<sub>4</sub> (Pr)

XRD. The sample showed the presence of zircon, 6% of cristobalite (SiO<sub>2</sub>), and 10% of monoclinic zirconia. The

last two compounds, precursors powders, evidence an incomplete chemical reaction during synthesis. A subtle shift of zircon diffraction lines toward lower angles suggests a small increase in the unit cell size.

*PAC.* Three hyperfine interactions,  $I_m$  of monoclinic zirconia,  $I_1$ , and  $I_2$  (see Table 1) were found to describe this sample. The interaction  $I_m$  reveals that an important amount of m-ZrO<sub>2</sub>, much greater than that determined by XRD, is present in the sample. The different intensities determined by both techniques can probably be explained as being due to the extremely localized character of the PAC technique in comparison with that of XRD. In fact, the degree of disorder  $\delta$  fitted for the hyperfine interaction indicates that PAC is sensitive to perfect crystalline configurations as well as disordered, nondiffractable ones.

The remaining two interactions describe rather ordered EFGs, and according to XRD, they should be associated with the presence of praseodymium within the zircon lattice to form a solid solution.

The interaction  $I_1$  appears with a low intensity. Considering its quadrupole frequency, smaller than that for pure zircon, it has been associated with the substitution of the Pr<sup>4+</sup> ions for the smaller Zr<sup>4+</sup> ions in the solid solution Pr<sub>x</sub>Zr<sub>1-x</sub>SiO<sub>4</sub>. This assignment matches the results obtained by Siggel *et al.* (10) and Ocaña *et al.* (11).

As compared with interaction I of pure zircon, the major interaction  $I_2$  exhibits the same quadrupole frequency but a somewhat lower asymmetry parameter. Substitution of Pr<sup>4+</sup> for Si<sup>4+</sup> is quite improbable considering the size mismatch between both cations. Thus, the hypothesis that this interaction describes the zircon lattice slightly modified by the localization of the remaining Pr<sup>4+</sup> ions at interstitial sites could be pertinent.

#### IV. CONCLUSIONS

From the analysis of the three samples studied, the following conclusions can be drawn:

1. The PAC technique, assisted by XRD, proved efficient to determine the modifications caused in the zircon lattice by the incorporation of V<sup>4+</sup> and Pr<sup>4+</sup> coloring ions. For each pigment, XRD revealed the formation of a solid solution and PAC allowed the characterization of the configurations associated with the dopant cations located at two different positions of the zircon lattice.

2. In both doped zircons the substitution of the coloring agent for zirconium is unambiguous. In the case of

vanadium-doped zircon this substitution is predominant, while in the case of praseodymium its occurrence is minor.

3. Concerning the second site, it cannot be decided if the remaining vanadium cations occupy Si<sup>4+</sup> sites or interstitial tetrahedral distorted sites. In the case of praseodymium, there is some evidence that the remaining doping cations could be located at interstitial sites.

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#### REFERENCES

1. C. A. Seabright, *Ceramic Pigments*, U.S. Patent 2,441,407, May 1948.
2. T. Demiray, D. K. Nath, and F. A. Hummel, *J. Am. Ceram. Soc.* **53**(1), 1 (1970).
3. K. Robinson, G. V. Gibbs, and P. H. Ribbe, *Am. Mineral.* **56**, 782 (1971).
4. P. Dawson, M. M. Hargreave, and G. R. Wilkinson, *J. Phys. C. Solid State Phys.* **4**, 240 (1971).
5. A. Beltrán, S. Bohm, A. Flores-Riveros, J. A. Igualada, G. Monrós, J. Andrés, V. Luaña, and A. Martín Pendás, *J. Phys. Chem.* **97**, 2555 (1993).
6. S. Di Gregorio, M. Greenblatt, J. H. Pifer, and M. D. Sturge, *J. Chem. Phys.* **76**(6), 2931 (1982).
7. P. Chandley, R. Clark, R. Angel, and G. D. Price, *J. Chem. Soc. Dalton Trans.* **9**, 1579 (1992).
8. M. Ocaña, R. González-Elipe, V. M. Orera, P. Tartaj, and C. J. Serna, *J. Am. Ceram. Soc.* **81**(2), 395 (1998).
9. H. Xiayou, B. Gui-Ku, and Z. Min-Guang, *J. Phys. Chem. Solids* **46**(6), 719 (1985).
10. A. Siggel and M. Jansen, *Z. Anorg. Allg. Chem.* **583**, 67 (1990).
11. M. Ocaña, A. Caballero, A. R. González-Elipe, P. Tartaj, and C. J. Serna, *J. Solid State Chem.* **139**, 412 (1998).
12. H. Frauenfelder and R. M. Steffen, in "Alpha-, Beta-, and Gamma-Ray Spectroscopy" (K. Siegbahn, Ed.), Vol. 2, Chapter 19. North-Holland, Amsterdam, The Netherlands, 1965.
13. P. C. Rivas, J. A. Martínez, M. C. Caracoche, A. R. López García, L. C. Klein, and R. S. Pavlik, Jr., *J. Am. Ceram. Soc.* **78**(5), 1329 (1995).
14. "Table of Isotopes" (M. Lederer and V. S. Shirley, Eds.), p. 1135. John Wiley and Sons, Inc., New York, 1978.
15. G. Monros, J. Carda, P. Escribano, and J. Alarcon, *J. Mater. Sci. Lett.* **9**, 184 (1990).
16. F. T. Booth and G. N. Peel, *Trans. Br. Ceram. Soc.* **61**(7), 359 (1962).
17. V. I. Matkovich and P. M. Corbett, *J. Am. Ceram. Soc.* **44**(3), 128 (1961).
18. P. Lacentre and M. C. Caracoche, *Radiation Effects Defects Solids* **129**, 181 (1994).
19. A. Vasquez, *Thesis*, Porto Alegre, Brazil, 1973.
20. M. C. Caracoche, M. T. Dova, A. R. López García, J. A. Martínez, and P. C. Rivas, *Hyperfine Interact.* **39**, 117 (1988).
21. P. Tartaj, T. González-Carreño, C. J. Serna, and M. Ocaña, *J. Solid State Chem.* **128**, 102 (1997).