Journal of Alloys and Compounds, *177* (1991) 143–147
JAL 0050

Synthesis, structural determination and magnetic behaviour of $Y_xGd_{1-x}VO_4$ phases ($x=0.25$, 0.50, 0.75)

J. Isasi, M. L. Veiga, Y. Laureiro, R. Saez-Puche and C. Pico
Departamento de Química Inorgánica I, Facultad de Ciencias Químicas, Universidad Complutense, E-28040 Madrid (Spain)

(Received June 6, 1991)

Abstract

Solid solutions of composition $Y_xGd_{1-x}VO_4$ ($x=0.25$, 0.50, 0.75) have been prepared and characterized. These phases are isomorphous with zircon, $ZrSiO_4$. The crystal structures were refined from X-ray powder diffraction data by the Rietveld method. The lattice parameters show a linear decrease with increasing yttrium content and the final reability factors are in agreement with the proposed structural model. In order to study the effect produced by the substitution of Gd^{3+} by diamagnetic Y^{3+} ions, the magnetic susceptibility of $Gd_{0.5}Y_{0.5}VO_4$ has also been measured in the temperature range 4.2–300 K.

1. Introduction

Rare earth ions in an oxide matrix have received considerable interest, mainly concentrated on the luminescent and magnetic properties of these ions. In fact, YVO_4 activated with Eu^{3+} is a highly efficient luminophor [1].

In the case of rare earth (R) vanadates, RVO_4, all the members crystallize in the tetragonal system, space group $I4_1/amd$, being isomorphous with mineral zircon, $ZrSiO_4$. The structural parameters of $ErVO_4$ [2], $DyVO_4$ [3] and $NdVO_4$ [4] have been reported previously, as well as the theoretical parameters for the other members of the series.

The rare earth vanadates (IV) have emerged as classic examples of materials which exhibit cooperative Jahn–Teller structural phase transitions [5–9]. Crystals of $GdVO_4$ and YVO_4 do not show structural phase changes [10].

In this paper we report the synthesis and structural characterization by X-ray powder diffraction of the solid solutions $Y_xGd_{1-x}VO_4$ ($x=0.25$, 0.50, 0.75). The magnetic behaviour of one member of this solid solution series has also been studied.

2. Experimental details

Microcrystalline materials $Y_xGd_{1-x}VO_4$ ($x=0.25$, 0.50, 0.75) were obtained by solid state reaction between the oxides Y_2O_3 (Merck) Gd_2O_3 (Merck)

0925-8388/91/$3.50

and V_2O_5, this last oxide being isolated by the method described in ref. 11. The initial mixture in stoichiometric ratio was heated in air for 92 h at 900 K.

Powder X-ray diffraction patterns were registered at a rate of 0.1° (2θ) per minute by means of a Siemens Kristalloflex diffractometer powered by a D500 goniometer using nickel-filtered Cu Kα radiation.

Magnetic susceptibility measurements were made using the Faraday method in the range 4.2–300 K with a DMS5 Pendule susceptometer. The maximum applied magnetic field was 15 kG with $H(\mathrm{d}H/\mathrm{d}Z) = 29$ kG^2 cm^{-1}. The equipment was calibrated with $Hg(Co(SCN)_4)$ and $Gd_2(SO_4)_3 \cdot 8H_2O$ and χ was independent of the field in the temperature range of the measurements. Values of effective magnetic moment (μ_B) and Weiss constant (θ) were obtained by least-squares fits from the linear part of the χ^{-1} *vs.* T plots.

3. Results and discussion

A 2θ scan of 0.04° was used and the Rietveld profile analysis method [12] was employed for refinement of X-ray diffraction results in the range 10°–120° (2θ) for 144 observed reflections. The structure of YVO_4 [1] was used as trial model. The Rietveld programme minimized the function $\chi^2 = (R_{WP}/R_{EXP})^2$.

The reflection conditions are $h+k+l=2n$ for $(h\ k\ l)$, $h, k=2n$ for $(h\ k\ 0)$, $k+l=2n$ for $(0\ k\ l)$, $2h+l=4n$ for $(h\ h\ l)$, $l=4n$ for $(0\ 0\ 1)$, $h=2n$ for $(h\ 0\ 0)$ and $h=2n$ for $(h\ \bar{h}\ 0)$, compatible with the space group $I4_1/amd$ ($Z=4$). The atoms occupy the following positions: yttrium and gadolinium in $4a$ $(0, \frac{3}{4}, \frac{1}{8})$, vanadium in $4b$ $(0, \frac{1}{4}, \frac{3}{8})$ and oxygen in $16h$ $(0, y, z)$.

The crystallographic parameters are presented in Table 1. As can be seen, the unit cell parameters decrease linearly with increasing the yttrium content.

The structure of these solids solutions is isomorphous with zircon [14] and can be described as chains of alternating RO_8 distorted polyhedra (with $R \equiv Y$ or Gd randomly distributed) sharing edges and corners with VO_4

TABLE 1

Crystallographic parameters of $Y_xGd_{1-x}VO_4$

Composition	Unit cell parameters (Å)		Oxygen position		Reliability factors	
	a	c	y	z	R_{WP}	R_P
$GdVO_4$ [13]	7.213	6.348				
$Y_{0.25}Gd_{0.75}VO_4$	7.164	6.315	0.435	0.212	13.52	8.22
$Y_{0.5}Gd_{0.5}VO_4$	7.143	6.310	0.440	0.201	12.50	7.19
$Y_{0.75}Gd_{0.25}VO_4$	7.136	6.300	0.436	0.202	14.68	5.31
YVO_4 [1]	7.123	6.292				

tetrahedra. Figure 1 shows a perspective of the structure in which chains of $VO_4(1)$–RO_8–$VO_4(1)$ are defined along the *c* axis direction. It can be seen that there is octa-coordination of R ions (black oxygen atoms), with VO_4 tetrahedra offering a common edge (labelled 1) or a vertex (labelled 2 and 3). This fact is reflected in two sets of R–O bond distances, whilst the V–O ones remain unchanged with the composition (Table 2).

The magnetic susceptibility of $Y_{0.5}Gd_{0.5}VO_4$ has also been measured in the temperature range 4.2–300 K as an example. These results show a quasi-Curie-like behaviour over the entire interval of measurements, as can be observed from Figure 2. This behaviour is characteristic of the ground state of Gd^{3+}, $^8S_{7/2}$, for which the crystal field splitting should be very small, *i.e.* less than 1 cm^{-1} [15], and can be neglected, and the magnetic moment takes the experimental value 8.01 μ_B, which agrees with the free-ion value of 7.94 μ_B [16].

The high symmetry of the ground state of Gd^{3+} yields a θ value for $Y_{0.5}Gd_{0.5}VO_4$ close to zero ($\theta = -0.42$). It is obvious that this negative Weiss constant value is due to the crystal field effects and non-cooperative interactions, *i.e.* antiferromagnetic coupling, present in this compound down to 4.2 K.

By substitution of Gd^{3+} by Y^{3+} ions the number of paramagnetic ions is reduced but the magnetic behaviour is scarcely modified with respect to $GdVO_4$ [11]. Analogous results are obtained for the remaining stoichiometries

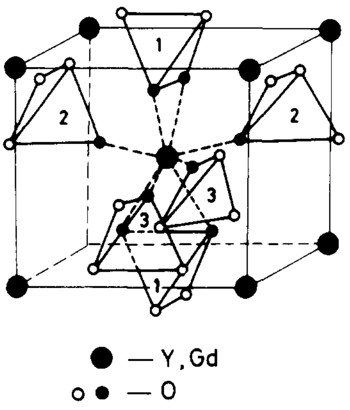

Fig. 1. VO_4 tetrahedra around yttrium or gadolinium atoms.

TABLE 2

Selected interatomic distances (angstroms) in $Y_xGd_{1-x}VO_4$ (R ≡ Y or Gd)

	$Y_{0.25}Gd_{0.75}VO_4$	$Y_{0.5}Gd_{0.5}VO_4$	$Y_{0.75}Gd_{0.25}VO_4$
R–O (×4)	2.29(3)	2.28(3)	2.31(9)
R–O (×4)	2.45(4)	2.50(8)	2.51(9)
V–O (×4)	1.71(5)	1.71(8)	1.71(9)

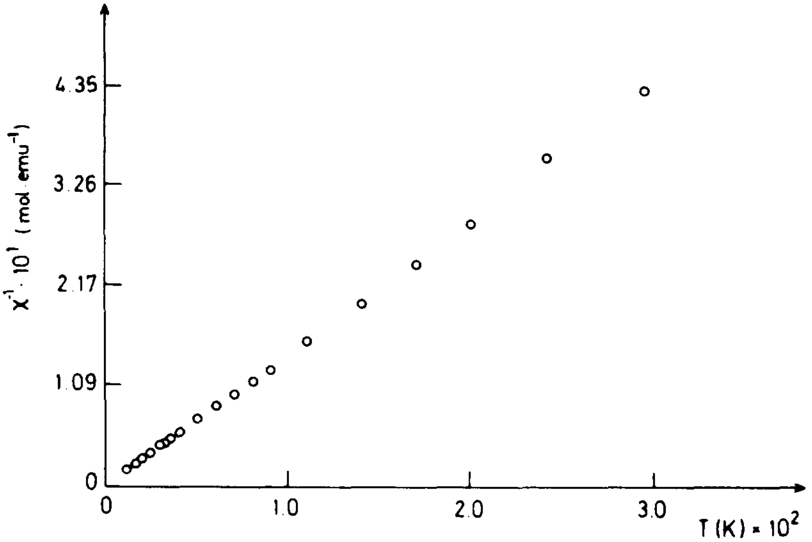

Fig. 2. Temperature dependence of reciprocal molar susceptibility in $Y_{0.5}Gd_{0.5}VO_4$.

in the solid solutions. From the crystal structure of these oxides one can conclude that in the whole range of composition paramagnetic ions are isolated, taking into account their location on 4*a* crystallographic sites. Therefore it is feasible to modulate the Gd^{3+} concentration in the material for different purposes.

Acknowledgments

We thank F. Rojas for the magnetic measurements. This work is supported by the CICYT PB 89-134 (Spain). J. Isasi is grateful to the UCM for a "Beca Complutense".

References

1 H. Schwarz, *Z. Anorg. Allg. Chem.*, *44* (1963) 323.
2 E. Patscheke, H. Fuess and G. Wiel, *Chem. Phys. Lett.*, *2* (1968) 47.
3 G. Willand and H. Schäfer, *J. Phys. Chem.*, *4* (1971) 811.
4 J. A. Baglio and O. J. Sovers, *J. Solid State Chem.*, *3* (1971) 458.
5 A. H. Cooke and C. J. Ellis, *Solid State Commun.*, *8* (1970) 689.
6 T. J. Glynn, R. T. Harley and R. M. Macfarlane, *J. Phys. C: Solid State Phys.*, *10* (1977) 2937.
7 R. T. Harley, W. Hayes, A. M. Perry, S. R. P. Smith, R. J. Elliot and I. D. Saville, *J. Phys. C: Solid State Phys.*, *7* (1974) 3145.
8 M. Schwab, *Phys. Status Solidi B*, *86* (1978) 195.
9 A. Kasten, H. G. Kahle, P. Klöfer and D. Schäfer-Siebert, *Phys. Status Solidi B*, *144* (1987) 423.
10 J. D. Cashion, A. H. Cooke, L. A. Hall, D. M. Martin and M. R. Wells, *Colloq. CNRS 180*, 1970, p. 417.

11 M. D. Guo, A. T. Aldred and D.-K. Chan, *J. Phys. Chem. Solids*, *48* (1987) 229.
12 J. Isasi, *Tesis de Licenciatura*, Universidad Complutense, Madrid, 1987.
13 J. Rodriguez-Carvajal, *Program FULLPROF*, ILL, Grenoble, 1990.
14 J. A. Baglio and G. Gashurov, *Acta Crystallogr. B*, *24* (1968) 292.
15 M. D. Guo, A. T. Aldred and S. K. Chang, *J. Phys. Chem. Solids*, *48* (1987) 229.
16 J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities*, Oxford University Press, Oxford, 1965.