Journal of Alloys and Compounds, 177 (1991) 251–257
JAL 0053

Synthesis, structure determination and magnetic susceptibilities of the oxides $Ln_3Li_5Sb_2O_{12}$ ($Ln \equiv Pr$, Nd, Sm)

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

(Received June 6, 1991)

Abstract

The oxides $Ln_3Li_5Sb_2O_{12}$ ($Ln \equiv Pr$, Nd, Sm) were prepared in air by heating a mixture of Ln_2O_3, $LiNO_3$ and Sb_2O_3 in the temperature range 1023–1243 K. Lattice parameters as well as atomic coordinates in the space group $I2_13$ ($Z=8$) are established from X-ray powder diffraction data by the Rietveld method. Magnetic susceptibilities from 4.2 to 300 K follow a Curie–Weiss law above 50 K ($Ln \equiv Pr$) or 70 K ($Ln \equiv Nd$). This is attributed to the splitting of the ground state associated with the Ln^{3+} ions by the influence of the crystal field. The magnetic moments, 3.54 and 3.61 μ_B for praseodymium and neodymium respectively, agree with those calculated by Hund's formula. The Sm^{3+} behaviour can be explained by taking into account that the splitting of the multiplets is not too large compared to kT. The magnetic moment observed at room temperature for this cation is 1.6 μ_B.

1. Introduction

A new series of mixed oxides, $Ln_3Li_5Sb_2O_{12}$ ($Ln \equiv La$, Pr, Nd, Sm, Eu), has recently been synthesized [1]. The unit cell is cubic (space group $I2_13$, $Z=8$).

In this paper we report the experimental magnetic susceptibilities for the oxides $Ln_3Li_5Sb_2O_{12}$ ($Ln \equiv Pr$, Nd, Sm) in polycrystalline samples, which were also characterized by X-ray powder diffraction data, refined on the basis of the Rietveld analysis method.

2. Experimental details

$Ln_3Li_5Sb_2O_{12}$ ($Ln \equiv Pr$, Nd, Sm) samples were prepared from Ln_2O_3, $LiNO_3$ and Sb_2O_3 (Merck). The initial mixture in stoichiometric ratio is heated to 1023 K for 6 h. The second step is a thermal treatment at 1243 K. In this process, sublimation of lithium oxide takes place and it is necessary to add an excess of 30%–40% $LiNO_3$. Therefore the stoichiometry of this compound could not be fixed, but the tentative chemical formula of the phase $La_3Li_5Sb_2O_{12}$

Elsevier Sequoia, Lausanne

[2] is proposed taking into account the structural analogy with the niobium (V) and tantalum (V) ternary oxides [3].

3. Results and discussion

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 generator using nickel-filtered Cu Kα radiation. A 2θ step scan of 0.04° was used and the Rietveld profile analysis method [4] was employed for refinement of X-ray diffraction patterns in the range 10°–120° (2θ) for 287 observed reflections. The structure of $La_3Li_5(Nb,Ta)_2O_{12}$ was used as a trial model. The Rietveld programme minimizes the function $\chi^2=(R_{WP}/R_{EXP})^2$. The reflection conditions are $h+k+l=2n$ for (h, k, l), $k+l=2n$ for $(0, k, l)$ and $h=2n$ for $(h, 0, 0)$, compatible with the space group $I2_13$. The structural data for $Ln_3Li_5Sb_2O_{12}$ (Ln ≡ Pr, Nd, Sm) are given in Table 1. The unit cell parameters decrease linearly in accordance with the lanthanide contraction effect. Table 2 lists the experimental bond lengths and angles of $Ln_3Li_5Sb_2O_{12}$ (Ln ≡ Pr, Nd, Sm).

The structure of these compounds is isomorphous to $La_3Li_5Sb_2O_{12}$ and can be described as a three-dimensional framework of lanthanide, antimony and oxygen atoms. The SbO_6 octahedra are located along the threefold axes of the unit cell and are associated with three lanthanide atoms, forming infinite chains of composition $(Ln_3Sb_2O_{12})_n$. These chains are bonded with others by means of lanthanide and lithium atoms. Figure 1 shows the orientation of $(Ln_3Sb_2O_{12})_n$ chains along a threefold axis.

Magnetic susceptibility measurements were made using the Faraday method in the temperature range 4.2–300 K with a DMS5 Pendule susceptometer. The maximum magnetic field applied was 1 kG with $H(dH/dZ)=29$ kG^2 cm^{-1}. The equipment was calibrated with $Hg(Co(SCN)_4)$ and $Cd_2(SO_4)_3\cdot 8H_2O$ and χ was independent of the field in the temperature range of the measurements. Values of effective moment (μ_B) and Weiss constant (θ) were obtained by least-squares fits from the linear part of the χ^{-1} *vs.* T plots.

The magnetic susceptibility of $Pr_3Li_5Sb_2O_{12}$ follows a Curie–Weiss law behaviour from 300 to 50 K. Below this temperature deviations upwards from linearity are observed, analogous to those found in some compounds of praseodymium [5, 6]. Since this cation has an even number of f electrons, the lowest crystal field level could be a singlet and the upward deviations observed at the lower temperatures are probably due to the population of this singlet level (see Fig. 2). The reciprocal molar magnetic susceptibility for $Nd_3Li_5Sb_2O_{12}$ obeys a Curie–Weiss law, $\chi=1.63/T+14.8$, above 70 K and the moment calculated from the χ^{-1} *vs.* T plot suggests that crystal fields effects are probably present (Fig. 2). Similar remarks have previously been reported for different neodymium compounds [7–9].

The observed and calculated magnetic moments and Weiss constants for Ln^{3+} in the oxides can be found in Table 3. In these cases negative

TABLE 1

Structural parameters for $Ln_3Li_5Sb_2O_{12}$

Ln ≡ Pr					Ln ≡ Nd					Ln ≡ Sm				
Atom	Site	x	y	z	Atom	Site	x	y	z	Atom	Site	x	y	z
Pr(1)	12*b*	0.118(9)	0.000	0.250	Nd(1)	12*b*	0.124(2)	0.000	0.250	Sm(1)	12*b*	0.116(6)	0.000	0.250
Pr(2)	12*b*	0.619(8)	0.000	0.250	Nd(2)	12*b*	0.622(9)	0.000	0.250	Nd(2)	12*b*	0.620(9)	0.000	0.250
Sb(1)	8*a*	0.000	0.000	0.000	Sb(1)	8*a*	0.000	0.000	0.000	Sb(1)	8*a*	0.000	0.000	0.000
Sb(2)	8*a*	0.250	0.250	0.250	Sb(2)	8*a*	0.250	0.250	0.250	Sb(2)	8*a*	0.250	0.250	0.250
Li(1)	24*c*	0.630(0)	0.307(2)	0.533(3)	Li(1)	24*c*	0.603(6)	0.307(4)	0.533(1)	Li(1)	24*c*	0.534(1)	0.284(2)	0.612(9)
Li(2)	24*c*	0.454(4)	0.383(3)	0.699(9)	Li(2)	24*c*	0.454(9)	0.382(5)	0.696(7)	Li(2)	24*c*	0.486(9)	0.385(1)	0.632(7)
O(1)	24*c*	0.323(0)	0.088(1)	0.241(4)	O(1)	24*c*	0.263(0)	0.094(8)	0.204(5)	O(1)	24*c*	0.310(8)	0.101(7)	0.225(1)
O(2)	24*c*	0.218(4)	0.395(4)	0.297(8)	O(2)	24*c*	0.234(4)	0.396(4)	0.332(9)	O(2)	24*c*	0.219(7)	0.423(0)	0.284(1)
O(3)	24*c*	0.312(0)	0.544(4)	0.430(4)	O(3)	24*c*	0.378(6)	0.544(2)	0.453(6)	O(3)	24*c*	0.360(8)	0.514(1)	0.423(6)
O(4)	24*c*	0.614(2)	0.470(5)	0.561(0)	O(4)	24*c*	0.663(2)	0.438(7)	0.529(2)	O(4)	24*c*	0.633(2)	0.460(8)	0.575(3)
Cell parameter (Å): $a = 12.745(2)$					Cell parameter (Å): $a = 12.674(5)$					Cell parameter (Å): $a = 12.577(0)$				
Volume (Å^3): 2070.23(4)					Volume (Å^3): 2035.82(1)					Volume (Å^3): 1989.44(1)				
Reliability factors (%):					Reliability factors (%):					Reliability factors (%):				
$R_P = 19.6$, $R_{WP} = 20.0$, $R_B = 8.33$, $R_F = 7.86$					$R_P = 18.2$, $R_{WP} = 21.0$, $R_B = 6.22$, $R_F = 6.67$					$R_P = 18.0$, $R_{WP} = 20.0$, $R_B = 8.87$, $R_F = 7.32$				

TABLE 2

Bond lengths (angstroms) and bond angles (degrees) of $Ln_3Li_5Sb_2O_{12}$

Ln ≡ Pr

Sb(1)–O(3)	2.61(7)	3×	Pr(1)–O(4)	2.43(9)	2×
Sb(1)–O(4)	1.69(1)	3×	Pr(1)–O(4)	2.60(6)	2×
Sb(2)–O(1)	2.26(7)	3×	Pr(1)–O(1)	2.83(3)	2×
Sb(2)–O(2)	1.90(5)	3×	Pr(1)–O(1)	2.90(4)	2×
Pr(2)–O(2)	2.62(5)	2×	Pr(2)–O(2)	2.54(2)	2×
Pr(2)–O(3)	2.39(5)	2×	Pr(2)–O(3)	2.52(0)	2×
Li(1)–O(1)	2.01(0)		Li(2)–O(1)	2.02(2)	
Li(1)–O(2)	2.19(5)		Li(2)–O(1)	2.34(3)	
Li(1)–O(2)	2.69(5)		Li(2)–O(2)	2.19(8)	
Li(1)–O(3)	2.21(1)		Li(2)–O(3)	2.19(4)	
Li(1)–O(3)	2.00(0)		Li(2)–O(4)	2.49(6)	
Li(1)–O(4)	2.11(2)		Li(2)–O(4)	2.52(2)	

O(4)–Pr(1)–O(4)	90.02	O(1)–Pr(1)–O(1)	140.80
O(2)–Pr(2)–O(2)	70.43	O(3)–Pr(2)–O(3)	59.69
O(3)–Sb(1)–O(4)	84.48	O(4)–Sb(1)–O(3)	87.54
O(1)–Sb(2)–O(2)	89.41	O(2)–Sb(2)–O(1)	110.38
O(3)–Li(1)–O(1)	65.67	O(1)–Li(1)–O(3)	81.44
O(3)–Li(1)–O(2)	94.95	O(2)–Li(1)–O(2)	73.68
O(2)–Li(1)–O(4)	93.04	O(4)–Li(1)–O(3)	91.55
O(2)–Li(2)–O(4)	92.26	O(4)–Li(2)–O(1)	124.03
O(1)–Li(2)–O(1)	63.08	O(1)–Li(2)–O(3)	55.77
O(3)–Li(2)–O(4)	89.74	O(4)–Li(2)–O(2)	90.02

Ln ≡ Nd

Sb(1)–O(3)	1.73(9)	3×	Nd(1)–O(4)	2.62(2)	2×
Sb(1)–O(4)	2.24(0)	3×	Nd(1)–O(4)	2.94(6)	2×
Sb(2)–O(1)	2.06(0)	3×	Nd(1)–O(1)	2.24(0)	2×
Sb(2)–O(2)	2.14(1)	3×	Nd(1)–O(1)	2.62(6)	2×
Nd(2)–O(2)	2.14(1)	2×	Nd(2)–O(2)	2.46(9)	2×
Nd(2)–O(3)	2.64(0)	2×	Nd(2)–O(3)	2.73(6)	2×
Li(1)–O(1)	2.55(1)		Li(2)–O(1)	2.14(6)	
Li(1)–O(2)	2.79(9)		Li(2)–O(1)	2.38(6)	
Li(1)–O(2)	2.09(6)		Li(2)–O(2)	2.42(7)	
Li(1)–O(3)	2.10(4)		Li(2)–O(3)	2.09(6)	
Li(1)–O(3)	2.46(3)		Li(2)–O(4)	2.08(0)	
Li(1)–O(4)	2.20(1)		Li(2)–O(4)	2.01(7)	

O(4)–Nd(1)–O(4)	78.47	O(1)–Nd(1)–O(1)	68.29
O(2)–Nd(2)–O(2)	72.06	O(3)–Nd(2)–O(3)	84.57
O(3)–Sb(1)–O(4)	77.65	O(4)–Sb(1)–O(3)	89.61
O(1)–Sb(2)–O(2)	92.79	O(2)–Sb(2)–O(1)	69.99
O(3)–Li(1)–O(1)	91.05	O(1)–Li(1)–O(3)	79.74
O(3)–Li(1)–O(2)	110.90	O(2)–Li(1)–O(2)	89.02
O(2)–Li(1)–O(4)	78.26	O(4)–Li(1)–O(3)	64.27
O(2)–Li(2)–O(4)	89.80	O(4)–Li(2)–O(1)	108.90
O(1)–Li(2)–O(1)	92.81	O(1)–Li(2)–O(3)	85.78
O(3)–Li(2)–O(4)	88.97	O(4)–Li(2)–O(2)	90.20

(*continued*)

TABLE 2. (*continued*)

Ln ≡ Sm					
Sb(1)–O(3)	2.00(3)	3×	Sm(1)–O(4)	2.62(5)	2×
Sb(1)–O(4)	1.90(7)	3×	Sm(1)–O(4)	2.26(1)	2×
Sb(2)–O(1)	2.04(1)	3×	Sm(1)–O(1)	2.77(4)	2×
Sb(2)–O(2)	2.24(0)	3×	Sm(1)–O(1)	2.93(8)	2×
Sm(2)–O(2)	2.26(6)	2×	Sm(2)–O(2)	2.79(7)	2×
Sm(2)–O(3)	2.20(2)	2×	Sm(2)–O(3)	2.39(8)	2×
Li(1)–O(1)	2.09(4)		Li(2)–O(1)	2.12(3)	
Li(1)–O(2)	2.84(2)		Li(2)–O(1)	2.40(6)	
Li(1)–O(2)	2.10(0)		Li(2)–O(2)	2.19(3)	
Li(1)–O(3)	2.09(9)		Li(2)–O(3)	2.09(6)	
Li(1)–O(3)	2.27(1)		Li(2)–O(4)	2.41(4)	
Li(1)–O(4)	2.39(1)		Li(2)–O(4)	2.19(5)	
O(4)–Sm(1)–O(4)		66.72	O(1)–Sm(1)–O(1)		69.03
O(2)–Sm(2)–O(2)		77.54	O(3)–Sm(2)–O(3)		61.92
O(3)–Sb(1)–O(4)		102.85	O(4)–Sb(1)–O(3)		90.38
O(1)–Sb(2)–O(2)		89.54	O(2)–Sb(2)–O(1)		77.62
O(3)–Li(1)–O(1)		88.81	O(1)–Li(1)–O(3)		83.96
O(3)–Li(1)–O(2)		98.99	O(2)–Li(1)–O(2)		79.44
O(2)–Li(1)–O(4)		99.42	O(4)–Li(1)–O(3)		84.55
O(2)–Li(2)–O(4)		73.07	O(4)–Li(2)–O(1)		137.57
O(1)–Li(2)–O(1)		70.70	O(1)–Li(2)–O(3)		119.33
O(3)–Li(2)–O(4)		96.61	O(4)–Li(2)–O(2)		88.81

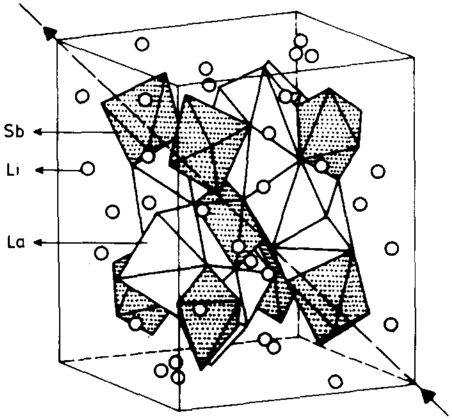

Fig. 1. A threefold axis along which chains of $(Ln_3Sb_2O_{12})_n$ (Ln ≡ Pr, Nd, Sm) are disposed and location of lithium atoms (circles).

values for the Weiss constant (θ) are found. It is obvious that the Weiss constant values are due to the crystal field effects.

A different behaviour in the temperature dependence of the magnetic properties of $Sm_3Li_5Sb_2O_{12}$ is observed (Fig. 3). The susceptibility of

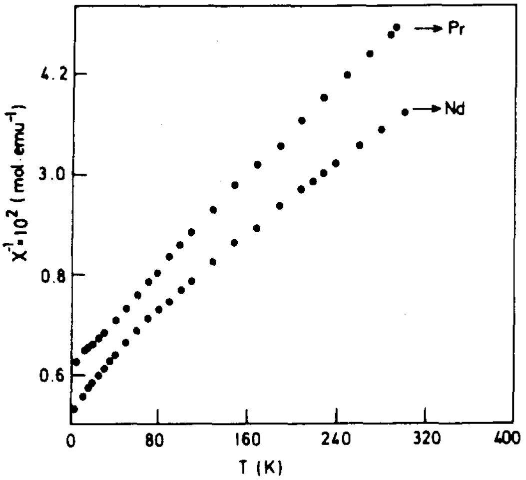

Fig. 2. Temperature dependence of reciprocal magnetic susceptibility for $Ln_3Li_5Sb_2O_{12}$ per mole of Ln^{3+} (Ln≡Pr, Nd).

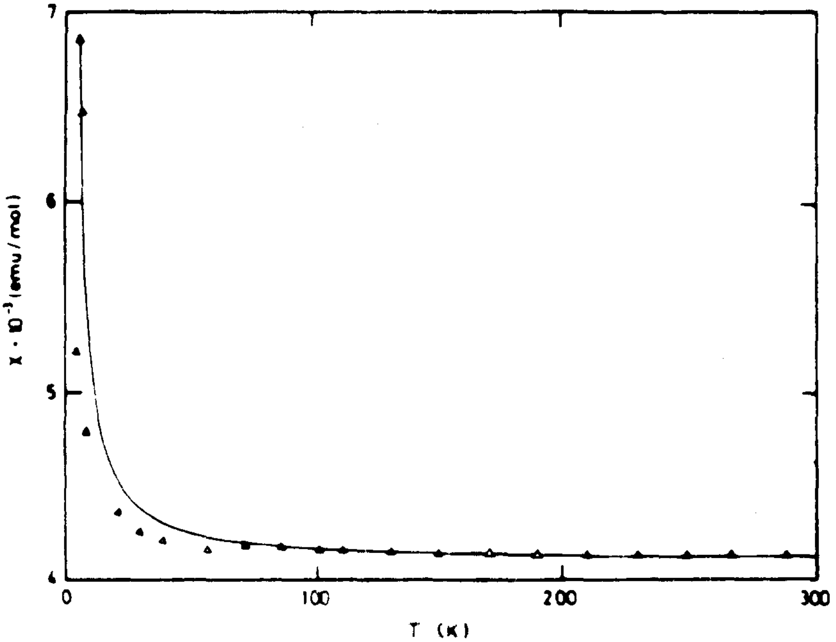

Fig. 3. Temperature variation of magnetic susceptibility per mole of $Sm_3Li_5Sb_2O_{12}$. Full lines represent calculated values.

$Sm_3Li_5Sb_2O_{12}$ remains almost constant between 100 and 240 K. This characteristic behaviour is attributed to the fact that the energy differences of the ^6H multiplet levels for Sm^{3+} are comparable to kT, and for this reason Van Vleck can be used in a first approximation [10], neglecting the J-mixing and crystal-field-splitting effects, although this gives a poor fit of the ex-

TABLE 3

Magnetic parameters for $Ln_3Li_5Sb_2O_{12}$

Ln	Ground state of the free ion	μ^c (μ_β)	μ^e (μ_β)	θ (K)
Pr	$^3H_4$	3.58	3.54	−16.0
Nd	$^4I_{9/2}$	3.62	3.61	−14.8
Sm	$^6H_{5/2}$	1.6	1.6[a]	–

[a]Calculated at 298 K.

perimental and calculated susceptibilities, as Fig. 3 shows, and a value of $\lambda = 298$ cm^{-1} for the orbit-coupling constant is obtained.

Acknowledgments

We thank F. Rojas for the magnetic measurements. This work is supported by the CICYT PB89-134 (Spain). J. Isasi is grateful to the UCM for a "Beca Complutense".

References

1 J. Isasi, M. L. Lopez, M. L. Veiga and C. Pico, *Anal. Quim.*, in the press.
2 J. Isasi, M. L. Veiga, A. Jerez and C. Pico, *J. Less-Common Met.*, *167* (1991) 381.
3 H. Hyooma and K. Hayashi, *Mater. Res. Bull.*, *23* (1988) 1399.
4 J. Rodriguez-Carvajal, *Program FULLPROF*, ILL, Grenoble, 1990.
5 R. Saez-Puche, M. Norton, T. R. White and W. S. Glaussinger, *J. Solid State Chem.*, *50* (1983) 281.
6 Y. Laureiro, M. L. Veiga, F. Fernandez, R. Saez-Puche, A. Jerez and C. Pico, *J. Less-Common Met.*, *167* (1991) 387.
7 L. Beaury, J. Derouet, P. Porcher, P. Caro and P. G. Fedman, *J. Less-Common Met.*, *126* (1986).
8 Y. Laureiro, M. L. Veiga, F. Fernandez, R. Saez-Puche, A. Jerez and C. Pico, *J. Less-Common Met.*, *335* (1990) 157.
9 M. L. Lopez, M. L. Veiga, F. Fernandez, A. Jerez and C. Pico, *J. Less-Common Met.*, *166* (1990) 367.
10 J. H. van Vleck, *The Theory of Electric and Magnetic Susceptibilities*, Oxford University Press, Oxford, 1965.