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Preparation and Study of the New Oxides $Ln_2Te_4O_{11}$ (Ln = Ce, Pr, Tb)

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Abstract

Three new oxides of composition $Ln_2Te_4O_{11}$ (Ln = Ce, Pr, Tb) have been prepared, by solid state reaction between rare earth oxides and TeO_2 *in vacuo* (Ln = Ce) or in air (Ln = Pr, Tb). The oxides are monoclinic, with lattice parameters which compare with those established for the known $Ln_2Te_4O_{11}$ oxides. X-ray diffraction data, infrared absorption spectra and the results of magnetic measurements for the three compounds are reported.

Introduction

The series of rare earth oxides $Ln_2Te_4O_{11}$ has been described [1] for all the lanthanide elements, with the exception of Ce, Pr and Tb. These compounds are monoclinic, space group *C2c* (No. 15) or *Cc* (No. 9). Unit-cell parameters, *a*, vary from 12.80 to 12.26 Å; *b*, from 5.278 to 5.058 Å; *c*, from 16.42 to 15.90 Å; and *β*, from 105.92 to 106.18° (in all cases, from La to Lu).

Incomplete series of oxocompounds of the rare earth elements have been frequently reported, in which the compounds of Ce, Pr or Tb are not included. Several examples [2–4] are: the series $Ln_2Ti_2O_7$ (Ln = Y, La, Nd, Sm–Lu); $LnScO_3$ (Ln = Y, La, Nd, Sm, Gd, Dy, Ho, Er, Tm); and Ln_3ReO_8 (Ln = La, Sm, Tb–Ho, Er–Lu). The difficulties which are found in preparing the compounds involving tervalent Ce, Pr or Tb are probably caused by the tendency of these elements to adopt intermediate (III)–(IV) oxidation states, as has been shown for cerium, in a recent study of the system Ce–O [5].

This study aims to complete the missing gap in the series $Ln_2Te_4O_{11}$ describing how to prepare the compounds of Ce, Pr and Tb and reporting their crystal, magnetic and infrared absorption characteristics.

Experimental

$Ln_2Te_4O_{11}$ (Ln = Pr, Tb) were prepared from mixtures of analytical grade Pr_6O_{11} or Tb_4O_7 and a slight excess of TeO_2 to prevent sublimation (Ln:Te = 1:2.1). After being ground in an agate mortar, the mixtures were heated in air at 923, 973 and 993 K (Ln = Pr), and 923, 973 and 1043 K (Ln = Tb). After each thermal treatment, which lasted one day, the materials were quenched, weighed and reground.

The synthesis of $Ce_2Te_4O_{11}$ was attempted by several routes: starting from a mixture of CeO_2 and TeO_2 (Ce:Te = 1:2.1) heated in air at 923, 973, 1023 and 1073 K; and from the following mixtures, which were heated *in vacuo* (10^{-3} mmHg) using Vycor ampoules; at 773 and 973 K, and quenched in air: Ce_2O_3 and TeO_2 (Ce:Te = 1:2); CeO_2, TeO_2 and Te (2:3.5:0.5); CeO_2, Ce and TeO_2 (1.5:0.5:4); Ce, TeO_2 and TeO_3 (2:1:3) and Ce, CeO_2, TeO_2 and TeO_3 (1.5:0.5:2:2).

A C.H.E.S.A. furnace was employed for thermal treatments. Temperatures were read with a calibrated Pt/Pt–Rh thermocouple, and are reliable to ±5 K.

The products of each thermal treatment were characterized by X-ray diffraction, using a Siemens Kristalloflex 810 diffractometer and a D-500 goniometer, with nickel-filtered copper radiation (λ = 1.540598 Å), provided with a graphite monochromator. The d-spacing measurements were made at a scanning rate of 0.1° 2θ min^{-1}, using Si (a = 5.43088(4) Å) as an internal standard. X-ray intensity data were collected by step-scanning from 11 to 74° 2θ, with increments of 0.02° 2θ. The counting time of each step was 4 s. The unit-cell parameters were refined by least-squares.

Infrared spectra were recorded between 1000 and 200 cm^{-1} using a Perkin-Elmer 325 spectrophotometer, and KBr disks.

The magnetic measurements were carried out on powder samples at 20 different temperatures from 77 to 300 K using a Faraday type magnetometer, equipped with a continuous flow cryostat designed by Oxford Instruments. A magnetic induction of

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about 10 kG was used. The independence of the susceptibility from the magnetic induction was checked at room temperature. The estimated absolute accuracy of temperatures is ±0.1 K. The relative accuracy on the apparent increase of the sample weight when the magnetic field is applied is about 1%.

Results and Discussion

$Ln_2Te_4O_{11}$ compounds (Ln = Pr, Tb) were synthesized in air, and $Ce_2Te_4O_{11}$ could only be prepared *in vacuo* by reaction between Ce_2O_3 and TeO_2. The remaining mixtures gave a mixture of phases.

X-ray Diffraction Data

The products were obtained as pale-coloured polycrystalline powders (Ce, yellow; Pr, green; Tb, white). The samples gave X-ray diffraction patterns which were indexed in the monoclinic system. The observed and calculated interplanar spacings and the observed intensities are listed in Table I. Crystal data are given in Table II. The densities were calculated assuming $Z = 4$. The observed unit-cell parameters compare with those previously established [1] for the known $Ln_2Te_4O_{11}$ oxides.

Infrared Spectra

Figure 1 shows the IR absorption spectra of $Ln_2Te_4O_{11}$ (Ln = Ce, Pr, Tb). The eleven bands, which occur in the region 800–250 cm^{-1}, behave in the same manner, shifting to higher frequencies as the atomic weight of the rare earth element increases. For instance, the strong band which occurs at 400 cm^{-1} for $Ce_2Te_4O_{11}$ appears at 404 and 427 cm^{-1} for Pr and Tb compounds, respectively. This

TABLE I. Observed (o) and Calculated (c) Interplanar Spacings and Observed Intensities for the Oxides $Ln_2Te_4O_{11}$

hkl	Ln = Ce			Ln = Pr			Ln = Tb		
	d_o	d_c	I_o	d_o	d_c	I_o	d_o	d_c	I_o
002	7.880	7.884	36	7.838	7.850	32	7.729	7.727	25
113	3.376	3.375	1000	3.362	3.363	1000	3.303	3.304	1000
$\bar{1}14$	3.227	3.229	22	3.214	3.216	26	3.165	3.162	28
$400-\bar{3}13$	3.062	3.061	929	3.050	3.049	911	2.991	2.994	993
204	2.965	2.963	14	2.953	2.952	18	2.899	2.902	17
$\bar{2}06$	2.699	2.700	241	2.687	2.687	228	2.648	2.646	214
020–006	2.623	2.624	165	2.615	2.615	170	2.565	2.565	195
115–313	2.516	2.517	6	2.506	2.507	12	2.461	2.465	11
$\bar{4}06$	2.338	2.338	6	2.329	2.327	7	2.291	2.290	12
$\bar{5}12-\bar{2}23$	2.282	2.281	53	2.287	2.290	49	2.239	2.240	59
206–116	2.205	2.204	199	2.196	2.200	181	2.159	2.160	154
$\bar{4}20$	1.993	1.992	213	1.986	1.985	210	1.947	1.948	224
$\bar{6}06$	1.884	1.884	244	1.876	1.874	250	1.842	1.843	264
$\bar{2}26$	1.881	1.881	253	1.876	1.874	245	1.840	1.842	236
$\bar{7}12-\bar{7}13-131$	1.719	1.717	141	1.712	1.710	165	1.678	1.679	127
$\bar{1}19-027$	1.706	1.706	176	1.700	1.700	190	1.675	1.673	170
226	1.688	1.688	137	1.682	1.682	134	1.652	1.652	132
133	1.625	1.626	105	1.620	1.620	115	1.591	1.590	133
$\bar{3}33-\bar{8}02$	1.586	1.586	97	1.581	1.581	93	1.551	1.551	90
$\bar{8}04-\bar{5}19$	1.581	1.581	123	1.574	1.575	121	1.550	1.547	122
$800-\bar{6}26$	1.530	1.530	75	1.525	1.525	124	1.497	1.497	134
$\bar{5}33$	1.433	1.433	58	1.427	1.428	43	1.401	1.401	44
319	1.415	1.415	85	1.410	1.410	82	1.386	1.386	75
$\bar{4}$ 0.12–0 2.10	1.349	1.350	46	1.344	1.344	33	1.325	1.324	28
625–820–533	1.323	1.323	110	1.318	1.318	97	1.292	1.293	80
0 0.12–$\bar{8}26$	1.313	1.314	66	1.308	1.308	46	1.288	1.288	64

TABLE II. Crystal Data for the Oxides $Ln_2Te_4O_{11}$ with e.s.d.s in Parentheses

Ln	*a* (Å)	*b* (Å)	*c* (Å)	*β* (°)	*V* ($Å^3$)	D_c ($Mg\ m^{-3}$)
Ce	12.734(4)	5.247(1)	16.403(8)	106.00(4)	1053.6(5)	6.09
Pr	12.685(5)	5.230(2)	16.329(9)	105.95(5)	1041.6(6)	6.17
Tb	12.458(7)	5.129(2)	16.08(1)	106.02(7)	987.6(8)	6.75

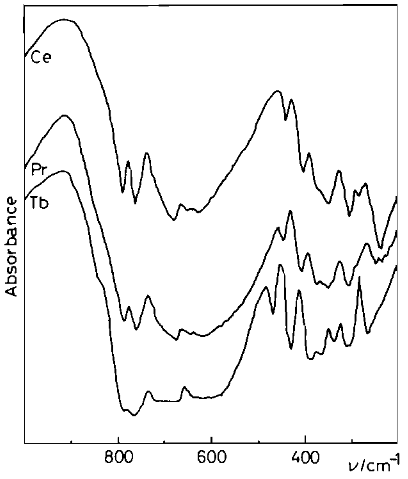

Fig. 1. Infrared absorption spectra for $Ln_2Te_4O_{11}$ (Ln = Ce, Pr, Tb).

TABLE III. Correlation Factors χ_m/T, Observed (o) and Calculated (c) Magnetic Moments, and Weiss Constants for the Oxides $Ln_2Te_4O_{11}$

Ln	r	μ_o (BM)	μ_c (BM)	$-\theta_w$ (K)
Ce	0.9975	2.407(7)	2.56	64.8
Pr	0.9993	3.46(1)	3.62	30.2
Tb	0.9984	9.72(4)	9.72	2.8

kind of correlation between the atomic mass and the frequencies of the bands can only be explained as an effect of lattice vibration.

Magnetic Measurements

The reciprocal magnetical susceptibilities obey the Curie–Weiss law. For the Ce compound, $\chi_m^{-1} = 1.393\ T + 90.2$; for Ln = Pr, $\chi_m^{-1} = 0.672\ T + 20.3$, and for Ln = Tb, $\chi_m^{-1} = 0.086\ T + 0.24$. Table III includes the correlation factors χ_m^{-1}/T, the observed Curie–Weiss constants and a comparison of observed magnetic moments and those calculated for the Ln^{3+} free ions. $Ln_2Te_4O_{11}$ (Ln = Ce, Pr, Tb) are paramagnetic in the range 77–300 K.

The good correlation factors (r) obtained, as well as the agreement between observed magnetic moments and those calculated for the free ions, confirm the oxidation state of the three lanthanide elements.

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