

A_2MoTiO_{7-x} (A≡rare earth or Y): a new series of oxide pyrochlores prepared by topochemical reduction of A_2MoTiO_8 scheelites

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Abstract

A series of anion-deficient pyrochlore oxides of the formula A_2MoTiO_{7-x} ($x \leq 0.5$), where A≡Sm, Gd, Tb, Dy, Ho, Er, Lu and Y, has been prepared by reduction of A_2MoTiO_8 scheelites. The scheelite-to-pyrochlore conversion is reversible, indicating that the reaction is likely to be topochemical. The oxidation states of molybdenum and titanium are most probably $Mo^{(III)}$ and $Ti^{(IV)}$ for the limiting composition of the pyrochlores $A_2MoTiO_{6.5}$. The new pyrochlores are non-metallic and paramagnetic as expected.

1. Introduction

Oxides of the formula $A_2B_2O_7$, where A is a trivalent rare earth or yttrium and B is a tetravalent metal, crystallizing in the pyrochlore structure continue to attract attention in view of their interesting electrical, magnetic and catalytic properties [1]. $A_2B_2O_7$ pyrochlores are known for several tetravalent metals such as for B≡Ti, V, Mn, Mo, Ru, Sn and Pb [1, 2]. The pyrochlore structure is versatile to accommodate multiple substitution at both the A and the B sites. Several multiply substituted charge-coupled pyrochlores of the type $AA'B_2O_7$ (A≡Ca, Cd; A'≡Ce; B≡Ti) and $A_2BB'O_7$ (A≡Ln or Bi; B≡Cr, Fe, Ga, Sc, In; B'≡Nb, Ta, Sb) have been reported [1, 3]. Multiply substituted $A_2B_2O_7$ pyrochlores containing two different transition metal atoms at the B site with partially filled d shells are rare. We report here the synthesis and characterization of A_2MoTiO_{7-x} ($x \leq 0.5$) pyrochlores where $Mo^{(III)}$ and $Ti^{(IV)}$ seem to occupy the B sites at the limiting composition. We have prepared the new pyrochlores by a novel method involving topochemical reduction of the corresponding A_2MoTiO_8 scheelites. The newly prepared A_2MoTiO_{7-x} pyrochlores are non-metallic paramagnets, unlike the $A_2Mo_2O_7$ pyrochlores [4–6].

2. Experimental details

A_2MoTiO_8 scheelites for A≡Sm, Gd, Tb, Dy, Ho, Er, Lu and Y were prepared [7] by reacting A_2O_3 , TiO_2 and MoO_3 at 1200 °C for 24 h. Reduction

TABLE 1

Lattice parameter a_c and oxygen content data for A_2TiMoO_{7-x} pyrochlores

A^{3+}	a_c^a (Å)	Oxygen content ^b
Sm ³⁺	10.410	6.50
Gd ³⁺	10.328	6.55
Tb ³⁺	10.282	6.70
Dy ³⁺	10.254	6.50
Ho ³⁺	10.220	6.60
Er ³⁺	10.180	6.70
Lu ³⁺	10.077	6.70
Y ³⁺	10.216	6.50

^aThe standard deviation in the last digit is 2–3.

^bDetermined by wet chemical analysis of the reducing power of the sample. The standard deviation in the oxygen content is within ± 0.02 .

of the scheelites was investigated in a flowing hydrogen atmosphere at various temperatures. It was found that single-phase oxides of the pyrochlore structure were formed when the reduction was carried out at 875–900 °C for 12–24 h. The reduced phases were characterized by powder X-ray diffraction, wet chemical analysis, IR spectroscopy, electrical conductivity and magnetic susceptibility measurements. Wet chemical analysis using $K_2Cr_2O_7$ as the oxidant enabled us to determine the oxygen content with an accuracy of ± 0.02 . Reoxidation of the pyrochlore to the scheelite was followed by thermogravimetry and powder X-ray diffraction. Lattice parameters and oxygen contents of the new pyrochlores synthesized are listed in Table 1.

3. Results and discussion

Reduction of A_2MoTiO_8 scheelites at 875–900 °C in hydrogen yields black single-phase cubic pyrochlore oxides for $A \equiv Sm, Gd, Tb, Dy, Ho, Er, Lu$ and Y (Table 1). We could not, however, obtain a pyrochlore phase for $A \equiv Pr, Nd$ and Eu by the reduction of the corresponding scheelites. A plot of the cubic unit-cell parameter a_c of the new pyrochlores against the radius of $A^{(III)}$ ions (eight coordination) [8] is linear (Fig. 1), indicating that an isostructural series of phases are formed. We have determined the oxygen content of the samples by wet chemical analysis as well as by thermogravimetry. The oxygen content of the new pyrochlores is between 6.5–6.7 (Table 1), indicating that the new pyrochlores are anion deficient. Several anion-deficient oxide pyrochlores such as $Pb_2Ru_2O_{6.5}$ and $Bi_2Rh_2O_{6.8}$ have been reported in the literature [9, 10], where the anion vacancy occurs at 8a sites of the $Fd3m$ space group.

There are two possible combinations of oxidation states corresponding to the limiting oxygen stoichiometry of 6.5 in the new pyrochlores: $A_2Mo^{(III)}Ti^{(IV)}O_{6.5}$ and $A_2Mo^{(IV)}Ti^{(III)}O_{6.5}$ where $A \equiv$ trivalent rare earth. In order

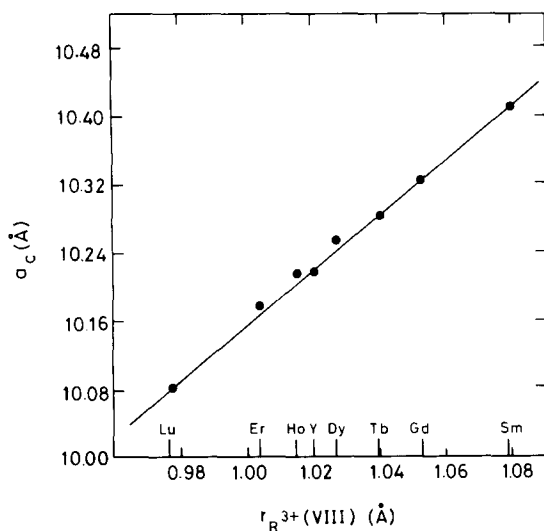


Fig. 1. Plot of cubic unit-cell parameter a_c of A_2MoTiO_{7-x} vs. the radius of A^{3+} .

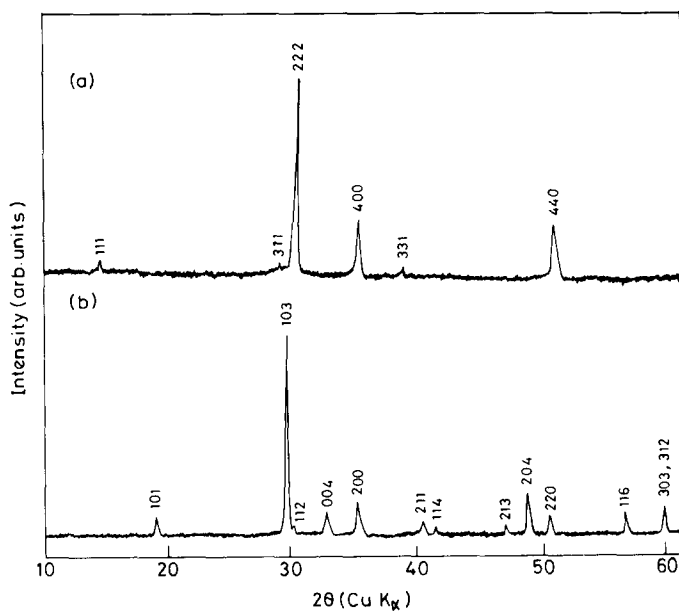


Fig. 2. X-ray powder diffraction patterns of Lu_2MoTiO_{7-x} pyrochlore (curve (a)) and its oxidation product, Lu_2MoTiO_8 , scheelite (curve (b)).

to distinguish between the two possibilities, we have carried out reduction of a titanium pyrochlore, $Y_2Ti_2O_7$, under similar conditions. Significantly we find no reduction at all in $Y_2Ti_2O_7$, the sample remaining white without any weight loss even after prolonged reduction at 900 °C in hydrogen. This result indicates that, in the molybdenum–titanium pyrochlores also, the titanium

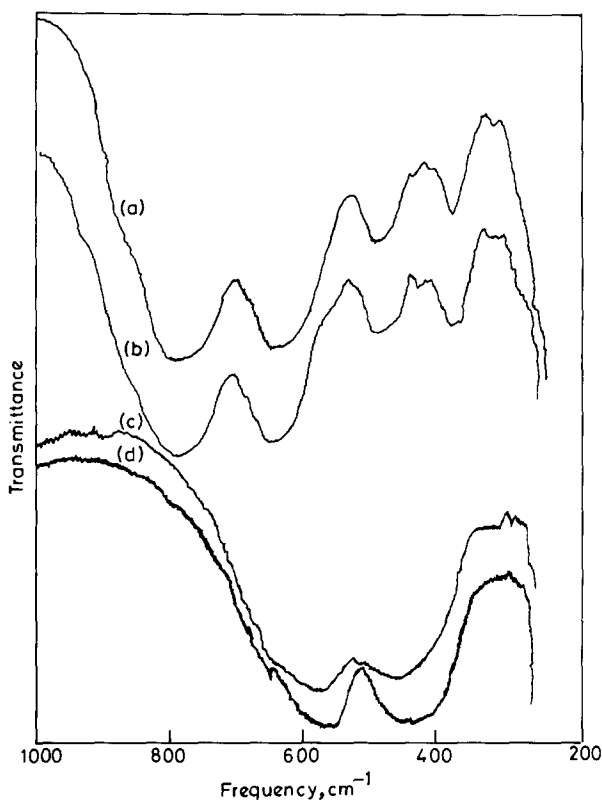


Fig. 3. IR absorption spectra of $\text{Dy}_2\text{MoTiO}_8$ (spectrum (a)), $\text{Gd}_2\text{MoTiO}_8$ (spectrum (b)), $\text{Dy}_2\text{MoTiO}_{7-x}$ (spectrum (c)) and $\text{Gd}_2\text{MoTiO}_{7-x}$ (spectrum (d)).

is most likely present in the titanium(IV) state; accordingly the correct formulation of the new pyrochlores is likely to be $\text{A}_2\text{Mo}^{(\text{III})}\text{Ti}^{(\text{IV})}\text{O}_{6.5}$. In cases where the oxygen stoichiometry is more than 6.5, both $\text{Mo}^{(\text{IV})}$ and $\text{Mo}^{(\text{III})}$ may be present together with $\text{Ti}^{(\text{IV})}$. Thus $\text{Lu}_2\text{MoTiO}_{6.7}$ would consist of $\text{Lu}_2\text{Mo}_{0.4}^{(\text{IV})}\text{Mo}_{0.6}^{(\text{III})}\text{Ti}^{(\text{IV})}\text{O}_{6.7}$.

It is well known that both the scheelite and the pyrochlore structures are related, being derived from the fluorite structure [11]. It is therefore likely that the transformation of A_2MoTiO_8 scheelites to $\text{A}_2\text{MoTiO}_{7-x}$ pyrochlores on reduction proceeds by a topochemical mechanism. Reoxidation of $\text{A}_2\text{MoTiO}_{7-x}$ in air at around 900 °C indeed transforms the pyrochlores to the parent scheelites (Fig. 2). The weight gain in the process is consistent with the oxygen content determined by chemical analysis. For example, the weight increase expected for the reaction, $\text{Y}_2\text{MoTiO}_{6.5} + \frac{3}{4}\text{O}_2 \rightarrow \text{Y}_2\text{MoTiO}_8$ is 5.64%, while the weight gain found by thermogravimetry is 5.68%.

We have recorded the IR spectra of A_2MoTiO_8 scheelites and $\text{A}_2\text{MoTiO}_{7-x}$ pyrochlores in order to characterize the change in the structure. It is known that in the ABO_4 scheelites the small cations occur in tetrahedral coordination,

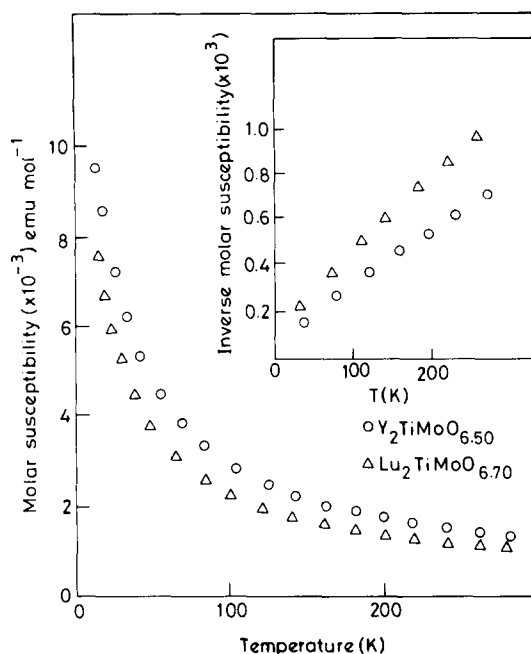


Fig. 4. Molar magnetic susceptibility *vs.* temperature plots for A_2MoTiO_{7-x} pyrochlores. The inset shows the corresponding inverse molar susceptibility *vs.* temperature plots.

TABLE 2

Magnetic data for A_2MoTiO_{7-x} pyrochlores

Compound	μ_A	μ_{calc}^a	μ_{found}	θ (K)
$Y_2TiMoO_{6.50}$	0	3.83	1.85	-22 ± 2
$Lu_2TiMoO_{6.70}$	0	2.49	1.50	-17 ± 2
$Gd_2TiMoO_{6.50}$	7.94	16.34	15.12	0

^a $\mu_{calc} = (2\mu_A^2 + \mu_{Mo}^{(III)2})^{1/2}$ for $A \equiv Gd$ and $\mu_{calc} = (0.6\mu_{Mo}^{(III)2} + 0.4\mu_{Mo}^{(IV)2})^{1/2}$ for $A \equiv Lu$.

while in the $A_2B_2O_7$ pyrochlores the B-site cations occur in near-octahedral oxygen coordination [11, 12]. Accordingly, the change in coordination of molybdenum and titanium from tetrahedral to octahedral geometry on reduction of the A_2MoTiO_8 scheelites to the pyrochlore structure is clearly seen in the IR spectra (Fig. 3). The scheelites show strong absorption bands due to the tetrahedral MO_4 groups [13] around 800 cm^{-1} (ν_3) and 400 cm^{-1} (ν_4). The A_2MoTiO_8 scheelites show two strong bands centred at around 800 cm^{-1} and 625 cm^{-1} which are probably due to ν_3 for the MoO_4 and TiO_4 groups respectively. These bands are clearly shifted to lower frequencies ($400\text{--}600\text{ cm}^{-1}$) in the pyrochlore structure, as expected. The IR spectra of A_2MoTiO_{7-x} showing absorption bands at 550 , 425 and 250 cm^{-1} are in general characteristic of the pyrochlore structure [14], providing further

evidence that reduction of A_2MoTiO_8 scheelites leads to the formation of pyrochlores.

Unlike the $A_2Mo_2O_7$ pyrochlores which are metallic or semimetallic ferromagnets for $A \equiv Nd, Sm$ and Gd [4–6, 15], A_2MoTiO_{7-x} pyrochlores are non-metallic and paramagnetic. The resistivity of A_2MoTiO_{7-x} pyrochlores varies from about 10^6 to about $10^3 \Omega \text{ cm}$ in the temperature range 150–300 K with an activation energy of about 0.20 eV. The non-metallic nature of A_2MoTiO_{7-x} pyrochlores in contrast with the metallic nature of $A_2Mo_2O_7$ pyrochlores is understandable because the octahedral sites of the A_2MoTiO_{7-x} pyrochlores are occupied by $Mo^{(III-IV)}$ and $Ti^{(IV)}$ and the presence of the latter with the $3d^0$ electronic configuration would not favour the formation of itinerant states.

Magnetic measurements reveal that the A_2MoTiO_{7-x} oxides are Curie–Weiss paramagnets. Plots of inverse molar susceptibility χ_M^{-1} vs. temperature T are linear down to 15 K (Fig. 4), showing small negative θ values. The paramagnetic moments determined from the slopes of the χ_M^{-1} vs. T plots are, however, much smaller than the spin-only value expected for the $Mo^{(III)}$: $4d^3$ configuration (Table 2). Possibly the low moment arises from the lower symmetry of the molybdenum sites in the A_2MoTiO_{7-x} pyrochlore structure. It is known that the octahedral site in the pyrochlore structure could be distorted to trigonal antiprismatic symmetry with unequal metal–oxygen bond lengths [16]. Further investigations are necessary to establish the structural details and their relation to the magnetic property of the interesting series of pyrochlore oxides.

In summary, we have synthesized a new series of oxide pyrochlores of the composition A_2MoTiO_{7-x} ($x \leq 0.5$) for $A \equiv Sm, Gd, Tb, Dy, Ho, Er, Lu$ and Y by reduction of the corresponding A_2MoTiO_8 scheelites. The scheelite-to-pyrochlore reduction is reversible, revealing that the reduction is likely to be topochemical. A_2MoTiO_{7-x} ($x \leq 0.5$) pyrochlores are non-metallic and paramagnetic down to 15 K, indicating that the $Mo^{III}-O-Ti^{IV}$ interaction does not produce itinerant states.

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