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Synthesis and characterization of charge-substituted garnets $YCaLnGa_5O_{12}$ (Ln = Ce, Pr, Tb)

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Abstract

A low temperature method is described for the preparation of the new garnet compounds $YCaLnGa_5O_{12}$ (Ln = Ce, Pr, Tb). In this set of compounds ($Ca^{2+} + Ln^{4+}$) replaces $2Y^{3+}$ in the parent gallium based garnet $Y_3Ga_5O_{12}$ in order to stabilize as effectively as possible the Ln^{4+} species in the eight-coordinate "A" site of the garnet structure. Characterization of the oxides by X-ray powder diffraction and thermogravimetric analysis is discussed with regard to the structural relationship of the substituted compound to the parent material. The tetravalent ions Pr^{4+} and Tb^{4+} exhibit increased thermal stability in reducing conditions as compared to the Ln^{4+} states in the fluorite (LnO_2) and perovskite ($BaLnO_3$) type structures. This result is discussed with reference to the complex crystal chemistry of these systems.

1. Introduction

Studies of the tetravalent state of the lanthanide elements Ce, Pr, and Tb currently make up a rather small part of the diverse chemistry of these rare earths. In particular, the oxide chemistry of these elements is primarily limited to the study of the fluorite-related systems LnO_{2-x}. However, the structural chemistry of the perovskites $BaLnO_3$ [1] and the oxometallates Li_8LnO_6 [2] and A_2LnO_3 [3] (A = alkali metal) indicates that there should exist a somewhat broader oxide chemistry associated with the 4+ state of these elements. Mainly, the difficulties have involved stabilizing the tetravalent state, as all three have trivalent states which are thermodynamically more stable in most environments [4]. We have been interested recently in exploring the various factors that determine the stability of tetravalent Ce, Pr and Tb in oxide lattices, and have attempted to prepare compounds that are charge-substituted relatives of well-established and very stable pyrochlore systems [5]. These materials have the composition $CaLnTi_2O_{7-x}$, the first member of the series being reported as $CaCeTi_2O_7$[6], where the $2Y^{3+}$ in the parent pyrochlore $Y_2Ti_2O_7$ have been replaced with ($Ca^{2+} + Ce^{4+}$). Our initial work with these systems, in which the Zr analogues were also studied, led to the result that the stoichiometric Ce^{4+} compounds could be prepared rather easily, but the Tb compounds have composition $CaLnM_2O_{6.5}$ (M = Ti, Zr), *i.e.* the lanthanide cation is trivalent rather than tetravalent. This result is not surprising, since the pyrochlore structure tolerates vacancies on both the cation and anion sublattices quite readily [7].

In an effort to find a system which might not have the tendency to allow the "reduction" of the tetravalent lanthanide cation to the trivalent state through the formation of oxygen vacancies, we have explored the possibility of charge substitution in the garnet framework of $Y_3Ga_5O_{12}$. The structure consists of a three-dimensional network of GaO_6 octahedra and GaO_4 tetrahedra with the Y^{3+} (or other trivalent rare earth) cations in eightfold oxide coordination within the array of Ga polyhedra. Since the structure is based on a three-dimensional array of polyhedra linking both vertices and edges, the formation of anion vacancies is expected to be substantially more difficult than vacancy formation in either the perovskite or pyrochlore materials, structures which are based on vertex-sharing of octahedra only, and can in many respects be considered two-dimensional as well as three-dimensional [8].

2. Experimental details

Garnet samples were prepared using a modification of a self-sustaining, or combustion, synthesis method, as recently described for garnets and related materials [9]. All reagents were obtained from Aldrich and used

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as received unless otherwise noted. In a typical experiment, 1.39 g (3.8 mmol) of $Y(NO_3)_3 \cdot 5H_2O$ and 0.90 g (3.8 mmol) of $Ca(NO_3)_2 \cdot 4H_2)O$ are dissolved in a small amount of H_2O, along with 7.57 g (19 mmol) of $Ga(NO_3)_3 \cdot 8H_2O$. The water of hydration associated with $Ga(NO_3)_3$ was determined by thermogravimetric analysis. For the Ce preparation, 1.65 g (3.8 mmol) of $Ce(NO_3)_3 \cdot 6H_2O$ (G.F. Smith Chemical Co.) is added to the solution. For the Pr and Tb preparations, stoichiometric amounts of Pr_6O_{11} or Tb_4O_7 were dissolved in 10 ml of concentrated HNO_3, and the acid solution added to the mixture as above. Finally, 4.6 g of urea (Merck) is added to the nitrate solution, and the solution is allowed to evaporate slowly with heating and gentle stirring until about 25 ml remain. A calculation of the amount of urea used as a fuel in the reaction has been discussed in depth previously [10] and is optimized based on the amount of nitrate (oxidizer) present in the reactants. The clear solution is then placed in a muffle furnace which has been maintained at 610 °C and in approximately 2 min, the combustion reaction is initiated, accompanied by the evolution of large amounts of brown NO_2 gas. When this reaction has subsided, the product appears light and porous, filling the reaction container. This product is ground fine with a mortar and pestle, and then pressed into pellets and fired at 1050 °C for 72 h in an atmosphere of flowing oxygen, with two intermediate grindings during this period. In general, the combustion synthesis alone is quite sufficient for the formation of the parent garnet $Y_3Ga_5O_{12}$, but the additional firing and grinding appears to be required for the formation of homogeneous materials in the charge substituted systems. Essentially, the combustion synthesis route is used to overcome the difficulties associated with the reaction of component binary oxides. Intimate contact of reactants is achieved through the low temperature route, and subsequent firing is therefore more effective.

Powder X-ray diffraction patterns were recorded in the 2θ range 10–65° using a Philips diffractometer with Ni-filtered Cu $K\alpha$ radiation, and cubic lattice parameters for the garnet phases were calculated using the least squares refinement program LCR-2 [11]. Elemental analyses using energy-dispersive X-ray fluorescence spectroscopy (EDAX) were carried out with an EG&G/ORTEC instrument interfaced to a Philips scanning electron microscope. Resulting spectra were matched with reference standards to give approximate compositions in atomic percent. Thermal stability in reducing conditions was measured by determining the temperature at which the reduction Ln^{4+} to Ln^{3+} took place in a 4% H_2/Ar atmosphere. A Mettler TA-2 Thermobalance was used to record the TGA data in the range 25–1125 °C.

3. Results and discussion

Calculated lattice parameters and associated data for the garnet phases obtained in the three preparations appear in Table 1. The cation radius for the dodecahedral eight-coordinate site in our charge-substituted garnet structures is derived from the average of the eight-coordinate crystal ionic radii for Ca^{2+}, Y^{3+} and Ln^{4+}, according to Shannon [12]. A predicted value for the lattice parameter is then based on interpolation of the standard values for the trivalent rare earth gallium garnets $Ln_3Ga_5O_{12}$[13]. For example, in the garnet phase $YCaCeGa_5O_{12}$, the calculated ionic radius for the eight-coordinate site is 1.173 Å, which is close to the crystal ionic radius of Tb^{3+} (eight-coordinate), 1.180 Å. We expect the compound $YCaCeGa_5O_{12}$ to have approximately the same cubic lattice parameter as that of the garnet $Tb_3Ga_5O_{12}$. Changes in the lattice parameter (Δa_0) representing the charge-substituted systems are given relative to the lattice parameter of the parent compound $Y_3Ga_5O_{12}$ ($a_0 = 12.277$ Å). Lattice parameter data for the charge-substituted garnets and the $Ln_3Ga_5O_{12}$ series are plotted in Fig. 1. Given the trend in lattice parameter with increasing Ln^{3+} ionic radius in the $Ln_3Ga_5O_{12}$ series, we expect a larger change in the lattice parameter of the charge-substituted compounds relative to $Y_3Ga_5O_{12}$ than we actually observe. However, the change appears to be consistently about half of the expected value, based on the lattice parameter of the appropriate $Ln_3Ga_5O_{12}$ garnet with the corresponding "A" site ionic radius, because only one of the "A" site cations is varying.

The samples exhibit a rather diverse crystal chemistry. For the Ce preparation, a two-phase mixture is formed which consists of the garnet phase along with CeO_2 as a minor phase. The Pr preparation likewise consists of a two-phase mixture, the major phase being the garnet, and the minor phase the tetragonal phase $CaPrGa_3O_7$, which is isostructural with melilite, $Ca_2MgSi_2O_7$ [14]. The approximate lattice parameters for $CaPrGa_3O_7$ ($a = 8.01$, $c = 5.21$) calculated from the powder data agree fairly well with what would be expected for this phase, in comparison with the slightly smaller sizes of Nd^{3+} and Sm^{3+} and the lattice parameters of the corresponding isostructural compounds $CaNdGa_3O_7$ and $CaSmGa_3O_7$ [15]. Unfortunately, it was not possible to index the melilite phase completely and obtain accurate lattice parameters using the X-ray data. This is due to the fact that many of the reflections were obscured by the more intense garnet peaks, and also because this class of compounds is rather poorly characterized in general. However, the melilite structure is closely related to that of garnet, having both dodecahedral (Ca) and tetrahedral (Mg, Si) coordination

TABLE 1. Physical properties of $YCaLnGa_5O_{12}$ preparations

	$YCaCeGa_5O_{12}$	$YCaPrGa_5O_{12}$	$YCaTbGa_5O_{12}$
Color, oxidized	Light green	Light brown	Dark tan
"A" site radius[a] (Å)	1.173	1.170	1.143
a_0, predicted (Å)	12.325	12.317	12.255
a_0, observed (Å)	12.298(3)	12.297(3)	12.267(3)
Δa_0, predicted[b] (Å)	+0.048	+0.040	−0.022
Δa_0, observed[c] (Å)	+0.021	+0.020	−0.010
a_0, reduced material (Å)	12.303(5)	12.301(4)	12.280(5)
Color, reduced	Yellow-green	Green	White

[a] See text. [b] $[a_0(\text{predicted}) - a_0(Y_3Ga_5O_{12})]$ where $a_0(Y_3Ga_5O_{12}) = 12.277$ Å. [c] $[a_0(\text{observed}) - a_0(Y_3Ga_5O_{12})]$.

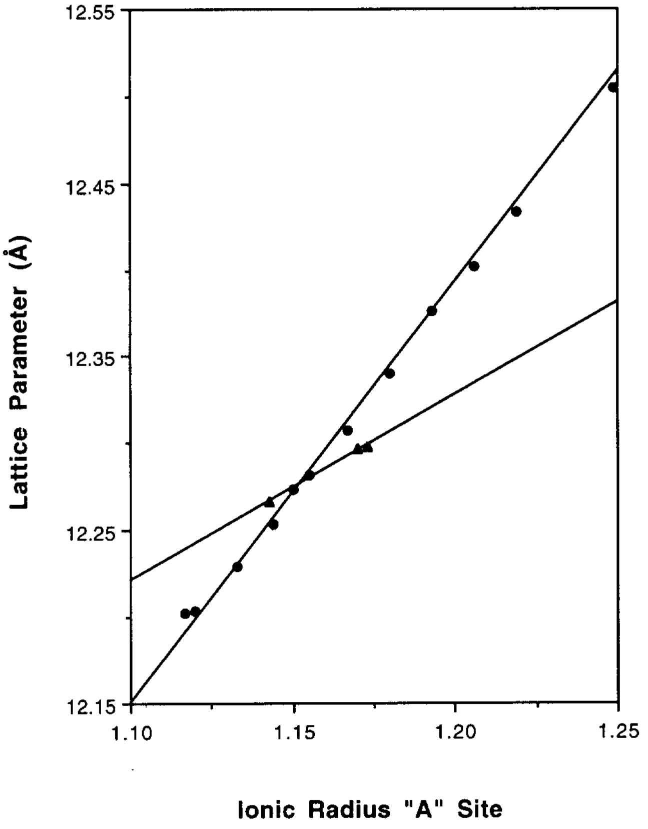

Fig. 1. Variation of cubic garnet lattice parameter with ionic size in "A" site. Circles, $Ln_3Ga_5O_{12}$ compounds; triangles, $YCaLnGa_5O_{12}$ systems as a function of average ionic radius in "A" site.

of cations. Unlike the Ce and Pr garnet samples, the Tb garnet sample is a single phase material.

X-Ray fluorescence data, presented in Table 2, show that the compositions of the samples are in the neighborhood of those expected based on the nominal chemical formulae of the expected garnet products, and also approximately the compositions of the starting reaction mixtures. Oxygen stoichiometry (and thus a determination of the oxidation state of the rare earth cation) in these systems cannot be accurately measured by TGA because the loss of oxygen is exceedingly slow.

TABLE 2. XRF data for garnet preparations (at.%)[a]

Ln	Y	Ca	Ln	Ga
Ce	3.8	5.4	4.1	27.0
Pr	5.0	5.0	3.9	26.2
Tb	5.9	6.1	4.2	24.2

[a] Calculated for $YCaLnGa_5O_{12}$: Y, Ca, Ln; 5.0%, Ga, 25.0%.

TABLE 3. Reduction temperatures[a] for Ln^{4+} in oxide lattices (°C)

Ln	LnO_{2-x}	$BaLnO_3$	$YCaLnGa_5O_{12}$
Ce	>1150	>1150	795
Pr	500	800	1040
Tb	440	570	1030

[a] Temperature at which reduction begins in 4% H_2/Ar.

Hence, no discrete transitions occur in the weight loss profile as a function of temperature, as the Ga^{3+} begins to be reduced concurrently with the rare earth.

Reduction temperatures for the samples are presented in Table 3, along with the relevant data for other tetravalent rare earth systems. The change in color upon reduction in all three samples is what we expect to see as the lanthanide cation goes from tetravalent to trivalent. A surprising result of the reduction experiments is that the tetravalent Ce appears to be less stable in the garnet lattice than in any of the other systems we have investigated, while the tetravalent Pr and Tb are much more stable than in the fluorite or perovskite lattices. The results for Pr and Tb are in accord with what we predict on the basis of our assumptions about the stability of the garnet lattice with respect to oxygen loss (reduction of $Ln^{4+}$to Ln^{3+}), although the increase in reduction temperature for the Tb^{4+} species is more dramatic than that for Pr^{4+}. X-Ray diffraction analysis of the products of the TGA experiments shows that the products of the reduction of the $YCaCeGa_5O_{12}/CeO_2$ mixture are: (1) a garnet phase which has a slightly increased lattice parameter; and (2) a melilite phase, presumably $CaCeGa_3O_7$ ($a = 7.923(8)$ Å, $c = 5.227(6)$ Å), with no CeO_2 remaining in the sample. The Pr preparation after reduction also shows a marginally increased lattice parameter for the garnet phase, and a noticeably increased amount of the melilite phase compared to the amount seen in the original diffraction pattern. Surprisingly, the Tb preparation after reduction shows only a garnet phase with a noticeably larger lattice parameter than that of the garnet before reduction.

With respect to thermal stability, we would initially conclude that the tetravalent Ce is unstable with respect to reduction in the Ga garnet framework because the dodecahedral site in the Ga garnet is optimal in size for smaller rare earths. This is implied by the fact that the Tb system does not phase separate under reducing conditions, but rather the Tb^{4+} is reduced to Tb^{3+}, and leads to a larger cubic lattice parameter, in keeping with the larger size of the trivalent cation as compared to the tetravalent cation. The dramatic increase in thermal stability (compared to TbO_2 or $BaTbO_3$) of Tb^{4+} upon charge substitution into the Ga garnet framework is then clearly tied to the stability of the garnet for smaller rare earths. This argument would also suggest that the Pr system should exhibit the same behavior as the Ce system, since both of these tetravalent cations are nearly identical in size. The same sort of phase separation takes place, as $CaPrGa_3O_7$ appears at the expense of the Pr garnet phase. However, the reduction temperature is much higher than that of the Ce system, indicating that tetravalent Pr is more stable than tetravalent Ce in the garnet lattice. The reduction (phase separation) temperature for the Ce system is most likely unusually low, rather than that for the Pr system being too high, because CeO_2 appears to be reacting with the garnet phase to generate the melilite phase and a reduced garnet, since the CeO_2 is consumed in the TGA reduction. This observation is indeed unusual since CeO_2 itself is reduced in H_2 only at temperatures in excess of 1200 °C. The driving force behind this reaction may be the stability of the melilite phase $CaCeGa_3O_7$. The temperature at which the phase separation takes place in the Ce system in this particular case is thus not an accurate indicator of the stability of the Ce^{4+} species in the garnet structure.

We are currently exploring other low temperature synthetic approaches which would eliminate the CeO_2 from the Ce garnet system. Neutron powder diffraction studies are also planned in order to more fully characterize the melilite-type phases present in these systems, and also to investigate the site occupancies of the three cations in the garnet framework as a function of temperature. Techniques such as EXAFS, which can probe the local environment about the cation sites in the structure, and XANES, which can identify the relative amounts of Ln^{3+} and Ln^{4+} present, will be useful in more fully characterizing the oxidation state and coordination environment of the rare earth species.

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