Lanthanide Titanates and $Ln_xBi_{4-x}Ti_3O_{12}$ Solid Solutions; their Raman Spectra

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Abstract

The formation of $Ln_xBi_{4-x}Ti_3O_{12}$ solid solutions, where x_{max} ranges from 0.08 for Lu to 2.92 for La, has been examined by Raman spectroscopy. A review of the literature concerning Ln_2O_3–$Ln_2Ti_2O_7$ solid solutions and Ln_2TiO_5 is presented and the Raman spectra of many of these phases are reported.

Introduction

The formation of substitutional solid solutions of lanthanide dititanates from heterotypic mixtures of lanthanide dititanates ($Ln_{2-x}\overset{*}{Ln}_xTi_2O_7$) and of bismuth-containing lanthanide dititanates ($Ln_{2-x}Bi_x$-Ti_2O_7), from mixtures of oxides have been studied earlier [1, 2]. A stability diagram was empirically constructed using as parameters the percent difference in ionic radii between lanthanide elements (or between lanthanide elements and bismuth) and the calculated volume of the unit cells. In the bismuth-containing lanthanide dititanate solid solutions the solubility of bismuth was found to increase as the ionic radius of the lanthanide element decreased. Wolfe and Newnham [3] found for another family of titanate solid solutions, $Ln_xBi_{4-x}Ti_3O_{12}$, that the solubility of rare earths in $Bi_4Ti_3O_{12}$ was also strongly dependent on the lanthanide element, with a maximum occurring for lanthanum and a minimum for lutetium. The structure of $Bi_4Ti_3O_{12}$ is described as orthorhombic by Aurivillius [4], as monoclinic by Cummins and Cross [5], and as monoclinic (*Pc*), but very nearly orthorhombic (*B2cb*) by Newnham *et al.* [6]. These authors agree that in all cases the compound consists of alternate layers of $Bi_2O_2^{2+}$ and perovskite-like layers of $Bi_2Ti_3O_{10}^{2-}$. Wolfe and Newnham [3] rationalize the solubility behavior of the lanthanide elements in $Bi_4Ti_3O_{12}$ on the basis of this model, suggesting that the larger lanthanide ions (La^{3+}–Gd^{3+}) have a strong preference for substitution in the perovskite-like layers, whereas the smaller lanthanide ions are too small to acquire the 12-fold coordination required in this layer.

In this work, we have examined the systems Ln_2O_3–TiO_2 and Ln_2O_3–Bi_2O_3–TiO_2 by Raman spectroscopy, for the purpose of determining the usefulness of this method for identifying the various phases occurring in these systems.

Available Information

Our intention of treating the Ln_2O_3–Bi_2O_3–TiO_2 system as a pseudobinary system ($Ln_4Ti_3O_{12}$–$Bi_4Ti_3O_{12}$) led us to review the existing data on Ln_2O_3–$Ln_2Ti_2O_7$ to ascertain whether or not species with stoichiometry $Ln_4Ti_3O_{12}$ exist for all the lanthanide elements.

A comprehensive review of lanthanide titanates was published by Shcherbakova *et al.*, in 1979 [7]. The authors review in some detail 6 phase diagrams known for TiO_2–Ln_2O_3 (where Ln = La, Gd, Y, Er, Tb, and Lu) and discuss the various phases reported. In addition a Tb_2O_3–TiO_2 phase diagram has been published by Shcherbakova *et al.* [8]. The region where solid solutions have been reported [8–18] is shown graphically in Fig. 1. The available data indicate that, in general, increasing the temperature expands the region of homogeneity of the cubic phase. Although it was impossible to represent all the data at the same temperature in Fig. 1, it is evident that the results of different authors do not agree. The data in Fig. 1 suggest that a decrease in the ionic radii of the lanthanide elements extends the range of homogeneity of the cubic (pyrochlore/fluorite) region toward higher Ln_2O_3 concentrations. Further clarification is needed as to the phase relationships in this region, since insufficient information is available to determine whether this region is truly homogeneous (with a gradual conversion from the pyrochlore to the fluorite structure with increasing lanthanide oxide content) or if the two cubic phases coexist in some region. A similar situation has been comprehensively reviewed and discussed for the systems Ln_2O_3–MO_2, Sc_2O_3–MO_2 (M = Hf, Zr) by Bevan and Summerville [19]. These authors use such examples to emphasize the uncertainty inherently involved in determining

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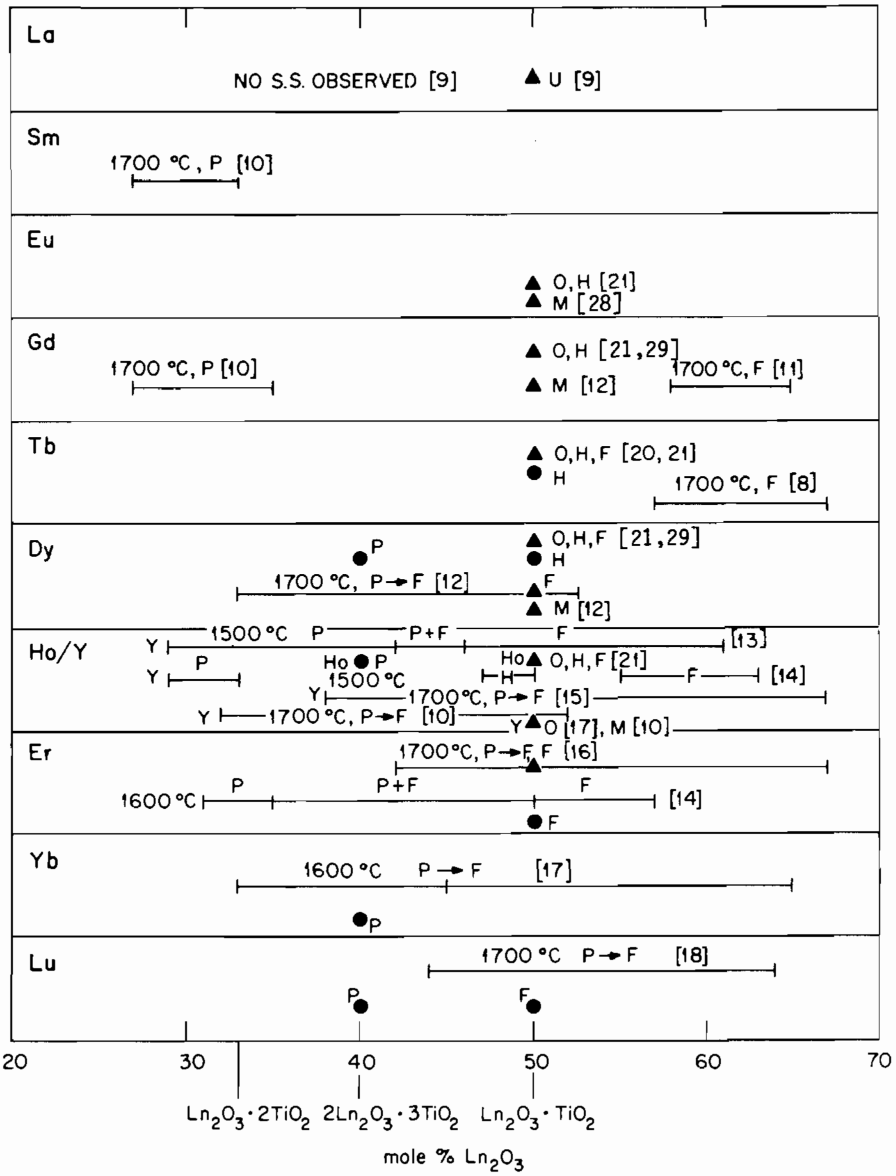

Fig. 1. Some of the compounds and phases reported in various $Ln_2O_3-TiO_2$ systems; U: structure unknown; P: pyrochlore; M: monoclinic; F: fluorite; O: orthorhombic, and H: hexagonal. Solid circles ●: this work; ▲: literature data. Numbers in brackets are text references.

equilibrium phase relationships in systems where regions of various degrees of heterogeneity may be present.

We reviewed the pertinent literature on monotitanates (Ln_2TiO_5) since by reaction with $Ln_2Ti_2O_7$, these compounds can be viewed as a source for the synthesis of $Ln_4Ti_3O_{12}$. The polymorphism of Ln_2TiO_5 compounds has been reviewed by Shcherbakova *et al.* [7], Sukhanova *et al.* [20] and Petrova *et al.* [21]. Shcherbakova *et al.* [7] list the cell parameters available at the time of their review for compounds with the monoclinic, orthorhombic and hexagonal structures (the monoclinic Y_2TiO_5 has been referenced incorrectly). The polymorphs quoted from the original references are represented in Fig. 1. The others authors [20] and [21], plot diagrams of regions of stability as a function of temperature and ionic radius of the lanthanide elements. Both diagrams show the existence of orthorhombic (low-temperature), hexagonal (high-temperature), and fluorite structures. The diagrams, essentially the same, differ slightly in the position and shape of the hexagonal-fluorite boundary.

Sukhanova *et al.* [20] and Petrova *et al.* [21] both describe the apparent similarity between the regions of stability of the polymorphs of the oxides Ln_2O_3

and those of the compounds Ln_2TiO_5. Sukhanova *et al.* [20] further indicate that the similarity extends to the phase behavior of lanthanide oxides and monotitanates formed under high (shock-wave) pressures and temperatures (*e.g.*, unstable phases, such as orthorhombic Yb_2TiO_5 can be synthesized under high pressures and low temperatures).

Experimental

The syntheses of solids with the compositions $Ln_2O_3 \cdot TiO_2$ and $2Ln_2O_3 \cdot 3TiO_2$ were accomplished by heating powdered mixtures of the oxides in platinum boats to 1700 °C in air for periods up to 35 h, followed by rapid cooling in air. Some of the preparations were quenched in water and were found to be identical to those cooled in air. All the preparations were examined by Raman spectroscopy and X-ray diffraction (XRD). The synthesis of $Ln_xBi_{4-x}Ti_3O_{12}$ solid solutions was done similarly but at temperatures below 1200 °C. The samples were ground and reheated repeatedly until their Raman spectra remained unchanged. Raman spectra were excited with the 514.5 or 488.0 nm line from a CW argon-ion laser. Spectra were observed with a Ramanor HG-2S spectrophotometer (Instruments SA) as previously described [22].

Results and Discussion

The Raman spectra of lanthanide dititanates ($Ln_2Ti_2O_7$) have been discussed by a number of authors [23]. Spectra of monoclinic dititanates containing the elements La to Nd have many Raman peaks while the remaining lanthanide elements show simpler Raman spectra characteristic of the cubic pyrochlore structure.

The Raman spectra of mixtures of Ln_2TiO_5 of fluorite or hexagonal structure with $Ln_2Ti_2O_7$ compounds showed only the presence of the latter, very likely due to its significantly stronger Raman activity. This was confirmed by the spectrum of the pure phases Dy_2TiO_5 (hexagonal structure) (Fig. 2b), and $Dy_2Ti_2O_7$ (pyrochlore structure) (Fig. 2a), and of their synthetic equimolar mixture (Fig. 2c) which only shows the $Dy_2Ti_2O_7$ spectrum. Orthorhombic Gd_2TiO_5 can, however, be identified by Raman spectroscopy in the presence of $Gd_2Ti_2O_7$. This was demonstrated by heating a mixture of $2Gd_2O_3$–$3TiO_2$ to 1080 °C. The product was found by X-ray diffraction (XRD) to contain orthorhombic Gd_2TiO_5 and $Gd_2Ti_2O_7$. A comparison of the Raman spectrum of this mixture (Fig. 3a) with those of $Gd_2Ti_2O_7$ (Fig. 3b) and orthorhombic Nd_2TiO_5 reported by [24] identified the presence of orthorhombic Gd_2TiO_5.

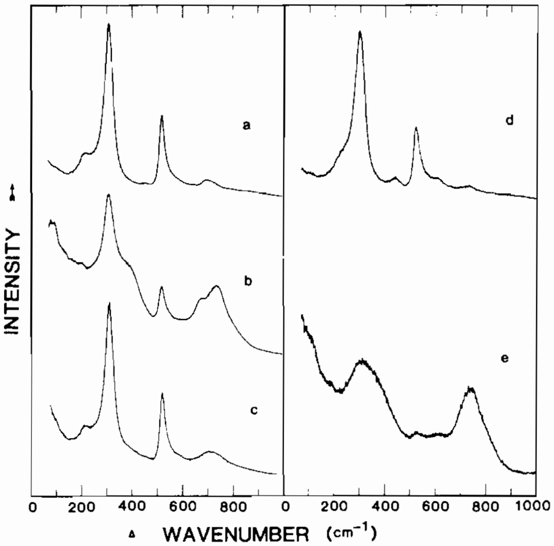

Fig. 2. Raman spectra excited with 514.5 nm radiation, of: (a) pyrochlore $Dy_2Ti_2O_7$; (b) hexagonal Dy_2TiO_5 obtained by heating to 1600 °C Dy_2O_3 + TiO_2; (c) mechanical mixture of equimolar amounts of (a) and (b); (d) pyrochlore $Yb_2Ti_2O_7$ and (e) fluorite Yb_2TiO_5, obtained by heating to 1700 °C a mixture of Yb_2O_3 + TiO_2.

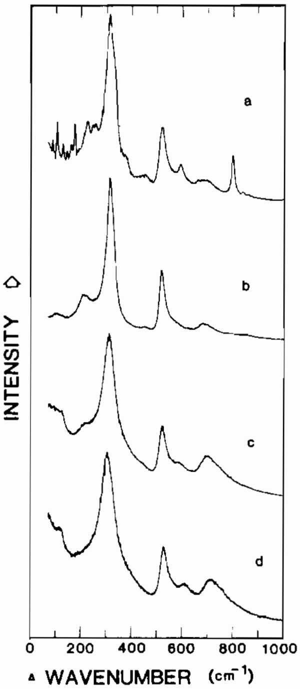

Fig. 3. Raman spectra excited with 514.5 nm radiation (except 488 nm for 3a and 3b) of: (a) a mixture of 'pyrochlore' $Gd_2Ti_2O_7$ and orthorhombic Gd_2TiO_5 obtained by heating to 1080 °C a mixture of $2Gd_2O_3$ + $3TiO_2$; (b) 'pyrochlore' $Gd_2Ti_2O_7$; (c) solid solution with stoichiometry $Dy_4Ti_3O_{12}$ and pyrochlore structure, obtained by heating to 1700 °C a mixture $2Dy_2O_3$ + $3TiO_2$, and (d) similar to (c) but $Yb_4Ti_3O_{12}$.

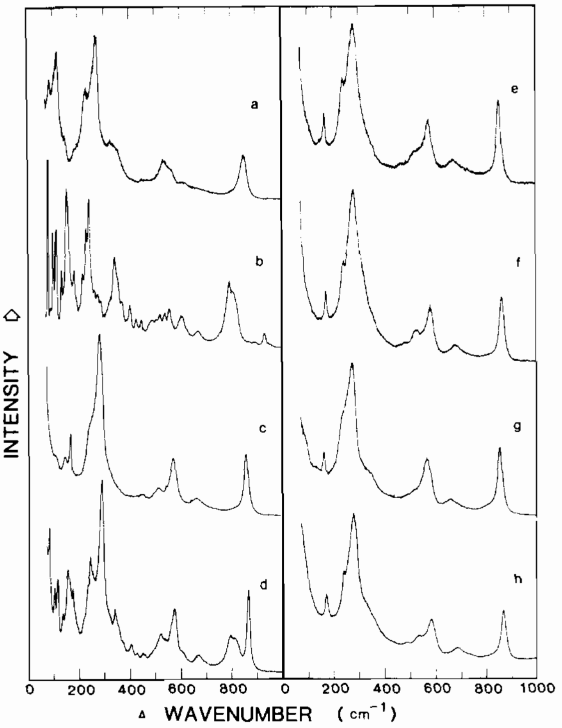

Fig. 4. Raman spectra excited with 514.5 nm radiation of: (a) 'orthorhombic' $Bi_4Ti_3O_{12}$; (b) monclinic $La_2Ti_2O_7$; (c) $La_2Bi_2Ti_3O_{12}$; (d) mixture of $La_{2.8}Bi_{1.2}Ti_3O_{12}$, unobserved La_2TiO_5, and $La_2Ti_2O_7$; (e) $Nd_2Bi_2Ti_3O_{12}$; (f) $Eu_2Bi_2Ti_3O_{12}$; (g) $Sm_{1.2}Bi_{2.8}Ti_3O_{12}$, and (h) $Gd_{1.6}Bi_{2.4}Ti_3O_{12}$. All the preparations were obtained by heating the corresponding mixtures of Ln_2O_3, Bi_2O_3, and TiO_2 between 1110° and 1170 °C.

The Raman spectra of the solid solutions Ln_2O_3–$Ln_2Ti_2O_7$ (Figs. 3c, 3d) with pyrochlore structure and composition corresponding to $Ln_4Ti_3O_{12}$ (where Ln = Dy and Yb) are similar to spectra of the pyrochlore type $Ln_2Ti_2O_7$ (Fig. 3b). In Fig. 4 the Raman spectra of $Bi_4Ti_3O_{12}$ (Fig. 4a) and monoclinic $La_2Ti_2O_7$ (Fig. 4b) and of various solid solutions $Ln_xBi_{4-x}Ti_3O_{12}$ (where Ln = La to Gd) which we identified as pure phases by XRD, (Figs. 4c, e, f, g, and h) are shown. The spectrum of a mixture of $La_{2.8}Bi_{1.2}Ti_3O_{12}$ with monoclinic $La_2Ti_2O_7$ and La_2TiO_5, the latter unobserved by Raman spectroscopy is shown in Fig. 4d. It should be pointed out, however, that we were not able in all cases to detect by Raman spectroscopy minor phases determined to be present by XRD in addition to the major phase $Ln_xBi_{4-x}Ti_3O_{12}$.

Attempts to correlate the unit cell volumes of $Ln_xBi_{4-x}Ti_3O_{12}$ determined by Wolfe and Newnham [3] with those obtained by means of empirical calculation in which Zen's equation [25] was applied to a pseudobinary system $Ln_4Ti_3O_{12}$–$Bi_4Ti_3O_{12}$ were not possible due to lack of sufficient data. The only unit cell volume available in addition to that of $Bi_4Ti_3O_{12}$ [3] was that for a composition $Dy_4Ti_3O_{12}$, of cubic structure reported by Queyroux [12]. These values gave unsatisfactory results in which the calculated unit cell volumes of solid solutions far exceeded the measured values. Hence, we plotted the empirical parameters δ and IR_{mean} of the phases obtained in the system Ln_2O_3–Bi_2O_3–TiO_2 to construct a stability diagram, shown in Fig. 5. δ is the percent difference of ionic radii between bismuth and the lanthanide element, $(100(IR_{Bi}-IR_{Ln})/IR_{Ln})$, and IR_{mean} is the average ionic radius of the cations in solid solution, weighed according to their composition. The ionic radii were estimated for coordination number (CN) = 12 by extrapolation of ionic radii reported for smaller coordination numbers [26]. A maximum lanthanide concentration in solid solution, $X_{Ln(max.)} = n_{Ln}/(n_{Ln} + n_{Bi})$ can be calculated from the boundaries in Fig. 5, which when plotted versus δ yields a useful function for interpolation of solubility data for other ions (Fig. 6). Because of our interest in actinide chemistry, we estimated the solubility of Am^{3+} and Pu^{3+} in solid solutions containing bismuth. Using ionic radii for Am^{3+} (1.255 Å) and Pu^{3+} (1.286 Å) with CN = 12 obtained by a linear extrapolation of ionic radius (IR) *vs.* CN and interpolating the corresponding values of δ in Fig. 6, we estimate that solid solutions of the type $An_xBi_{4-x}Ti_3O_{12}$, where An = actinide element, could exist containing up to about 56 and 62 atom % of, respectively Am^{3+} and Pu^{3+}. If, however, one uses the value of 1.38 Å for

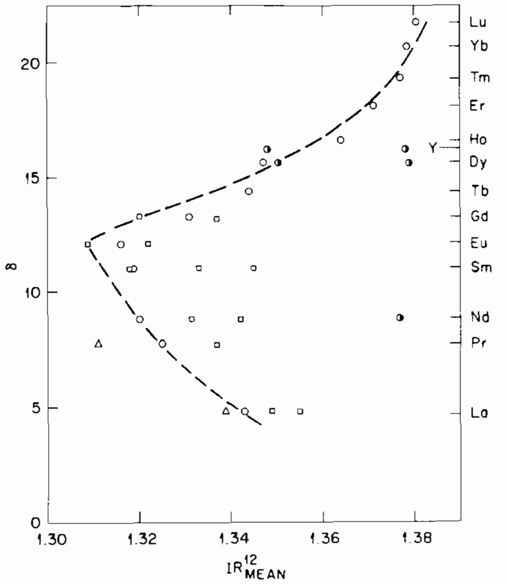

Fig. 5. Stability diagram for solid solutions $Ln_xBi_{4-x}Ti_3O_{12}$ as a function of $\delta = 100\ (IR_{Bi}-IR_{Ln})/IR_{Ln}$ and IR_{mean} the mean ionic radii of cations. ◑ orthorhombic symmetry, measured by [3]; ○ orthorhombic symmetry, calculated from [3]; □ orthorhombic symmetry, calculated, this work; △ restricted miscibility, this work.

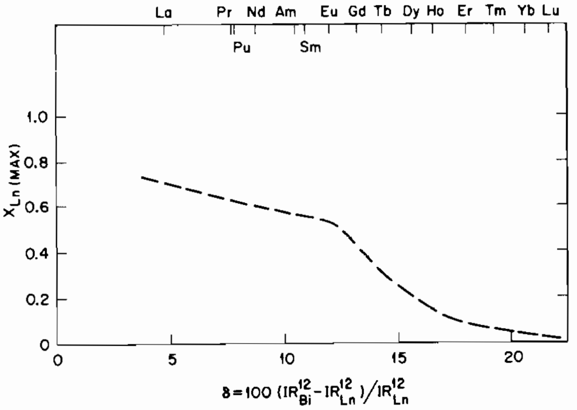

Fig. 6. Solubility of lanthanide elements, $X_{Ln} = n_{Ln}/(n_{Ln} + n_{Bi})$ in $Bi_4Ti_3O_{12}$ as a function of δ. The data was taken from the boundaries drawn in Fig. 5.

the ionic radius of Pu^{3+} with CN = 12, calculated by Russell *et al.* [27], then a prediction for the solubility of Pu^{3+} in $Bi_4Ti_3O_{12}$ results in a value larger than 70%.

Conclusions

Raman spectroscopy of the compounds and solid solutions studied revealed that while pure phases of Ln_2TiO_5 are easily distinguishable from others such as $Ln_2Ti_2O_7$, their mixtures are less easily identified. The spectra of solid solutions Ln_2O_3–$Ln_2Ti_2O_7$ with compositions near $Ln_4Ti_3O_{12}$ are also too similar to those of $Ln_2Ti_2O_7$ for proper identification. Raman spectra of solid solutions $Ln_xBi_{4-x}Ti_3O_{12}$ resemble that of the stable 'parent' compound $Bi_4Ti_3O_{12}$. Only small shifts in the frequencies of the peaks have been observed among solid solutions with compositions very near $Ln_2Bi_2Ti_3O_{12}$ where Ln = La to Sm. The preparation of $Ln_xBi_{4-x}Ti_3O_{12}$ solid solutions was found to agree well with the solubilities of lanthanide elements in $Bi_4Ti_3O_{12}$ established by Wolfe and Newnham [3]. A representation of the solubility data as a function of the percent difference in ionic radii between bismuth and lanthanide elements (rather than atomic number) allows for the prediction of the solubility in $Bi_4Ti_3O_{12}$ of other tervalent ions such as Pu^{3+} and Am^{3+}.

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