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Substitutional Solid Solutions of Bismuth-Containing Lanthanide Dititanates, $Ln_{2-x}Bi_xTi_2O_7$*

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The formation of solid solutions $Ln_{2-x}Bi_xTi_2O_7$, where Ln = La to Lu and Y, except Ce, Pm, and Eu, has been studied by Raman spectroscopy and to a lesser extent by X-ray diffraction. It has been established that the solubility of bismuth increases with decreasing ionic radius of the lanthanide element. No evidence was experimentally found in this work for the existence of $Bi_2Ti_2O_7$. © 1985 Academic Press, Inc.

Introduction

Heterotypic lanthanide dititanates form substitutional solid solutions ($Ln_{2-x}\overset{*}{Ln}_xTi_2O_7$) in which the mutual solubility of the compounds with different structures (monoclinic for the larger lanthanides and cubic pyrochlore for the smaller lanthanides) can be correlated with an empirical parameter derived from the ionic radii of the lanthanide ions (*1*). In order to test that correlation further, it was deemed of interest to study the effect of replacing one of the lanthanide ions by another tervalent metal ion of comparable ionic radius, and bismuth was used as a suitable replacement. A set of solid solutions of $Y_{2-x}Bi_xT_2O_7$ has been prepared and analyzed by Knop *et al.* (*2*); they found that the solid solutions are cubic and that their lattice parameters increase linearly with bismuth content. An attempt to fit the data from (*2*) for $Y_{2-x}Bi_xTi_2O_7$ into the stability diagram developed in (*1*) for $Ln_{2-x}\overset{*}{Ln}_xTi_2O_7$ did not give satisfactory results. The position of the unit cell volumes of the cubic Bi-containing compounds extended from the cubic region far into the restricted miscibility region. Since the ionic radii of Bi^{3+} (1.13 or 1.17 Å) and of La^{3+} (1.16 Å) (*3*) are very similar, we suspected that the difference in electronic structure of these ions, $5d^{10}6s^2$ and $5s^25p^6 4f^0$ respectively, may have a stronger effect on the solid solution formation than initially considered. This merited further exploration and was studied by means of the synthesis and analysis of mixed bismuth, lanthanide dititanates of most of the lanthanide elements. An interesting problem that arose initially in this study was concerned with the existence of $Bi_2Ti_2O_7$, which we had planned to mix with $Ln_2Ti_2O_7$ (Ln = lan-

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thanide element) for the preparation of some of the solid solutions. Although the existence of $Bi_2Ti_2O_7$ has been reported (*4*, *5*) subsequent hydrothermal synthesis of bismuth titanates (*6*) did not confirm its existence. It is interesting to note that in (*5*) single crystals of $Bi_4Ti_3O_{12}$ and $Bi_2Ti_4O_{11}$ were obtained from melts containing TiO_2, Bi_2O_3, and V_2O_5, while $Bi_2Ti_2O_7$ could only be obtained from similar melts to which 10 mol% ZnO had been added. This $Bi_2Ti_2O_7$ was identified by X-ray diffraction as face-centered cubic with $a_0 = 20.68$ Å.

We first reexamined the existence of some bismuth titanates and then investigated the formation of $Ln_{2-x}Bi_xTi_2O_7$ solid solutions. Raman spectroscopy and X-ray diffraction were used for identification of the compounds and their mixtures; the former because we had found it to be very sensitive to the different dititanate structures (*1*) and because it is a very rapid technique.

Experimental

(*a*) *Bismuth Titanates*

Examination by Raman spectroscopy and X-ray diffractometry of solids resulting from heating, up to 1175°C, mixtures of $Bi_2O_3:TiO_2$ (1 : 1, 2 : 3, 1 : 2, 1 : 3, and 1 : 4) indicated the formation of $Bi_4Ti_3O_{12}$ (2 : 3) and $Bi_2Ti_4O_{11}$ (1 : 4) as pure phases, while mixtures of these two compounds were found when other initial proportions (1 : 1, 1 : 2) were used. No evidence was found for the formation of $Bi_2Ti_2O_7$ under our preparative conditions. Raman spectra of the pure compounds 2 : 3 and 1 : 4, together with that of a mixture of both resulting from the reaction

$$Bi_2O_3 + 2TiO_2 \rightarrow 0.2Bi_2Ti_4O_{11} + 0.4Bi_4Ti_3O_{12}, \quad (1)$$

are shown in Fig. 1.

(*b*) *General*

Because we had established (above) that $Bi_2Ti_2O_7$ did not form under our experimental conditions while $Y_{2-x}Bi_xTi_2O_7$ solid solutions do (*2*), our preparations of solid solutions $Ln_{2-x}Bi_xTi_2O_7$ were made using the corresponding oxides as starting materials. The oxides (Bi_2O_3: Baker 99.8%, TiO_2: "certified" Fisher Scientific Co., and Ln_2O_3: 99+% from several suppliers) were thoroughly mixed by grinding, and the powders were placed in covered platinum containers and fired in air at various temperatures up to 1200°C for periods of 17 hr. The products were ground, examined by Raman spectroscopy and reheated; this operation was repeated until the Raman spectra did not change. The weights of the preparations

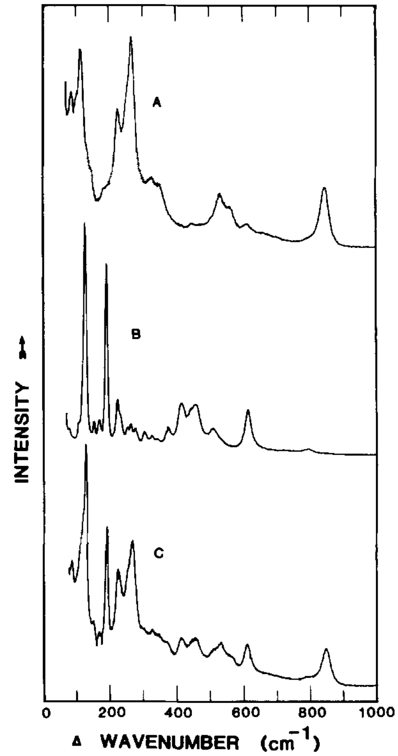

Fig. 1. Raman spectra of (A) $Bi_4Ti_3O_{12}$ and (B) $Bi_2Ti_4O_{11}$ excited with 488 nm light and (C) mixture of $Bi_4Ti_3O_{12}$ and $Bi_2Ti_4O_{11}$ resulting from the reaction of Bi_2O_3 and TiO_2 (1 : 2) at 1085°C excited with 514.5 nm light.

were recorded and the stoichiometries of the resulting solid solutions were inferred assuming that the weight losses were due to volatilization of Bi_2O_3. The Raman spectra were obtained on a Ramanor HG-2S spectrometer with either 488.0 or 514.5 nm excitation from an argon-ion laser. The instrumentation used has been described elsewhere (*7*). X-Ray diffraction data were recorded using Cu$K\alpha$ radiation and either Debye–Scherrer cameras or a diffractometer described previously (*1*).

Results and Discussion

Because the ionic radius of Bi^{3+} and of the lighter lanthanides are quite similar and there are known compounds in which such ions behave similarly (e.g., the formation of orthophosphates with analogous crystal structures and similar lattice parameters (*8*) we expected $Bi_2Ti_2O_7$ to form and strongly resemble the light lanthanide dititanates. Under our experimental conditions this did not occur, but we were able to prepare many solid solutions of the type $Ln_{2-x}Bi_xTi_2O_7$. Based on their identification by Raman spectroscopy and X-ray diffractometry, the preparations were designated cubic (C), monoclinic (M), and of restricted miscibility (R), where the latter refers to mixtures of $Ln_2Ti_2O_7$ with $Bi_4Ti_3O_{12}$ and $Bi_2Ti_4O_{11}$. The Raman spectra of the cubic and monoclinic phases were similar to those of dititanates containing only lanthanide elements (*1*). Measured lattice parameters of cubic phases were used to determine the volumes of unit cells (V_m), of the solid solutions. Additionally, the volume of a hypothetical unit cell (V_{Bi}) of cubic $Bi_2Ti_2O_7$ was obtained by extrapolation from linear plots of V_m vs the cationic fraction of bismuth, $X_{Bi} = [n_{Bi}/(n_{Bi} + n_{Ln})]$. Using the volumes of pure lanthanide dititanates (V_{Ln}) obtained from reported lattice parameters (*2*) at $X_{Bi} = 0$ the lines converge to $X_{Bi} = 1$ giving $V_{Bi} = 1110 \pm 2.5$ Å^3. This value of V_{Bi} agrees with that of 1106 Å^3 which is one-eighth of the volume calculated from (*5*). The value of V_{Bi} together with unit-cell volumes of the lan-

TABLE I

SELECTED SOLUBILITY VALUES FOR BISMUTH IN $Ln_2Ti_2O_7$

Lanthanide element	X_{Ln}[a] Initial	Final	Temperature (°C)	Duration (hr)	Phase observed[b]	δ[c]	V_c[d] (Å^3)	V_m[e] (Å^3)	V_{sat}[f] (Å^3)	$X_{Bi(sat.)}$[a]
Lu	0.80	0.82	1170	36	C	19.75	1024.7	1028.5		
	0.70	0.73	1170	36	C		1034.1	1033.3		
	0.25	0.26	1125	57	C		1083.1	1084.5		
									1087.0	0.78
Tm	0.50	0.55	1133	18	C	17.71	1058.4	1061.2		
	0.25	0.27	1125	57	C		1084.8	1085.1		
									1086.0	0.74
Tb	0.75	0.76	1170	37	C	12.50	1061.6	1061.2		
	0.49	0.50	1140	30	C		1078.3	1080.0		
	0.25	0.26	1170	37	R		1093.6	1091.1		
									1082.0	0.56
Sm	0.63	0.72	1170	42	C	8.43	1081.1	1081.9		
	0.50	0.52	1140	30	R		1089.2	1084.5		
									1081.9	0.28

[a] X_i: atom fraction (cations).

[b] C: cubic, R: restricted miscibility (polyphasic).

[c] $\delta = 100(IR_{Bi} - IR_{Ln})/IR_{Ln}$; coordination number = 8 used for IRs from (*3*).

[d] $V_c = X_{Bi}(V_{Bi} - V_{Ln}) + V_{Ln}$; V_{Bi} estimated to be ≈ 1110 ± 2.5(Å)^3 and V_{Ln} calculated from data in (*2*).

[e] Calculated from measured lattice parameters which had an uncertainty of ±0.0003 Å.

[f] Calculated from boundary in Fig. 2.

thanide dititanates (V_{Ln}) was used to estimate the unit-cell volumes of solid solutions. Representative measured (V_m) and calculated volumes (V_c) of cubic unit cells of solid solutions are listed in Table I; the satisfactory agreement obtained gave us confidence in the estimated volumes of those solid solutions whose lattice parameters were not measured. The data obtained are represented in the form of a stability diagram shown in Fig. 2, as a function of the arbitrary parameters $\delta = 100(\mathrm{IR_{Bi}} - \mathrm{IR}_{Ln})/\mathrm{IR}_{Ln}$, and V (V_m or V_c). The ionic radii, IR, were taken from Shannon's tabulation for coordination number 8 (*3*). We have used the value of 1.17 Å for Bi^{3+}, which corresponds to an ion in which the character of its lone pair electrons is dominant, instead of 1.13 Å where this character is constrained and more in line with Shannon's estimate of the ionic radius in a pyrochlore structure (*3*), for cosmetic reasons, i.e., to avoid obtaining negative values of δ for the La–Bi and Pr–Bi pairs. Use of the latter value would have little effect on the shape of the curve in Fig. 2, but would shift all points to lower values of δ. We have elected not to show in Fig. 2 any of the solid solutions containing La, Pr, and Nd which appeared to be single-phase monoclinic because their bismuth content ($X_{Bi} \leq 0.07$) was too low to be ascertained with confidence by Raman spectroscopy or X-ray diffraction. The boundary for solid solutions containing the elements La to Nd is shown as a dashed line to reflect larger uncertainties; this portion of the line was drawn using the volumes of $La_2Ti_2O_7$ and $Pr_2Ti_2O_7$ as limiting values for the volumes of their respective bismuth-containing solid solutions. The data in Fig. 2 indicate that there is a limiting mean size for the cations, corresponding to a cell volume of ~1085 Å^3, above which pyrochlore formation does not occur. This can be better visualized in Fig. 3 where the solubility of bismuth, as $X_{Bi(sat)}$, in $Ln_{2-x}Bi_xTi_2O_7$ solid solutions is shown as a function of δ. The values of $X_{Bi(sat)}$ were calculated from the values of

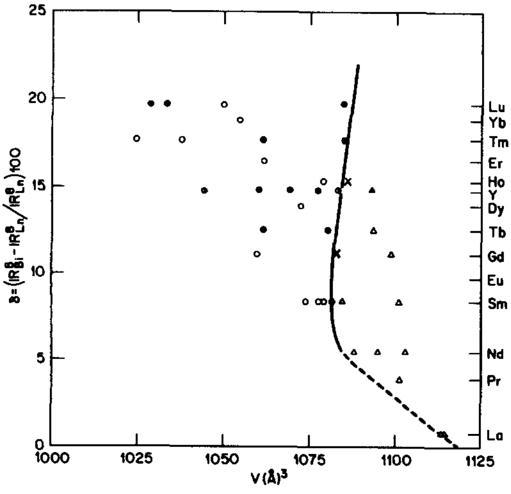

FIG. 2. Stability diagram of substitutional solid solutions $Ln_{2-x}Bi_xTi_2O_7$. δ is the percentage difference in ionic radii of Bi and Ln with CN = 8 and V the unit-cell volume; ● and ○: cubic phase, respectively, measured and calculated; X and △: restricted miscibility, respectively, measured and calculated; ◑ and ▲: data from Knop *et al.* (*2*), respectively cubic phase and restricted miscibility.

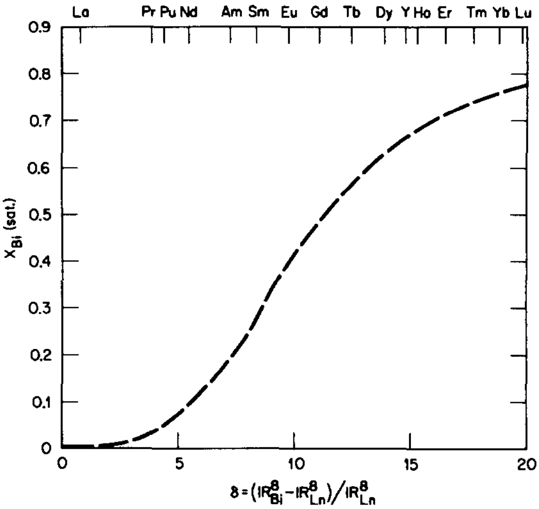

FIG. 3. Solubility of bismuth as X_{Bi}, bismuth cationic atom fraction, in various $Ln_2Ti_2O_7$ at ≤1175°C as a function of δ, the percentage difference in atomic radii of the cations.

the volumes of solid solutions on the boundary drawn in Fig. 2 between the monophasic cubic and polyphasic regions by means of the equation $[X_{\mathrm{Bi}} = (V_{\mathrm{c}} - V_{Ln})/(V_{\mathrm{Bi}} - V_{Ln})]$ (*9*).

Our interest in actinide chemistry leads us to draw on the analogy between lanthanides and trivalent actinides for predicting the extent of formation of solid solutions of the type $An_{2-x}\mathrm{Bi}_x\mathrm{Ti}_2\mathrm{O}_7$, where *An* is a trivalent actinide element. Using Shannon's value of 1.09 Å for the ionic radius of Am^{3+} (*3*) and a value extrapolated by us for Pu^{3+} of 1.12 Å (both with coordination number 8) to calculate values of δ and interpolating them in Fig. 3, we conclude that if cubic solid solutions of titanates containing Bi and Pu or Am form, they would contain less than 20 at.% bismuth.

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