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Synthesis and Characterization of Substitutional Solid Solutions $a\mathrm{Ln_2O_3} \cdot (1 - a)\mathrm{Bi_2O_3} \cdot 4\mathrm{TiO_2}$*

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The solubility of 10 lanthanide elements and of scandium is solid $Bi_2Ti_4O_{11}$ has been determined using Raman spectroscopy and X-ray diffraction. The data obtained were used to construct a diagram of solubility as a function of the ionic radii of bismuth and the lanthanide elements. The thermal stability of the solid solutions as a function of temperature and duration of thermal treatment has been qualitatively established.

Introduction

The study of substitutional solid solutions of titanates containing pairs of lanthanide elements or of a lanthanide element and bismuth is of general interest because knowledge is lacking about what effect the sizes of the substituting cations have on the formation of solid solutions. In earlier work, we have examined the formation of solid solutions with compositions $Ln_{2-x}\overset{*}{Ln}_x Ti_2O_7$(1), $Ln_{2-x}Bi_xTi_2O_7$(2), $Ln_xBi_{4-x}Ti_3O_{12}$(3), and $Ln_{2-x}\overset{*}{Ln}_xTi_yO_{2y+3}$(4). It was found that, using parameters based on the ionic radii of both cations, the data in each system could be correlated and stability fields defined which indicated solubility limits and, where appropriate, solid solution polymorphs. In extending our earlier work we have elected to study solid solutions formed by partial substitution of the bismuth in $Bi_2Ti_4O_{11}$ by lanthanide elements.

Experimental

The methods of preparation and instrumentation used has been described in detail previously (*1–4*). In summary, the synthesis of the solid species were accomplished by heating, at temperatures up to 1100°C, intimate mixtures of the powdered oxides Ln_2O_3 (Ln = lanthanide element), Bi_2O_3, and TiO_2 contained in platinum boats in air. The rutile TiO_2 used was obtained by heating anatase TiO_2 from Fisher ("certified") in air for 1 hr at 1000°C in a covered platinum dish. Lanthanide oxides and scandium oxide of 99+% purity were obtained from various suppliers. The weight losses of the preparations after each thermal treatment were monitored to detect and reject, if necessary, any preparation in which substantial vaporization of Bi_2O_3 may have oc-

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curred. This was not necessary, however, since the losses were found to be 1 wt% or less.

Raman spectra were obtained from powdered samples sealed in ~2 mm o.d. glass "melting point" tubes. A Ramanor HG-2S spectrometer (Instruments S.A.) equipped with photon counting electronics and a signal averaging system (described previously (*5*)) was used to record the spectra. All the spectra were excited with the 514.5-nm line of an argon-ion laser (except those of Er-containing compounds which were excited with 488.0 nm) at power levels of ~50 mW. X-ray diffraction data were recorded with 11.4-cm-diam. Debye-Scherrer cameras using Cu$K\alpha$ radiation.

Results and Discussion

Exploratory Experiments

Because it had been reported that $\mathrm{TiO_2}$ does not appear to dissolve in $\mathrm{Bi_2Ti_4O_{11}}$ (*6*) and because we had established that in solid solutions $\mathrm{Ln}_{2-x}\overset{*}{\mathrm{Ln}}_x\mathrm{Ti}_y\mathrm{O}_{2y+3}$ the value of y is very likely 4.33 with an upper limit near 4.50 (*4*), initial attempts to synthesize the solid solutions $\mathrm{Ln}_{2-x}\mathrm{Bi}_x\mathrm{Ti}_z\mathrm{O}_{2z+3}$ were made with values of z ranging from 4 to 4.36. It was soon found, however, that preparations with $z > 4.10$ yielded products that contained unreacted $\mathrm{TiO_2}$.

The Raman spectra of preparations previously heated to temperatures in the range 1000–1200°C indicated that above 1000°C decomposition of the solid solutions with formation of rutile ($\mathrm{TiO_2}$) and other products had occurred. Thus, it was decided to attempt the preparations starting at 850°C. The Raman spectra and the X-ray diffraction (XRD) powder diagrams of many of the preparations at 900°C resembled sufficiently that of $\mathrm{Bi_2Ti_4O_{11}}$ to warrant their preliminary identification as solid solutions. Examples of the Raman spectra are shown in Figs. 1a–c. Identification by Raman spectroscopy could be accomplished much quicker than by XRD and in consequence we relied more on the former method. To establish limits for the sensitivity of Raman spectroscopy, we prepared, by grinding together, several mixtures of either $\mathrm{Bi_2Ti_4O_{11}}$ or preparations identified earlier by XRD to be monophasic solid solutions with one of the following: anatase, rutile, bismuth sesquioxide, several lanthanide oxides, lanthanide dititanates ($\mathrm{Ln_2Ti_2O_7}$), or solid solutions of the type $\mathrm{Ln}_x\mathrm{Bi}_{4-x}\mathrm{Ti_3O_{12}}$. It was observed that the $\mathrm{Ln}_x\mathrm{Bi}_{2-x}\mathrm{Ti_4O_{11}}$ solid solutions exhibit such a markedly larger scattering cross section compared to those of the oxides of bismuth and of lanthanide elements, that the spectra of the oxides could not be seen in mixtures which contained less than 11 wt% $\mathrm{Bi_2O_3}$ or $\mathrm{Ln_2O_3}$. $\mathrm{TiO_2}$ in the anatase form could be clearly seen at a concentration of ~3 wt% (Fig. 1d). The two most intense Raman peaks of rutile (445 and 610 $\mathrm{cm^{-1}}$) overlap with minor peaks of $\mathrm{Bi_2Ti_4O_{11}}$ or its solid solutions, so that the presence of rutile could not be directly established. However, the presence of rutile could be approximately determined from the ratio I_{127}/I_{610}, the ratio of intensity of the strongest Raman peak of the solid solutions (127 $\mathrm{cm^{-1}}$) to that of the peak at 610 $\mathrm{cm^{-1}}$; in $\mathrm{Bi_2Ti_4O_{11}}$ this ratio had a value which ranged from 4.9 and 5.6. Because of our inability to detect unreacted bismuth and lanthanide oxides by Raman spectroscopy, detecting the presence of unreacted anatase and rutile by their Raman peaks was important for determining if saturation of the $\mathrm{Ti_4O_{11}^{6-}}$ solid solutions by the lanthanide ion had occurred. We speculated that the excess of lanthanide oxide over saturation could form other phases such as $\mathrm{Ti_2O_7^{6-}}$ or $\mathrm{Ti_3O_{12}^{12-}}$, and that the lanthanide oxide would probably remain unreacted at the lower temperatures (~850°C). This in turn would leave unreacted $\mathrm{TiO_2}$. A test of our ability to identify the structure of $\mathrm{TiO_2}$ was also required because most our our prepa-

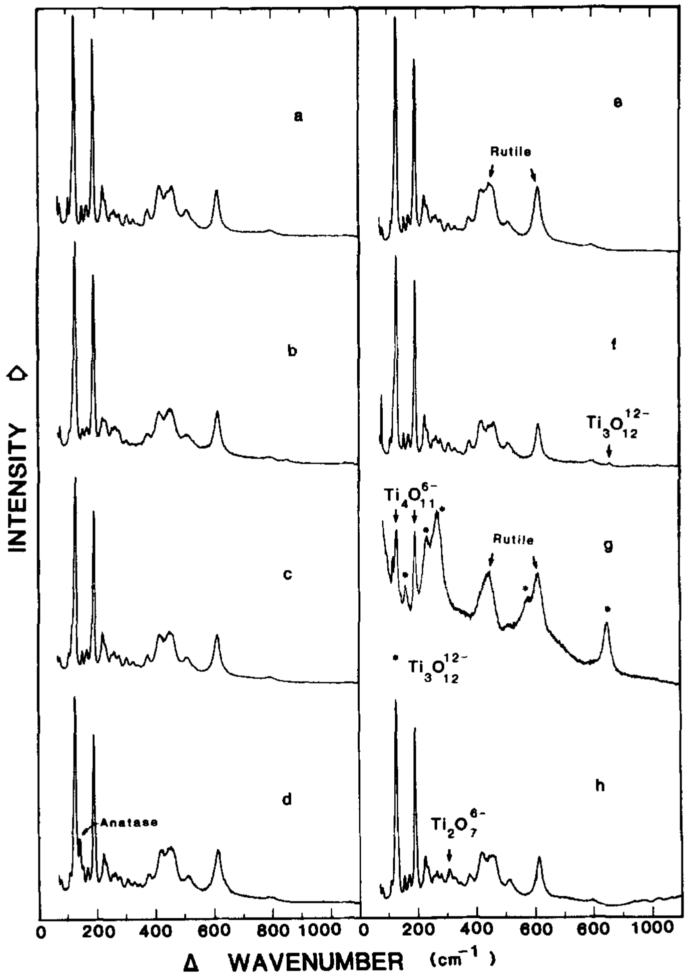

FIG. 1. Raman spectra, obtained with 514.5-nm excitation, of (a) $Bi_2Ti_4O_{11}$; (b) $Pr_{0.22}Bi_{1.78}Ti_4O_{11}$; (c) $Lu_{0.40}Bi_{1.60}Ti_4O_{11}$; (d) $Lu_{0.40}Bi_{1.60}Ti_4O_{11}$ mixed mechanically with 3.4 wt% anatase; (e) $Lu_{0.40}Bi_{1.60}Ti_4O_{11}$ mixed mechanically with 3.4 wt% anatase; (e) $Lu_{0.40}Bi_{1.60}Ti_4O_{11}$ mixed mechanically with 9.8 wt% rutile; (f) $Nd_{0.20}Bi_{1.80}Ti_4O_{11}$ mixed mechanically with 11 wt.% $Nd_{1.6}Bi_{2.4}Ti_3O_{12}$; (g) mixture estimated to be composed of 0.6 $Nd_{0.20}Bi_{1.80}Ti_4O_{11}$, 0.2 $Nd_{2.40}Bi_{1.60}Ti_3O_{12}$, and 1 TiO_2 (rutile), obtained by reacting 0.30 Nd_2O_3 + 0.70 Bi_2O_3 + 4 TiO_2 for 24 hr at 900°C; (h) $Bi_2Ti_4O_{11}$ mixed mechanically with 14 wt% $Sm_2Ti_2O_7$.

rations were done with anatase and we established that under our experimental conditions, anatase remained practically unchanged after 18 hr at 900°C. (Heating for 85 hr at 900°C, or 1 hr at 1100°C converted anatase into rutile). Thus, preparations at 850 and 900°C could contain either one or both forms of TiO_2 depending on the duration of the thermal treatment. To prove that long term (~60 hr) thermal treatments at 900°C yielded the same solid solution, independent of the TiO_2 polymorph used as starting reagent, we determined the peak ratios I_{127}/I_{610} of duplicate preparations containing initially rutile or anatase, as a function of time. After heating 60 to 80 hr, the ratios indeed converged to the same values.

The presence of $Ti_3O_{12}^{12-}$ in mixtures with $Ti_4O_{11}^{6-}$ was established by a peak at 856 cm^{-1} where the latter showed no Raman scattering and the former has a medium intensity peak. The detection limit was found to be 10 wt% of $Ti_3O_{12}^{12-}$ (Figs. 1f and g). The presence of $Ti_2O_7^{6-}$ in mixtures with $Ti_4O_{11}^{6-}$ can just be seen (at 300 ± 10 cm^{-1}), when the concentration of $Ti_2O_7^{6-}$ is about 14 wt%. (Fig. 1h).

The products resulting from heating the ground mixtures to 900°C yielded, independent of the duration of heating, homogeneous but unsintered powders. Since the melting point of Bi_2O_3 has been reported to be 860°C, it may be speculated that liquid Bi_2O_3 acts as a "mineralizer" and increases the rate of formation of these solid solutions. It was also found that preparations containing 10–30 at.% praseodymium did not exhibit the characteristic green color of Pr^{3+} but were gray when heated 47 hr at 900°C. Only after 15 hr at 1000°C was the color of the preparation green. The Raman spectra of the gray-colored preparations were similar to those of other monophasic $Ti_4O_{11}^{6-}$ solid solutions, while the spectra of the green-colored preparations unequivocally showed the presence of significant amounts of $Ti_3O_{12}^{12-}$. The UV and visible reflectance spectra indicated qualitatively that the gray-colored preparations contained only a very small amount of Pr^{3+}[1]. Since the green-colored praseodymium compounds once obtained, did not suffer discoloration, we ruled out the possible explanation that on cooling in air, surface oxidation had occurred to yield gray-colored compounds. We speculated that the virtual absence of Pr^{3+} in the gray compounds was due either to the fact that praseodymium with a valence higher than 3+ could be incorporated into solid solution or, more likely, that the unreacted TiO_2 (due to unreacted 10 at.% praseodymium) was present at concentrations below the limit of detection by Raman spectroscopy and XRD.

Solubility of Lanthanide Elements in $Bi_2Ti_4O_{11}$ and Stability of the Resulting Solid Solutions

The solubility of 10 lanthanide elements and of scandium in $Bi_2Ti_4O_{11}$ was determined by applying mainly Raman spectroscopy to products obtained by heating various mixtures $a Ln_2O_3 + (1 - a) Bi_2O_3 + b TiO_2$ with values of a ranging from 0.1 to 0.7 and those of b initially from 4.00 to 4.37. Table I lists the experimental preparative conditions, and the phases observed in selected preparations which were examined by XRD as well as by Raman spectroscopy.

Only very minor differences were observed among the Raman spectra of $Bi_2Ti_4O_{11}$ and of solid solutions containing different lanthanide elements or scandium; this can be be seen in Figs. 1a–c. When the Raman spectra appeared to belong to a monophase we relied on data obtained from both methods, and only on Raman measurements when the latter showed unequivocally the presence of more than one phase. The data obtained was represented in a diagram (Fig. 2) using as coordinates X_{Ln}, the lanthanide content and δ, function of the ionic radii of bismuth and the lanthanide elements. These coordinates are defined as follows: $X_{Ln} = n_{Ln}/(n_{Ln} + n_{Bi})$, where n_i are the number of gram-atoms of each cationic species; $\delta = 100 (IR_{Bi}^8 - IR_{Ln}^8)/IR_{Ln}^8$, where IR_i are the ionic radii taken from Shannon (7) and the superscript 8 refers to the arbitrarily chosen coordination number 8. The boundary separating the monophasic solid solutions from a polyphasic region in Fig. 2 indicates the maximum solubility of scandium and the lanthanide elements in $Bi_2Ti_4O_{11}$.

As previously found for other Bi-containing solid solution titanates, the solubility of the lanthanide element in $Bi_2Ti_4O_{11}$ is a function of its ionic radius. In this case,

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[1] The authors express their gratitude to J. P. Young, Analytical Chemistry Division, ORNL, for obtaining the reflectance spectra of praseodymium compounds.

TABLE I

SELECTED PREPARATIONS EXAMINED BY RAMAN SPECTROSCOPY AND XRD

Lanthanide element[a]	$n_{Bi_2O_3}$	n_{TiO_2}	T(°C)	Time (hr)	Phases observed in addition to solid solution		I_{127}/I_{610}[b]
					By XRD	By Raman spectroscopy	
—	1	4	900	139			4.97
La	0.89	4.04	850	106		Trace of $Ti_3O_{12}^{12-}$	4.00
	0.53	4.36	850	150		Rutile, anatase, $Ti_3O_{12}^{12-}$	ND[c]
Pr	0.89	4.00	850	106			4.97
Nd	0.90	4.05	850	106		Trace of $Ti_3O_{12}^{12-}$	4.76
	0.78	4.35	850	150		$Ti_3O_{12}^{12-}$, rutile	2.41
	0.54	4.37	850	20	$Nd_2Bi_2Ti_3O_{12}$	Strong anatase, minor $Ti_3O_{12}^{12-}$	ND
Sm	0.78	4.14	850	150		Rutile?	3.63
	0.53	4.34	850	150	$Sm_2Ti_2O_7$ and rutile	Very strong rutile and $Ti_2O_7^{6-}$	ND
Eu	0.75	4.01	900	139	ND	Rutile	3.00
	0.66	3.99	850	106	$Eu_2Ti_2O_7$	Rutile	2.98
Tb	0.51	4.02	900	24	Tb_6O_{11}, rutile	Rutile	2.61
Dy	0.80	4.05	900	156			
	0.67	4.04	850	106	Dy_2O_3	Rutile	3.74
Ho	0.41	4.02	900	24	Rutile + unidentified phase	Rutile	3.00
Er	0.80	4.05	900	156		Rutile?	
	0.72	4.06	900	139	ND	Rutile?	3.17
	0.64	4.01	850	106	Er_2O_3?	Rutile?	2.77
Lu	0.80	4.10	900	156			4.55
	0.70	4.05	900	139	ND	Trace of rutile	3.58

[a] $n_{Ln_2O_3} = 1 - n_{Bi_2O_3}$.

[b] Ratio of Raman peak intensities at 127 and 610 cm^{-1}.

[c] Not determined.

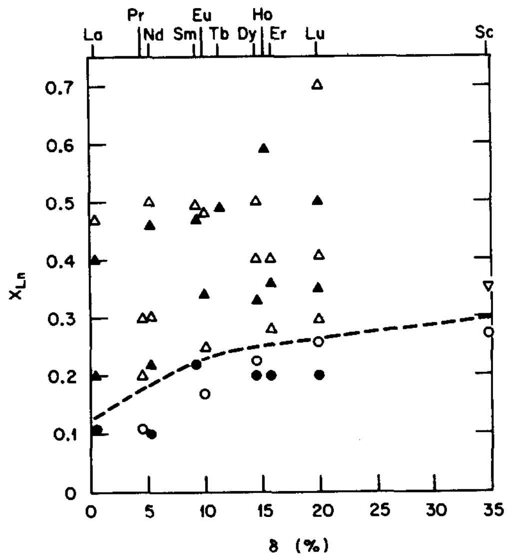

FIG. 2. Solubility at 900°C of Ln in $Ln_{2-x}Bi_xTi_4O_{11}$ expressed in terms of X_{Ln} ($= n_{Ln}/(n_{Ln} + n_{Bi})$) as a function of δ ($= 100(IR^8_{Bi} - IR^8_{Ln})/IR^8_{Ln}$) Triangles: polyphasic region; circles: solid solution; open symbols: Raman spectroscopy; filled symbols: Raman spectroscopy and XRD.

however, the opposite to what has been observed with the other Ln–Bi titanate systems (*2*, *3*) occurs; the solubility increases as the ionic radius of the lanthanide element decreases.

The peak ratio I_{127}/I_{610} as a function of time, of preparations at 1000°C, remained relatively constant for up to 40 hr and decreased with 100–140 hr of isothermal treatment, indicating the slow exsolution of rutile (Fig. 3). The presence of other phases, such as $Ti_3O_{12}^{12-}$ or $Ti_2O_7^{6-}$, however, was not unequivocally determined by Raman spectroscopy. Additional examination by XRD of two of the preparations kept at 1000°C revealed that the Pr-containing solution remained a pure phase throughout the heating period (102 hr), while the Er-containing solid solution, a pure phase after 24 hr, showed, after 137 hr, the presence of $Er_2Ti_2O_7$ and a phase whose diffraction pattern resembled closely that of rutile. The rate of decomposition of these solid solu-

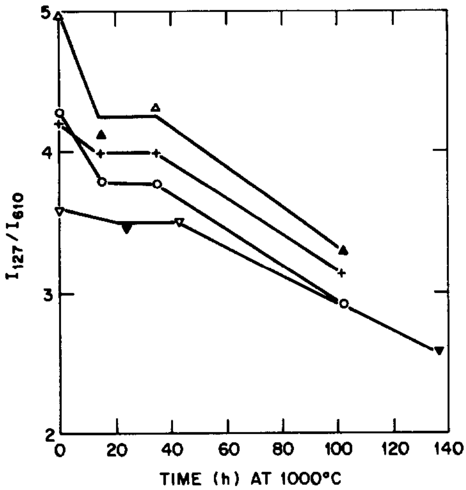

FIG. 3. Ratio of Raman peak intensities (height) at 127 and 610 cm^{-1} (I_{127}/I_{610}) of solid solutions prepared at 1000°C, as a function of time. ○, $La_{0.22}Bi_{1.78}Ti_4O_{11}$; △, $Pr_{0.22}Bi_{1.78}Ti_4O_{11}$; +, $Nd_{0.20}Bi_{1.80}Ti_4O_{11}$. All the above preparations were previously heated 106 hr at 850°C and 47 hr at 900°C. ▽, $Er_{0.40}Bi_{1.60}Ti_4O_{11}$, previously heated 22 hr at 850°C and Solid symbols represent additional analysis by XRD.

tions was found to increase with increasing temperature. The products of decomposition which were not detected by Raman spectroscopy in preparations held for 180 hr at 900°C became evident in the Raman spectra of those heated for shorter times (~60 hr) at or above 1000°C. This led us to speculate that even at temperatures lower than 1000°C the solid solutions $Ln_{2-x}Bi_x Ti_4O_{11}$ may be metastable. Some of the Raman spectra of preparations heated to above 1000°C showed, in addition to rutile, broad peaks covering the frequency range where the peaks of $Ti_2O_7^{6-}$ and $Ti_3O_{12}^{12-}$ appear, while others showed unequivocally peaks due only to the presence of $Ti_3O_{12}^{12-}$ and rutile. Since the composition of $Bi_{4-x}Ln_xTi_3O_{12}$ solid solutions at saturation are known from earlier work (*4*), we were able to estimate, by material balance, the composition of the phases generated by thermal decomposition of the $Ti_4O_{11}^{6-}$ solid solutions. The following two examples illustrate the thermal decomposition schemes of solid solutions estimated near their saturation point:

$$La_{0.2}Bi_{1.8}Ti_4O_{11} \rightarrow 0.5La_{0.4}Bi_{3.6}Ti_3O_{12} + 2.5TiO_2 \quad (1)$$

and

$$Lu_{0.5}Bi_{1.5}Ti_4O_{11} \rightarrow 0.383Lu_{0.08}Bi_{3.92}Ti_3O_{12} + 0.235Lu_2Ti_2O_7 + 2.38TiO_2 \quad (2)$$

The $Ti_3O_{12}^{12-}$ solid solution obtained in Eq. (1) is well below the La-saturation value, while in Eq. (2) Lu is saturating the $Ti_3O_{12}^{12-}$ solid solution phase (*4*).

Conclusions

We have established that lanthanide elements and scandium can partially substitute bismuth in $Bi_2Ti_zO_{2z+3}$, (where z ranges from 4.00 to 4.10) to form solid solutions. The solubility data was correlated as a function of the ionic radii of the lanthanide elements and bismuth. We have also found, qualitatively, that the rate of thermal decomposition of the solid solutions increases with temperature.

The exsolution of rutile TiO_2 from the solid solutions was the first effect of the thermal decomposition which could be detected by Raman spectroscopy. This rutile exsolution as a function of time of heating at constant temperatures led us to infer that all the solid solutions may be metastable.

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