

NON-STOICHIOMETRY AND OPTICAL SPECTRA
OF Nd(III) SUBSTITUTED PbTiO₃

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(Received April 19, 1976; Communicated by G. H. Jonker)

ABSTRACT

The non-stoichiometry of the perovskite (ABO₃)-type phase in the system PbO-TiO₂-Nd₂O₃ has been studied. Monophasic compounds of composition Pb_{1-αx}Nd_xTiO_{3+x(1.5-α)} with $x \leq 0.21$ and $0.09 \leq \alpha \leq 1.5$ were prepared. The ferroelectric Curie temperature (T_C) shows a decrease of 18.5 K/at% Nd with increasing value of x . T_C shows an increase of 3.5 K/mol % PbO with decreasing value of α (increasing content of PbO). The observed effect of α on optical spectra can be interpreted by assuming that Nd(III) ions partly occupy B sites in compounds with $\alpha < 1.5$.

Introduction

The perovskite (ABO₃)-type phases in the systems PbO-TiO₂-Ln₂O₃ (Ln = La, Sm) are highly non-stoichiometric (1,2). Unit-cell dimensions and dielectric properties of these phases depend strongly on composition. We have interpreted this non-stoichiometry on the basis of a defectstructure with variable numbers of both Ln(III)-ions and vacancies distributed over A and B sites in the perovskite structure (1). A defectstructure of the same type has been proposed for the perovskite-type phase in the system SrO-TiO₂-La₂O₃ which shows comparable non-stoichiometry (3). The defectstructures proposed are based on the results of X-ray diffraction studies.

Additional evidence for these defectstructures, especially concerning the occurrence of Ln(III) at two different crystallographic sites, might be obtained from optical spectra of these titanates substituted with suitable rare earth ions. Lindop and Goodwin (4) studied EPR and optical spectra of CaO.2Al₂O₃ doped with Nd(III) ions (4f³ electronic configuration). They concluded that Nd(III) ions occupy four different sites in this compound.

In this paper we report results of our investigations on the homogeneity range, Curie temperature and optical spectra of Nd(III) substituted PbTiO_3 .

Experimental part

Ceramic samples of composition $\text{Pb}_{1-\alpha}\text{Nd}_\alpha\text{TiO}_{3+x(1.5-\alpha)}$ with $x = 0.10, 0.18$ and 0.21 , respectively, and various values of α ($0.8 \lesssim \alpha \lesssim 1.5$) were prepared using standard techniques (1). Sintering was performed at 1520 K. The measured densities of the products were higher than 95% of the theoretical densities. The compositions of the samples were determined by X-ray fluorescence analysis. Homogeneity and unit-cell dimensions were determined from X-ray powder diffraction patterns. Curie temperatures were deduced from DTA curves.

Diffuse reflectance, normal transmission and scattered transmission spectra in the frequency range $6,000\text{--}25,000\text{ cm}^{-1}$ at room temperature were recorded using a Varian Cary 17I spectrophotometer. Low-temperature (down to 32 K) transmission spectra were recorded with a Perkin Elmer E14 spectrophotometer. Thin ($\sim 100\text{ }\mu\text{m}$) polished ceramic slices were used for transmission measurements.

Homogeneity range and Curie temperature

Table I gives a survey of the unit-cell dimensions and Curie temperatures of monophasic samples. For compounds with $x = 0.21$ no Curie temperatures could be detected from DTA measurements. The heat effects accompanying the ferroelectric-paraelectric transition are obviously below detection limit for this composition. From the results of the investigations on homogeneity range and Curie temperature of the perovskite-type phase, the following conclusions can be drawn.

- i) Pure compounds with $0.9 \lesssim \alpha \lesssim 1.5$ could be prepared. This means that the width of the homogeneity range (expressed in units of α) at fixed Nd/Ti ratio (x) far from the solubility

TABLE I

Unit-cell Parameters and Curie Temperatures for various Compounds of Composition $\text{Pb}_{1-\alpha}\text{Nd}_\alpha\text{TiO}_{3+x(1.5-\alpha)}$.

x	α	a(Å)	c(Å)	c/a	V(Å ³)	T _c (K)
0.10	1.42	3.9042	4.0555	1.039	61.82	589
	1.25	3.9048	4.0559	1.039	61.84	591
	1.09	3.9065	4.0579	1.039	61.92	598
	0.99	3.9095	4.0637	1.039	62.11	603
0.18	1.54	3.9064	3.9733	1.017	60.63	422
	1.42	3.9066	3.9788	1.018	60.72	433
	1.20	3.9139	3.9866	1.019	61.07	444
	1.10	3.9175	3.9923	1.019	61.27	454
	0.99	3.9177	3.9958	1.020	61.33	462
0.21	1.48	3.9074	3.9573	1.013	60.42	-
	0.95	3.9211	3.9786	1.015	61.17	-

limit of Nd(III) in PbTiO_3 ($x_{\text{max}} \approx 0.4$) equals almost the corresponding widths of the homogeneity ranges of La(III) and Sm(III) substituted PbTiO_3 (1).

- ii) An increase of the Nd/Ti ratio (x) of the phase at fixed value of α leads to a slight increase of the a -axis, and to decreasing values of c -axis, axial ratio c/a , unit-cell volume V and Curie temperature T_C . The decrease of T_C is about 18.5 K/at.% Nd(III). The corresponding values of La(III) and Sm(III) substitutions are 19.5 and 18.0, respectively (1).
- iii) An increase of the PbO content (decreasing α) at fixed Nd/Ti ratio leads to greater values of $a, c, c/a, V$ and T_C . The increase of T_C is about 3.5 K/mol% PbO. The corresponding values for La(III) and Sm(III) substitutions are 2 and 5, respectively (1).

Obviously, the effect of Nd(III) substitution on various properties is intermediate between those of La(III) and Sm(III) substitutions. This is in accordance with the intermediate value of the ionic radius of Nd(III).

Optical spectra

The spectra show absorption bands at frequencies which are in good agreement with literature data on spectra of Nd(III) ions (4,5). Figures 1 and 2 show transmitted intensity (I_t), in arbitrary units, vs. wave number ($\bar{\nu}$) for the two compounds with $x = 0.21$ (Table I). In the figures and in the discussion of the spectra α values of 1.5 and 1.0, respectively, are used for the sake of simplicity. Fig. 1 shows the influence of temperature on the shape of the absorption band around $17,000 \text{ cm}^{-1}$, which is due to transitions from $^4I_{9/2}$ ground state levels to $^4G_{5/2}$ and $^2G_{7/2}$ levels. Two effects can be distinguished.

- i) Resolution becomes better with decreasing temperature.
- ii) The absorption peak at about $16,600 \text{ cm}^{-1}$, which is present in the spectra recorded at room temperature and at 100 K, is absent in the spectrum recorded at 32 K. This indicates that this peak is due to a transition from a Stark level (belonging to the $^4I_{9/2}$ manifold) which must be close (of the order of 100 cm^{-1}) above the ground level.

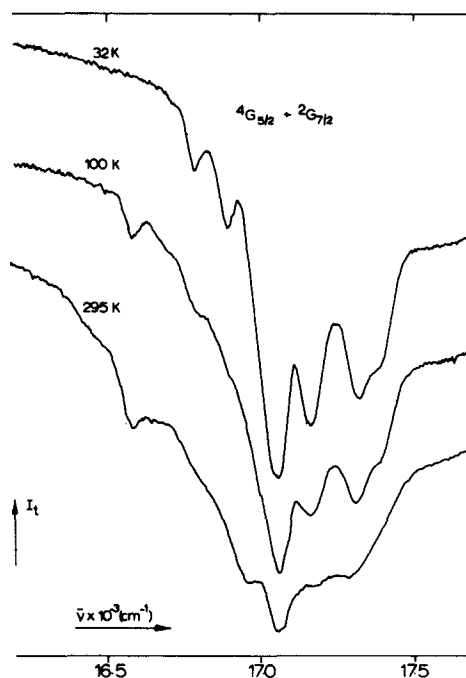


FIGURE 1

Transmitted intensity vs. wave number for the absorption band around $17,000 \text{ cm}^{-1}$ of a compound with $x = 0.21$ and $\alpha = 1.0$ at 32, 100 and 295 K, respectively.

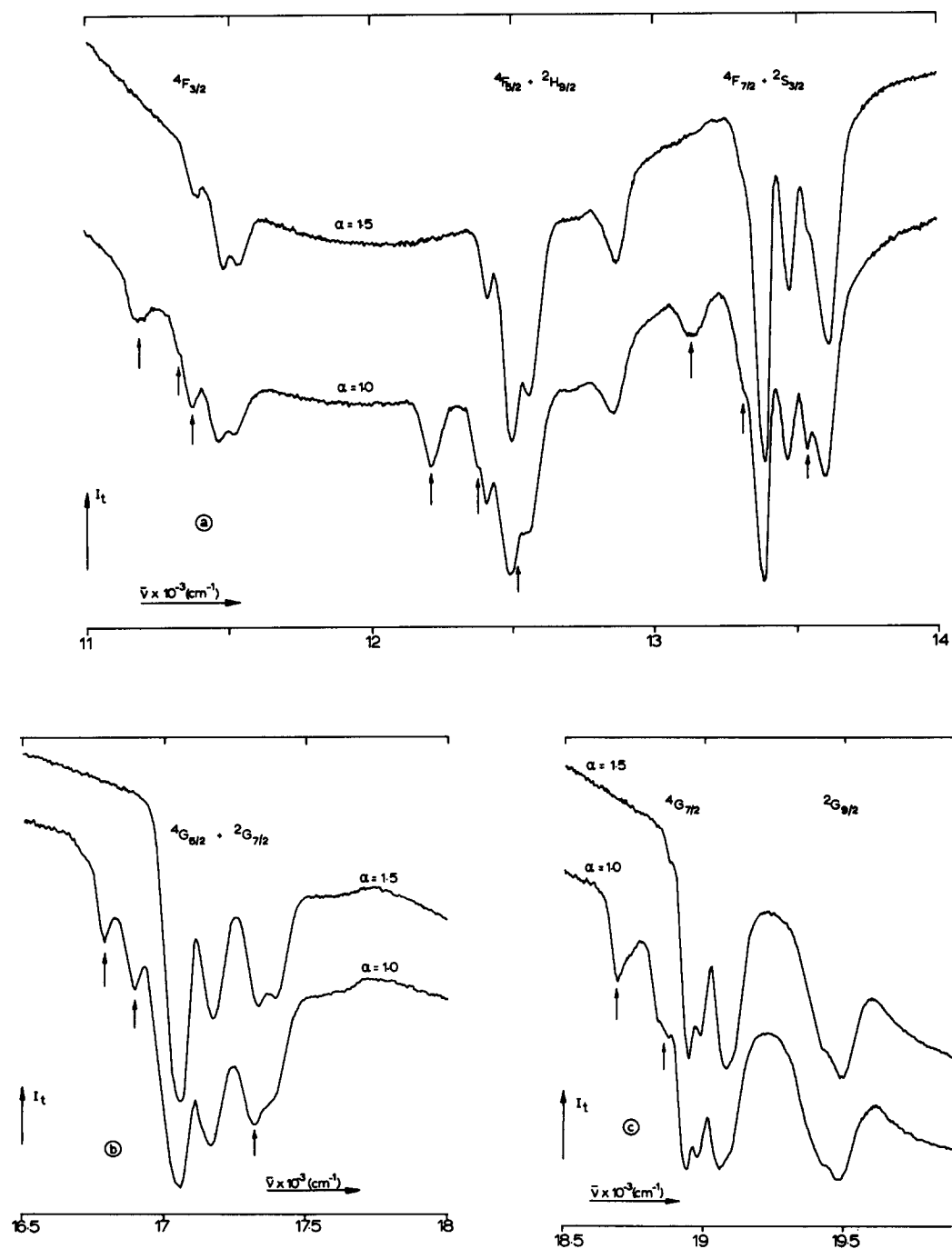


FIGURE 2

Transmitted intensity vs. wave number for two compounds with $x = 0.21$, and $\alpha = 1.5$ and 1.0 , respectively, at 32 K in the wave number regions $11,000\text{--}14,000 \text{ cm}^{-1}$ (a), $16,500\text{--}18,000 \text{ cm}^{-1}$ (b) and $18,500\text{--}19,900 \text{ cm}^{-1}$ (c). The arrows indicate the additional absorption phenomena in the compound with $\alpha = 1.0$.

The effect of α on the spectrum of compounds with $x = 0.21$ at 32 K can be seen from Fig. 2 (a,b and c), which shows different spectral regions. The spectra of the two compounds studied, viz. with $\alpha = 1.5$ and 1.0, are very similar, except for some additional small absorption peaks and shoulders in the spectrum of the compound with $\alpha = 1.0$. Throughout the spectrum these additional absorptions are found at slightly lower wave numbers than those of the main absorption peaks. With decreasing electron-electron repulsion energy or internal electric field strength for a particular site, all absorption peaks of a spectrum are shifted to lower wave numbers. This indicates that a small part of the Nd(III) ions occupies a second site in this compound.

From spectra, recorded at room temperature (not shown here), it can be seen that the absorption bands corresponding to the second site, distinctly increase with decreasing α values. However, the relatively large spectral bandwidths do not allow to calculate the oscillator strengths of the individual bands. Therefore, a quantitative interpretation cannot be given.

The features, which the spectra of compounds with different values of α have in common, must be due to Nd(III) ions at A sites. Merely on the basis of the spectroscopic results, it cannot be concluded yet that the second site, which Nd(III) obviously occupies in compounds with $\alpha < 1.5$, is indeed the B site of the perovskite structure. However, this conclusion appears to be justified by the results of our X-ray diffraction studies on La(III) substituted PbTiO_3 (1) and SrTiO_3 (3). These results have shown that a defectstructure with both La(III) ions and vacancies distributed over A and B sites is most likely for these compounds.

In the defectstructure proposed no B-site defects exist in compounds with $\alpha = 1.5$ (Table 2). Hence, in these compounds the rare earth ions occupy A sites only, giving rise to rather simple optical spectra. The defect concentrations in compounds with $\alpha < 1.5$ are not fully determined by composition. Two extreme cases which are characterized by a negligible number of rare earth ions at B sites (case I), and a negligible number of B-site vacancies (case II), respectively, must be distinguished. The

TABLE 2

Number of Defects per Unit Cell for Ln(III) substituted PbTiO_3 or SrTiO_3 with $x = 0.20$ and $\alpha = 1.5$ and 1.0, respectively. For the Compound with $\alpha = 1.0$ separate Numbers are given for the two extreme Cases I and II.

defect type	number $\alpha = 1.50$	number $\alpha = 1.00$	
		case I	case II
Ln_A	0.20	0.194	0.162
V_A	0.10	0.032	0.064
Ln_B	-	-	0.032
V_B	-	0.032	-

defect concentrations in a compound with $x = 0.20$ and $\alpha = 1.0$, are given in Table 2 for these cases. The actual defect concentrations are intermediate (1,3).

It is likely that this defectstructure also holds for Nd(III) substituted PbTiO_3 . Therefore, it is to be expected that some 10% of the Nd(III) ions occupy B sites in a compound with $x = 0.21$ and $\alpha = 1.0$, giving rise to additional optical absorption phenomena. This means that the observed effect of α on optical spectra supports, at least qualitatively, the defectstructure proposed.

Acknowledgements

We are highly indebted to H.J.L. van der Valk of the University of Groningen for making available the Perkin Elmer spectrometer and for his assistance in the low-temperature measurements. We wish to thank G.C. Tiekstra, H. Kruidhof and F.J. Carelsen for their technical assistance and A.J. Burggraaf and P.J. Gellings for useful discussions.

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