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Synthesis of $Ba(V_{1-x}Ti_x)S_3$ ($0 \leqq x \leqq 1.0$) Compounds and Their Structural Transitions

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The two-layer hexagonal perovskites $Ba(V_{1-x}Ti_x)S_3$ ($0 \leqq x \leqq 1.0$) are prepared in a H_2S stream. A structural phase transition from a hexagonal to an orthorhombic form takes place for the powder samples with $0 \leqq x \leqq 0.4$ and their transition temperatures are determined to be 250 K for $x = 0$, 240 K for $x = 0.1$, 222 K for $x = 0.2$, 195 K for $x = 0.3$, and 160 K for $x = 0.4$, respectively. The phase transformation does not occur down to 90 K for the materials above $x = 0.5$.

Introduction

$BaVS_3$ is a two-layer hexagonal perovskite-like compound which is characterized by metallic behavior at room temperature. Gardner *et al.* (*1*) found that, in the case of $BaVS_3$, at about 180 K a gradual crystal structural transformation to the phase tentatively indexed as an orthorhombic form took place, and that a metallic to semiconductive transition occurred at 130 K. Assuming the existence of distorted $-V^{4+}-V^{4+}-$ chains, they concluded that the structural change was undoubtedly associated with the electrical transition.

In order to make further investigation on the structural and physical property changes in $BaVS_3$, Takano *et al.* (*2*) conducted X-ray diffraction, electrical resistivity, and magnetic susceptibility measurements down to 4.2 K. They observed a sharp increase in resistivity and a clear peak in the magnetic susceptibility at 70 K. Therefore it is considered that the change in resistivity at 70 K appears to be associated with an antiferromagnetic transition rather than the structural modification at 258 K. Massenet *et al.* (*3*) found that the stoichiometric $BaVS_3$ behaved like a quasi-one-dimensional antiferromagnetic and, in case of the sulfur-deficient $BaVS_3$, three-dimensional ferromagnetic order took place below 16 K.

Recently, Massenet *et al.* (*4*) prepared complete solid solution $BaV_xTi_{(1-x)}S_3$ powder samples and discussed the effects of changing the population of *d*-electrons along the V–Ti chains by the results of X-ray, magnetic, and resistivity measurements.

In order to examine the crystallographic transition of two-layer perovskite sulfides, an attempt to synthesize the solid solution series of $Ba(V_{1-x}Ti_x)S_3$ ($0 \leqq x \leqq 1.0$) was made. In this paper, we report some results

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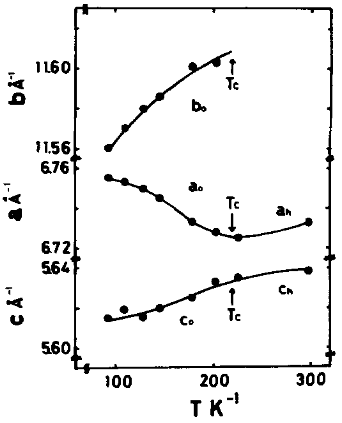

FIG. 1. The individual lattice parameters of hexagonal and orthorhombic $Ba(V_{0.8}Ti_{0.2})S_3$ as a function of temperature.

of the structural transition with respect to the effect of Ti^{4+} ions.

Experimental

All the $Ba(V_{1-x}Ti_x)$ ($0 \leq x \leq 1.0$) samples were prepared using the standard technique. Powders of $BaCO_3$, V_2O_5, and TiO_2 were weighed in the desired proportions and milled for 24 hr with acetone. After drying at 100°C, the mixed powders were heated repeatedly in a H_2S stream to convert them to sulfide. With increasing x, the firing temperatures were increased from 650 to 750°C to synthesize the single phase. The final heat treatment was made at 600°C for 12 hr to ensure stoichiometry for all samples. All powdered samples of $Ba(V_{1-x}Ti_x)S_3$ were pressed into a pellet 10 mm in diameter and 1 mm in thickness under 10 kbar at room temperature to measure the X-ray diffraction patterns over the temperature range 90 to 300 K using a low-temperature X-ray diffractometer. After the sample was maintained at the desired temperature for 30 min, the X-ray measurements were carried out maintaining the temperature constant within ±5 K.

Experimental Results and Discussion

X-Ray powder diffraction patterns of all samples having the composition $Ba(V_{1-x}Ti_x)S_3$ measured at 300 K were completely indexed as the two-layer hexagonal-like perovskite structure. The relation between compositions, and lattice parameters are in good agreement with those reported by Massenet *et al.* (*4*).

The results of X-ray diffraction data of the $Ba(V_{0.8}Ti_{0.2})S_3$ sample down to 90 K are indicated in Fig. 1 for individual lattice parameters. As seen in this figure, it was found that the structural phase transition from a hexagonal (h) to an orthorhombic (o) form occurred at 222 ± 5 K. In Fig. 2,

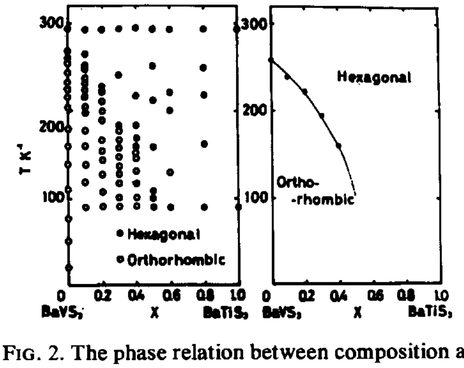

FIG. 2. The phase relation between composition and temperature in the solid solution $Ba(V_{1-x}Ti_x)S_3$.

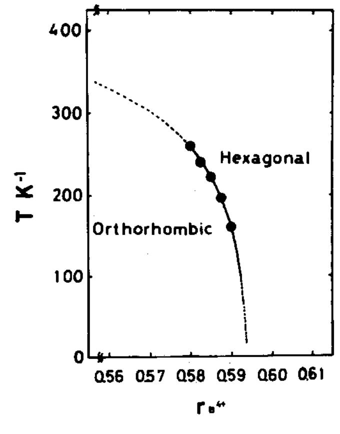

FIG. 3. The phase relation between the ionic radius of the B^{4+} cation and temperature for $BaB^{4+}S_3$.

results of X-ray diffraction measurements down to 90 K for all solid solution samples are illustrated. The phase transformation from hexagonal to orthorhombic form was observed for the specimen with $x \leqq 0.4$, but above $x = 0.5$ no phase change occurred down to 90 K. By an extrapolation of the present results, it is expected that in the $Ba(V_{1-x}Ti_x)S_3$ system the high-temperature hexagonal phase would be stable at about 0 K for the compound with $x > 0.6$.

The present data of the phase transition from hexagonal to orthorhombic form were represented as the relation between the ionic radius of the B^{4+} cation and the transition temperature using Shannon's ionic radius (*5*). In the case of the $Ba(V_{1-x}Ti_x)S_3$ system, the ionic radius of the B^{4+} cation was calculated by using the following equation: $r_{B^{4+}} = (1 - x)r_{V^{4+}} + xr_{Ti^{4+}}$. The results are shown in Fig. 3. It is expected that the sample with the low-temperature orthorhombic phase is stable at 300 K, when the ionic radius of the B^{4+} cation is about 0.575 Å in the $BaB^{4+}S_3$ compound.

Consequently, the close relation of lattice parameters between the hexagonal and the orthorhombic phase illustrates the second-order character of the phase transitions; very slight movement of V($\|a$) and S($\|c$) with the E_{2u} mode, and of Ba($\|b$) and S($\perp c$) with the E_{2g} mode, from their respective sites in the high-temperature hexagonal structure (D_{6h}^4), brings about the orthorhombic form of space group D_2^5. In this manner, when the ionic radius of the B^{4+} cation becomes larger, it is expected that the E_{2u} mode would be quenched and the high-temperature hexagonal phase would become more stable.

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