

Notes

Low-temperature Preparation of Sillenite Phases in Bi-M-O (M=Mn, Fe, Co) Systems†

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γ -Bi₂O₃-related sillenite phases in Bi-M-O (M=Mn, Fe, Co) systems have been prepared by a low-temperature 'wet' method employing strong alkaline medium. For M=Fe or Co, the method yields two different sillenite phases: one rich in bismuth (Bi₂₅MO₄₀) and the other rich in M. In the manganese system, only a manganese-rich sillenite phase (Bi₁₃Mn₁₃O₄₀) is obtained. The phases have been characterized by X-ray powder diffraction, IR spectroscopy and magnetic susceptibility measurements.

Sillenite phases, Bi_{26-x}M_xO_{40-y} (M=Si, Ge, Sn; x=2; and M=Fe, Zn etc., x<2; y depends on the oxidation state of M) crystallize in the γ -Bi₂O₃ structure, the prototype example¹ being Bi₂₄Ge₂O₄₀. Sillenite phases exhibit piezoelectricity, nonlinear electrooptic effect and optical activity and find use for applications in electrooptic devices, microwave acoustics and holographic information storage^{2,3}. We have shown earlier that bismuth atoms at the 24f sites of the sillenite structure can be substituted by M (M=Mg, Co or Ni)⁴. Since sillenites are metastable phases, we felt that they could be prepared by a low temperature route. Adopting the low-temperature technique of Longo and Horowitz⁵ for the synthesis of pyrochlore oxides in alkaline medium, we have now been able to synthesize new sillenite phases in the Bi-M-O (M=Mn, Fe, Co) systems.

The phases have been characterized by chemical analyses, X-ray diffraction (Philips diffractometer PW 1050/70), IR spectroscopy (Perkin-Elmer model 580) and magnetic susceptibility (Faraday balance) measurements in the temperature range 20-300K.

Aqueous solutions of bismuth nitrate (~1M) and M(Mn, Fe, Co) nitrates (~1M) in varying molar proportions (total volume, 50 ml) were added dropwise to a strong KOH solution (~50 ml) with continuous stirring. The final pH was ~13. Oxygen was passed through the solution, keeping the temperature around 300K. After about 24 hr, the crystalline products were filtered, washed free of alkali and dried in air. In the case of iron and cobalt, two distinct phases were

Table 1—Unit Cell Parameters, Chemical Analyses and Magnetic Susceptibility Data of Sillenite Phases in the Bi-M-O (M=Mn, Fe, Co) Systems

Composition	Colour	Bi/M		a(Å)	μ_{eff} per M (B.M.)
		Found	Calc.		
Bi ₂₅ FeO ₄₀	Red	24.81	25.00	10.140	5.87
Bi ₂₅ CoO ₄₀	Green	24.40	25.00	10.118	5.00
Bi _{11.5} Fe _{14.5} O ₃₉	Red	0.70	0.79	10.153	5.11
Bi _{9.5} Co _{16.5} O ₃₈	Black	0.57	0.58	10.120	4.30
Bi ₁₃ Mn ₁₃ O ₄₀	Brown	1.02	1.00	10.146	4.20

obtained, one heavier and the other lighter. The heavier phase which settled down was easily separable from the lighter phase.

X-ray diffraction, chemical analyses and IR spectra of the phases obtained in the Bi-M-O (M=Mn, Fe, Co) systems revealed that sillenite phases could be prepared by reaction of the aqueous metal nitrates in a strong alkali medium. Chemical compositions and unit cell parameters of the phases prepared are listed in Table I. In the Bi-Fe-O system, a well-crystallized single phase Bi₂₅FeO₄₀ could be obtained and its structural parameters agree well with the data reported by Craig and Stephenson⁶ on a sample prepared by solid state reaction. The temperature-magnetic susceptibility profile (Fig.1) of Bi₂₅FeO₄₀ shows that the trivalent iron is in the high spin ($S=5/2$) state. The result is in agreement with that of Devalette *et al.*⁷, indicating that the phase has to be formulated as (Bi⁵⁺ Fe³⁺)Bi₂₄O₄₀. When the concentration of iron in the preparation was increased, an additional phase also

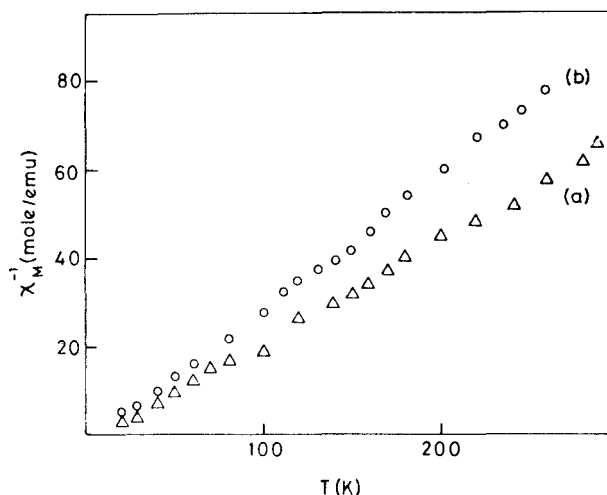


Fig. 1—Temperature-magnetic susceptibility profiles of (a) Bi₂₅FeO₄₀ and (b) Bi₂₅CoO₄₀

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possessing the sillenite structure was obtained. Starting from an equimolar solutions of bismuth and ferric nitrates, an iron-rich phase of approximate composition $\text{Bi}_{11.5}\text{Fe}_{14.5}\text{O}_{39}$, in addition to $\text{Bi}_{25}\text{FeO}_{40}$, could be obtained. Chemical analyses indicated that all the iron in the iron-rich phase is present in the +3 state and its μ_{eff} is 5.11 B.M.

The behaviour of Bi-Co-O system is similar to that of Bi-Fe-O system and a bismuth-rich phase, $\text{Bi}_{25}\text{CoO}_{40}$, could be easily obtained. The structural parameters (Table 2) and magnetic data are similar to those reported by Devalette *et al.*⁷ on a sample of $\text{Bi}_{25}\text{CoO}_{40}$ prepared by solid state reaction of oxides. $\text{Bi}_{25}\text{CoO}_{40}$ is a unique oxide containing Co(III) with four unpaired electrons ($\mu_{\text{eff}}=5.00$ B.M.) in the tetrahedral (2a) sites of the sillenite structure. Both $\text{Bi}_{25}\text{FeO}_{40}$ and $\text{Bi}_{25}\text{CoO}_{40}$ do not show any evidence for magnetic ordering down to low temperatures. Chemical analyses and magnetic susceptibility data reveal that cobalt in the cobalt-rich phase is present partially in +2 state, the likely charge distribution being $(\text{Co}_2^{2+}) [\text{Bi}_{9.5}^{3+} \text{Co}_{14.5}^{3+}] \text{O}_{38}$. In the Bi-Mn-O system, only a manganese-rich phase of approximate composition $\text{Bi}_{13}\text{Mn}_{13}\text{O}_{40}$ could be obtained (Table I). Chemical analyses indicated that part of manganese is in +4 state and its magnetic moment is 4.20 B.M.

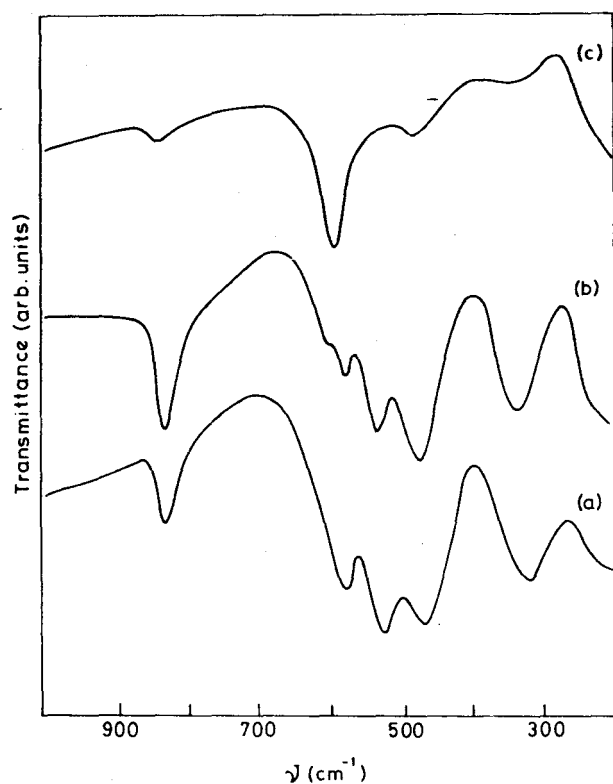


Fig. 2—IR spectra of (a) $\text{Bi}_{25}\text{FeO}_{40}$ (b) $\text{Bi}_{25}\text{CoO}_{40}$ and (c) $\text{Bi}_{9.5}\text{Co}_{16.5}\text{O}_{38}$

Table 2—X-ray Powder Diffraction Data of $\text{Bi}_{25}\text{CoO}_{40}$

<i>hkl</i>	<i>d</i> (Å)		<i>I</i>	
	Obs.	Calc. ^a	Obs.	Calc. ^b
220	3.576	3.577	14	12
310	2.198	3.199	53	60
222	2.914	2.920	11	14
321	2.706	2.704	40	42
400	2.529	2.529	6	3
411	2.385	2.386	5	4
330				
420	2.262	2.262	7	6
332	2.156	2.157	9	6
422	2.066	2.065	6	7
431	1.983	1.984	10	9
510				
521	1.846	1.847	5	2
530	1.735	1.736	21	26
433				
600	1.686	1.687	9	11
442				
611	1.641	1.641	14	17
532				
631	1.492	1.492	12	13
710	1.431	1.431	13	7
550				
543	1.376	1.376	6	3
721				
552	1.284	1.284	3	3
633				
651	1.245	1.246	0	1
732				
741	1.209	1.209	13	11
811				
554	1.192	1.192	10	9
653				
660	1.192	1.192	10	9
822				

(a) $a = 10.118 \text{ \AA}$.

(b) Intensities were calculated assuming the positional parameters of $\text{Bi}_{24}\text{Ge}_2\text{O}_{40}$ and were refined to a $R_w = 10.4\%$. The refined positional parameters are: (Bi + Co) (2a), 0, 0, 0; Bi (24f), 0.826, 0.683, 0.995; O(1) (24f), 0.866, 0.748, 0.515; O(2) (8c), 0.802, 0.802, 0.802 and O(3) (8c), 0.098, 0.098, 0.098.

IR spectra of $\text{Bi}_{25}\text{FeO}_{40}$ and $\text{Bi}_{25}\text{CoO}_{40}$ recorded in KBr pellets (Fig. 2) are characteristic of the sillenite phases reported in the literature^{7,8}. The high frequency ($\sim 820 \text{ cm}^{-1}$) strong band is due to the ν_3 mode of

MO_4 tetrahedra⁷, while a group of sharp bands in the region $400\text{--}600\text{ cm}^{-1}$, observed in all the sillenite phases, is attributed to the $(\text{Bi}_{24}\text{O}_{40})$ framework⁸. IR spectra of M-rich phases are different from those of normal sillenite phases (Fig. 2). A strong band at 575 cm^{-1} appears in the M-rich phases while the 820 cm^{-1} band is nearly extinct. The spectral features in the $400\text{--}600\text{ cm}^{-1}$ region are also different. The changes in the spectra are consistent with substitution of bismuth by M atoms at the 24f sites of the sillenite structure. Metal-rich sillenite phases are metastable decomposing at relatively low temperatures (500 K) to yield normal sillenite phases and $\text{Bi}_2\text{M}_4\text{O}_9$ (ref. 9).

While Horowitz *et al.*¹⁰ obtained pyrochlore phases in Bi–Ru–O and Bi–Ir–O systems by the alkali medium route, no such pyrochlore phases were formed in the presently investigated Bi–M–O (M = Mn, Fe, Co) systems. It is noteworthy that no ternary oxide could be prepared in the Bi–Ni–O system by this method.

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