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RAPID COMMUNICATION

# Structural and dielectric properties of a novel $Bi_2O_3$–$(1-x)WO_3$–$x$CuO solid solution

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**Abstract.** A novel solid solution in the system Bi–W–Cu–O has been synthesized and its structural and dielectric properties studied. The solid solution $Bi_2O_3$–$(1-x)WO_3$–$x$CuO exists up to $x = 0·7$; the solid solutions up to $x = 0·65$ are orthorhombic but stabilize in tetragonal structure in a narrow range around $x = 0·7$. The solid solutions are non-centrosymmetric and exhibit ferroelectric behaviour similar to their parent phase $Bi_2WO_6$. The Curie point of the solid solution is found to decrease with increase in $x$.

**Keywords.** Dielectric properties; ferroelectricity.

## 1. Introduction

Bismuth tungstate, $Bi_2WO_6$, is a $n = 1$ member of the Aurivillius layered-perovskite family of oxides having the general formula, $(Bi_2O_2)(A_{n-1}B_nO_{3n+1})$, where $n$ represents the number of $BO_6$-octahedra in the perovskite layer (Aurivillius 1949, 1950). $Bi_2WO_6$ is orthorhombic (space group *Pba*2) in the ferroelectric state with its Curie point at 1223 K (Wolfe *et al* 1969; Dorrian *et al* 1971; Wolfe *et al* 1971). Recently, we reported the synthesis of a novel Bi–W–Cu–O system (Sharma *et al* 1994). It is found that the solid solution $Bi_2O_3$–$(1-x)WO_3$–$x$CuO exists up to $x = 0·7$. Phases up to $x = 0·65$ adopt orthorhombic structure, while those in the narrow range around $x = 0·7$ stabilize with a tetragonal structure. In this report, we document the structural and dielectric properties of the Bi–W–Cu–O system.

## 2. Experimental

While $Bi_2WO_6$ was obtained by the conventional solid-state route, the samples of the solid solution belonging to the system Bi–W–Cu–O were prepared by melting 1 mole of $Bi_2O_3$, $(1-x)$ moles of $WO_3$ and $x$ moles of CuO. The melts were held at temperatures ranging between 1123–1323 K for 24 h and then quenched to room temperature in ambient air. X-ray powder diffraction (XRD) patterns of these samples were recorded on a STOE/STADI-P diffractometer in transmission geometry using $CuK_\alpha$ radiation. Samples were also characterized using EDAX on a scanning electron microscope (SEM) model S-150 Stereoscan, Cambridge (UK).

Samples were pelletized by double-end compression in a steel die. The pellets were sintered at 973 K and coated with gold paint on both flat ends. Dielectric constants of these samples were measured both as a function of temperature (300–1100 K) and frequency (100 Hz to 5 MHz) using a 4194 A HP Impedance/Gain Phase Analyser coupled to an IBM-PC. The room temperature ferroelectric ($P$ vs $E$) hysteresis-loops on the samples were also obtained employing a Sawyer-Tower circuit operating at 50 Hz.

## 3. Results and discussion

Typical X-ray powder diffraction patterns for the parent phase $Bi_2WO_6$, and $Bi_2O_3$–$(1-x)WO_3$–$xCuO$ solid solutions with nominal compositions $x = 0{\cdot}3$ and $0{\cdot}7$ are shown in figure 1. A single phase $Bi_2WO_6$-like solid solution is found to exist (Sharma *et al* 1994). The $x = 0{\cdot}3$ solid solution is orthorhombic with lattice parameters $a = 5{\cdot}448(4)$, $b = 5{\cdot}436(9)$, $c = 16{\cdot}458(6)$ Å, while the pattern of $x = 0{\cdot}7$ is indexable in a tetragonal system with $a = 3{\cdot}973(5)$ and $c = 16{\cdot}852(6)$ Å. $Bi_2O_3$–$0{\cdot}7WO_3$–$0{\cdot}3CuO$ solid solution has the XRD pattern similar to $Bi_2WO_6$ which is non-centrosymmetric with a space group *Pb2a* and point group *mm*2. By contrast, a careful examination of the observed reflections in the XRD pattern of $Bi_2O_3$–$0{\cdot}3WO_3$–$0{\cdot}7CuO$ solid solution suggests that the lattice is primitive tetragonal having the point group symmetry 4*mm*. The compositional variation for $Bi_2O_3$–$0{\cdot}3WO_3$–$0{\cdot}7CuO$ solid solution as obtained from EDAX is shown in figure 2. The analysis indicates good agreement between the expected and observed elemental ratios in the solid solution (table 1).

The data for room temperature variation of dielectric constant with frequency in 100 Hz–5 MHz range for the $x = 0$, $0{\cdot}3$ and $x = 0{\cdot}7$ compositions of the solid solution $Bi_2O_3$–$(1-x)WO_3$–$xCuO$ are shown in figure 3. While the dielectric constant value remains almost invariant with frequency for the composition $Bi_2O_3$–$0{\cdot}7WO_3$–$0{\cdot}3CuO$ much akin to the parent-phase $Bi_2WO_6$, the dispersion in dielectric constant with frequency is significant for $x = 0{\cdot}7$ solid solution in the frequency range 100 Hz–10 kHz.

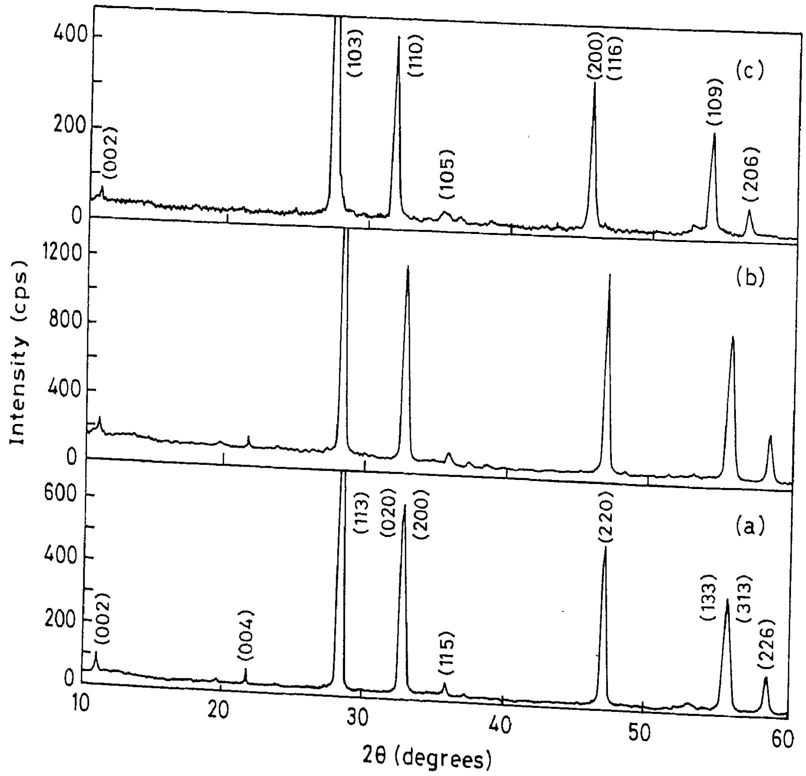


**Figure 1.** X-ray powder diffraction patterns for (**a**) $Bi_2WO_6$, (**b**) $Bi_2O_3$–$0{\cdot}7WO_3$–$0{\cdot}3CuO$, and (**c**) $Bi_2O_3$–$0{\cdot}3WO_3$–$0{\cdot}7CuO$.

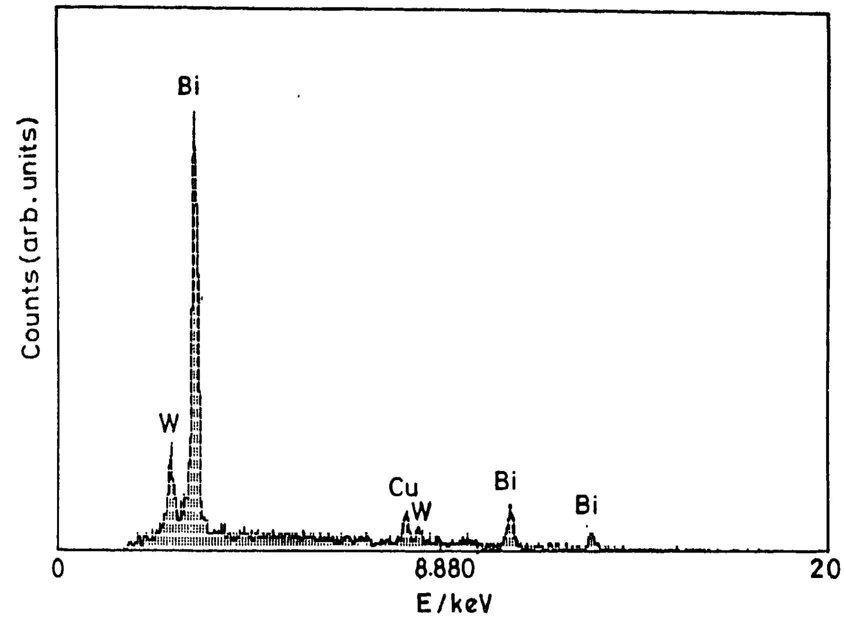


**Figure 2.** Compositional profile of $Bi_2O_3$–0·3$WO_3$–0·7CuO as obtained by EDAX.

**Table 1.** Composition of $Bi_2O_3$–0·3$WO_3$–0·7CuO as obtained by EDAX.

| Elemental ratios | Expected | Observed |
|---|---|---|
| Bi:W | 6·67:1 | 7:1 |
| Bi:Cu | 2·86:1 | 3·1:1 |
| Cu:W | 2·33:1 | 2:1 |

The variation in dielectric constant of these samples on changing to platinum electrodes is shown in the inset in figure 3. Unlike the data obtained with gold electrodes, a small dispersion in dielectric constant for $x = 0·3$ solid solution is observed. Such a behaviour could be attributed to electrode polarization caused by the space-charge effect.

Figure 4 shows the variation of dielectric constant as a function of temperature at 100 kHz for the $x = 0$, 0·3, and 0·7 members of $Bi_2O_3$–$(1-x)WO_3$–$x$CuO solid solution. The dielectric constant increases with temperature showing a maximum around 1022 and 970 K for $x = 0·3$ and $x = 0·7$ samples, respectively. However, in the case of the parent phase $Bi_2WO_6$, the dielectric constant remains almost invariant with temperature in the range of the study. The Curie point for this sample lies beyond 1150 K (Yanovskii *et al* 1975). The room temperature value of dielectric constant for the parent $Bi_2WO_6$ obtained at 100 kHz is in the range of values already reported in the literature (Yanovskii *et al* 1975). The corresponding values of the dielectric constants for the $x = 0·3$ and $x = 0·7$ solid solutions are relatively high and this may be attributed to the oxide–ion conductivity resulting from the oxide–ion vacancies.

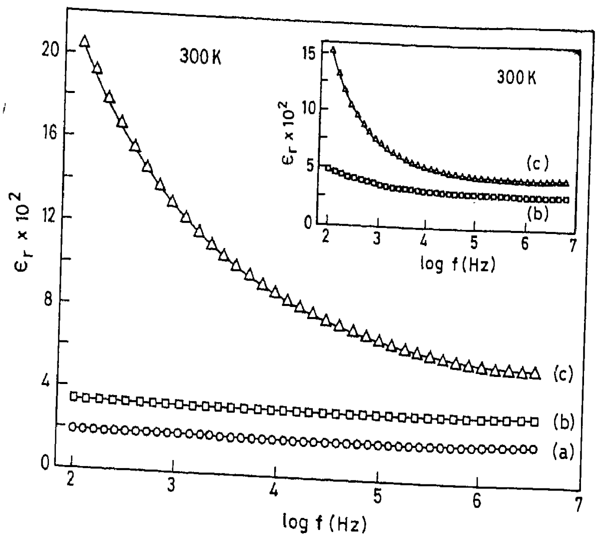


**Figure 3.** Frequency dependence of dielectric constant data at 300 K for (**a**) $Bi_2WO_6$, (**b**) $Bi_2O_3$–0·7$WO_3$–0·3CuO, and (**c**) $Bi_2O_3$–0·3$WO_3$–0·7CuO. The inset shows the data for (b) and (c) with platinum electrodes.

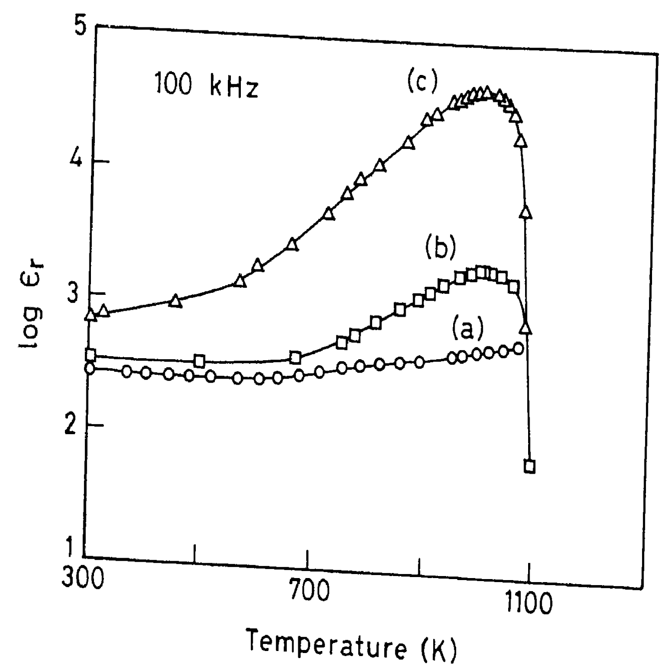


**Figure 4.** Variation of dielectric constants with temperature at 100 kHz for (**a**) $Bi_2WO_6$, (**b**) $Bi_2O_3$–0·7$WO_3$–0·3CuO, and (**c**) $Bi_2O_3$–0·3$WO_3$–0·7CuO.

The *P–E* hysteresis loops obtained (figure 5) for the $Bi_2O_3$–$(1-x)WO_3$–$x$CuO solid solutions of compositions $x = 0{\cdot}3$ and $x = 0{\cdot}7$ at 300 K indicate their ferroelectric nature. Though these are similar to that of $Bi_2WO_6$, the coercive fields are low. These studies confirm that the solid solutions are non-centrosymmetric polar at room temperature.

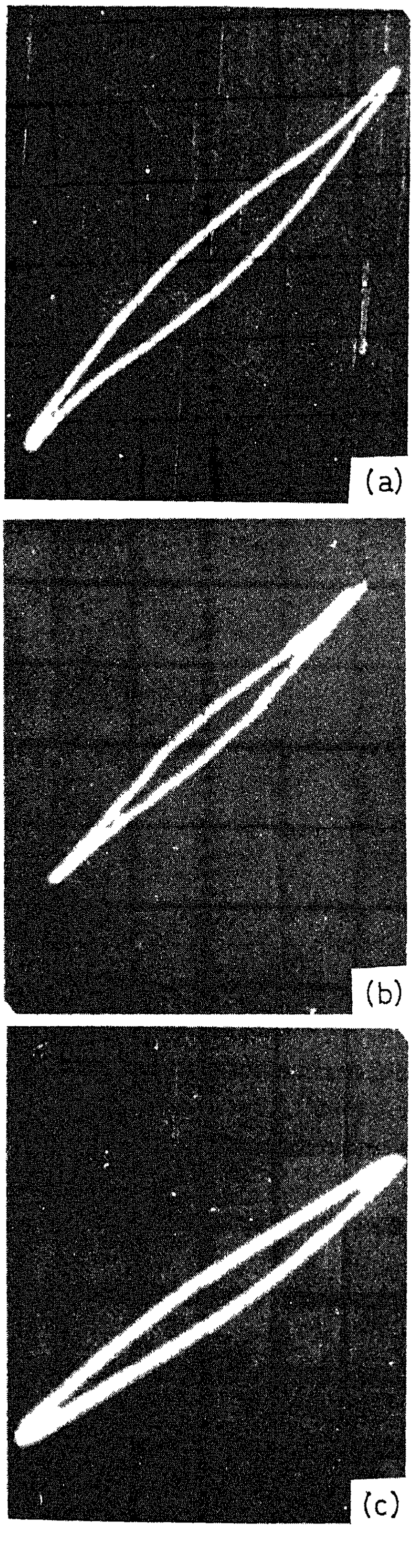


**Figure 5.** Ferroelectric hysteresis-loops for (**a**) $Bi_2WO_6$, (**b**) $Bi_2O_3$–0·7$WO_3$–0·3CuO, and (**c**) $Bi_2O_3$–0·3$WO_3$–0·7CuO recorded at 300 K.

## 4. Conclusions

In the light of the present study, we surmise that: (a) members of the $Bi_2O_3$–$(1-x)$ $WO_3$–$x$CuO ($0 < x \leqslant 0{\cdot}7$) solid solutions are non-centrosymmetric and (b) the dielectric constant values for $Bi_2O_3$–$(1-x)WO_3$–$x$CuO ($0 < x \leqslant 0{\cdot}7$) increase while the Curie point decreases with increase in $x$.

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