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The electronic properties of complex oxides of bismuth with the mullite structure

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Abstract

Bismuth forms double oxides with the oxides of aluminium, gallium, iron and manganese, all of which have the mullite structure. Since other bismuth-based complex oxides show useful functional properties including high-temperature pyroelectricity and piezoelectricity, the electronic and magnetic properties of the mullite-structured bismuth compounds are of potential interest.

In the present study, all the above compounds were synthesised in pure form by solid-state reaction, and their thermal behaviour and structures characterised by thermal analysis, powder X-ray diffraction, solid-state MAS NMR and Mőssbauer spectroscopy as appropriate.

The thermal analysis information allowed highly sintered polycrystalline samples to be produced. After the application of silver electrodes, the electronic properties of the pellet samples were determined as a function of frequency and temperature up to 900 °C. Frequency-dependent inflexions in the relative permittivity and loss angle curves of the ferrate and gallate may be due to losses due to dielectric relaxation, but the most notable and consistent electronic phenomenon in all samples is a steep rise in the dc conductivity at higher temperatures. The *P–E* hysteresis loops for the ferrate and manganate indicate that these are very poor ferroelectric materials, consistent with the centrosymmetric crystal structure of all these compounds.

Keywords: Bismuth compounds; Powders-solid state reaction; Spectroscopy; X-ray methods; Electrical properties

1. Introduction

In the last decade, ceramic materials previously considered interesting for their mechanical or engineering properties have increasingly been reinvestigated for other potentially useful functional properties, especially their electronic properties. The aluminosilicate mullite is an example of a material with excellent thermal and mechanical properties at elevated temperatures, making is an important engineering material.[1] Pure mullite is an insulator, allowing it to be used as a substrate for electronic devices,[1] but doping with transition metals is reported[2] to lower the resistivity by two orders of magnitude, to about $10^{11}\ \Omega\,\mathrm{cm}$ at room temperature.

The dielectric properties of aluminosilicate mullite, which are also important in determining its usefulness as an electronic substrate material, have also been determined.[3,4] The spread in the reported dielectric constants of 6.7–7.5 at 1 MHz has been ascribed to differences in chemical composition and microstructure of the ceramic samples, and in the proportion of glassy intergranular phases.[3] The dielectric constants remain more or less constant over a wide frequency range, up to 14 GHz.[4] These data, and the low dielectric loss of pure mullite confirm its useful high-frequency insulating properties.

These conclusions are not unexpected, but indicate that materials with the mullite structure which may also display useful electronic functions should be sought in systems containing other elements. One such group of mullite-structured compounds based on bismuth oxide (bismuth aluminate, ferrate, gallate and manganate) was first reported by Levin and Roth[5] without supporting X-ray structural data. The mullite-related structures of the aluminate and ferrate compounds were determined by single-crystal X-ray studies in the same year by Koizumi and Ikeda,[6] with X-ray determinations of the manganate[7] and gallate[8] following in 1967 and 1971, respectively. Subsequent refinements of these crystal structures[9–12] indicate that they all have orthorhombic unit cells in the space group *Pbam* with $z = 2$. The unit cell parameters are shown in Table 1, together with mullite for comparison.

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Table 1
X-ray structural data for bismuth aluminate, ferrate, gallate and manganate, with mullite, for comparison

	$Bi_2Al_4O_9$	$Bi_2Fe_4O_9$	$Bi_2Ga_4O_9$	$Bi_2Mn_4O_{10}$	Mullite
Space group	*Pbam*	*Pbam*	*Pbam*	*Pbam*	*Pbam*
$a \pm 0.005$	7.712	7.950	7.934	7.540	7.545
$b \pm 0.005$	8.112	8.428	8.301	8.534	7.689
$c \pm 0.005$	5.708	6.005	5.903	5.766	2.884
Z	2	2	2	2	1

Cell parameters taken from reference[12], mullite parameters from reference[1].

In the structures of the Al, Fe and Ga compounds all these atoms are distributed evenly across the tetrahedral M1 and octahedral M2 sites. By contrast, in the structure of the Mn compound, which has the formula $Bi_2Mn_4O_{10}$,[12] the Mn atoms are evenly distributed over the tetrahedral M2 and square pyramidal M3 sites. The Bi M4 atoms are three-coordinated, with three more oxygens in the outer sphere.[12] A view of the bismuth aluminate structure, looking down the octahedral chains, is shown in Fig. 1, together with the same view of mullite, for comparison.

Table 1 shows that the by comparison with mullite, the Bi double oxides have two formula units in the unit cell, resulting in the doubling of their *c*-axis dimensions. In the *c*-axis direction, an identical unit cell in mullite would be rotated by 180° in the Bi-compounds. The structural features common to the Bi-compounds and mullite are the columns of octahedral chains cross-linked by tetrahedral units (Fig. 1).

Although Bi compounds in general often display interesting electronic properties, not a great deal of work has been reported on the properties of these mullite-structured materials. The electric conductivity of the aluminate, reported to be 10^{-2} S cm^{-1} at 800 °C[13] was suggested to be largely, but not completely, ionic. A more detailed mechanism has been proposed for oxide ion conductance in this compound, invoking the polarizability of the Bi 6 s^2 lone pairs of electrons.[14]

Although the magnetic properties of the ferrate have been more extensively investigated,[15–23] suggesting the occurrence of a paramagnetic-to-antiferomagnetic transition at a Neel temperature of −9 °C the electronic properties of this and the other isostructural compounds have not been investigated systematically. The present study aims to remedy this deficiency by investigating the electronic behaviour of a series of well-characterized sintered polycrystalline samples as a function of temperature and frequency. Although all the structures as represented in Table 1 and Fig. 1 are centro-symmetric and would not therefore be expected to show ferroelectric properties, the possibility that small variations in the structure, stoichiometry or grain-boundary phases may contribute to electronic effects was thought to justify the present study.

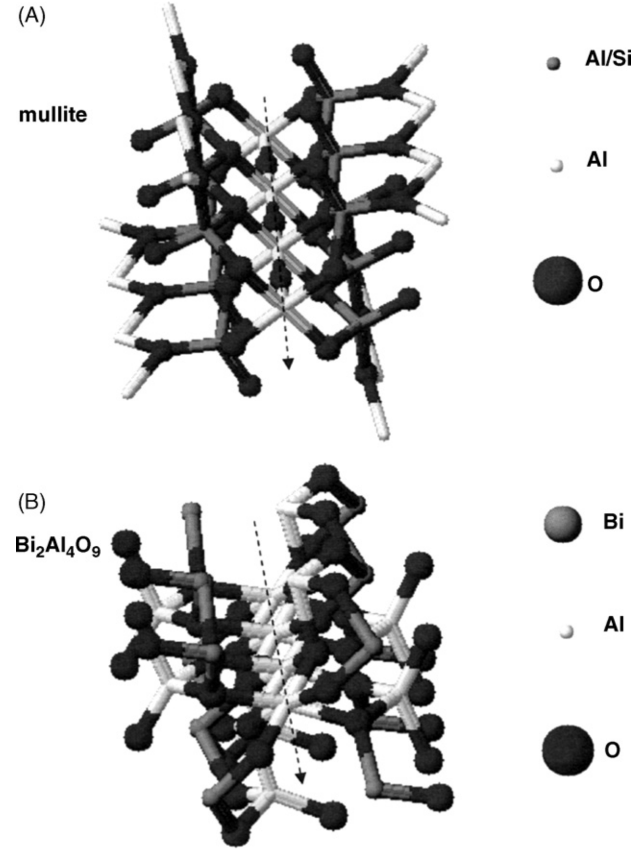

Fig. 1. View down the octahedral columns of (A) mullite and (B) $Bi_2Al_4O_9$, showing the tetrahedral cross-linking chains. Diagram prepared using ACD Chemsketch 3D software.

2. Experimental

The starting materials were Bi_2O_3, 99.9 mass%, −325 mesh (Cerac Specialty Inorganics), calcined Al_2O_3, 99.5 mass% (AnalaR), Fe_2O_3, 99.5% (Alfa), Ga_2O_3, 99.99 mass% (Aldrich) and Mn_2O_3, 99 mass%, −325 mesh (Aldrich). The double oxides were synthesised by solid-state reaction between 1:2 mixtures of the reactant powders. Before firing, the mixtures were homogenised by ball-milling in 2-propanol for 12 h. After removal of the solvent by rotary evaporation at 105 °C, the powders were formed into pellets by uniaxially pressing at 10 MPa, or by CIPing at 250 MPa. Firing and sintering was carried out in static air in an Amalgams CH5 chamber furnace at temperatures determined on the basis of TGA/DSC measurements (Rheometrics STA 1500 thermal analyser, heating rate 10 °C min^{-1}, in flowing air, 50 ml min^{-1}). The maximum firing temperatures to avoid decomposition of the samples were determined in this way to be 865 °C for $Bi_2Al_4O_9$, 920 °C for $Bi_2Fe_4O_9$, 865 °C for $Bi_2Ga_4O_9$ and 760 °C for $Bi_2Mn_4O_{10}$.

After synthesis, the products were ground and checked for phase purity by X-ray powder diffraction (Philips PW 1700 computer-controlled diffractometer with Co Kα radiation and graphite monochromator). The Mössbauer spectrum of the ferrate was recorded using a conventional microcomputer-controlled spectrometer operating in the sinusoidal mode, using a ^{57}Co/Rh source with a maximum activity of 1.85 G Bq. The spectrum was fitted using RECOIL Mössbauer software and the isomer shifts are quoted with respect to natural iron. The ^{27}Al MAS NMR spectrum of the aluminate was acquired at 11.7 T using a Varian Unity 500 spectrometer and Doty MAS probe spun at 10–12 kHz. The spectrometer frequency was