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# Synthesis and characterization of mixed melilite-type oxides

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ABSTRACT

The melilite-type oxides are potential targets for exploring interesting magnetic and electronic properties as well as multiferroicity and magnetoelectric effects. Polycrystalline samples of $Ba_2Cu_{1-x}Mn_xGe_2O_7$ have been synthesized by solid state reaction method. The morphology and chemical composition of the samples have been investigated by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). By using powder X-ray diffraction, the phase composition of the synthesized compounds and the evolution of their crystallographic axes as a function of the doping have been systematically studied. The synthesis of the polycrystalline compounds reported in this work is a prerequisite for the growth of high quality single crystals of mixed melilite-type oxides essential for the investigations of the complex magnetic phase diagram of these non-centrosymmetric systems.



## 1. Introduction

Multiferroics are an interesting group of materials which show simultaneous ferroelectric and magnetic ordering [1,2]. Among them, those where a large magnetoelectric coupling exists are particularly attracting because they could offer the possibility of achieving the mutual control of the electric and magnetic properties [3,4].

So, they can be the basis for a new device generation, for example, non-volatile, dense, fast, and low energy cost memories [5,6].

For these reasons, during the last few years, there have been a continuous effort to identify new multiferroics, with large magnetoelectric coupling. Furthermore, the interest of the scientific community has recently expanded to include materials with more complex structures than the class of perovskite oxides, to which many of the conventional ferroelectrics and magnets belong [7–9].

One possibility is offered by layered transition-metal oxides because of interesting magnetic and electronic properties and their low-dimensional characteristics [10,11].

Among them, the melilite-type oxides are one of the most fascinating systems. They have the general formula $A_2TM'_2O_7$, where A is a large cation, such as alkali earth or lanthanide ions, T is a small cation, generally a divalent or trivalent transition metal and M′ is a trivalent or tetravalent ion, normally silicon or germanium.

They typically crystallize in a tetragonal structure with non-centrosymmetric space group P -4 *21m and* crystallographic axes $a \approx 8$ Å and $c \approx 5$ Å.

In this structure, the T and M′ ions occupy not equivalent tetrahedral sites: T forms $TO_4$ tetrahedra and M′ is located in $M'_2O_7$ units. All the tetrahedra are corner – sharing and linked together along the *a*–*b* plane to form sheets, stacked along the *c*-axis, while the larger A cations lie among these sheets.

The melilite oxides present a large variety of magnetic behaviors, going from a 2D antiferromagnetism [12] to ferrimagnetism [13] and more complex 2D commensurate or incommensurate spiral ordering [14].

Indeed, the interplay of spin-orbit coupling and hopping interactions between the metal ion and the surrounding oxygens leads to the appearance of electric polarization whose origin is essentially local [15–17]. This could represent a new and alternative route by which magnetically-induced ferroelectricity can be reached, without requiring the onset of a frustrated magnetic ordering [18]. Furthermore, a mechanism for the appearance of local electric dipoles, whose origin may lie in the Jahn-Teller instabilities of non-centrosymmetric units has been recently devised [19].

Several studies exist for the melilite oxides containing silicon and strontium [13,20], whereas the systems based on barium and germanium are relatively less investigated. Reported synthesized materials of the class of $Ba_2TGe_2O_7$ (BTGO) compounds comprise $T$=Mn, Co, Cu [18,21], even though a comprehensive experimental analysis of structural, magnetic and ferroelectric properties exists only for the $Ba_2CoGe_2O_7$ (BCoGO) that is particularly interesting, as it shows spontaneous multiferroic properties [22–24].

Some studies exist also in the case of $Ba_2CuGe_2O_7$ (BCGO) because it has been proved that it develops helical magnetism at low

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temperatures via the Dzyaloshinskii-Moriya (DM) mechanism [25,26]. This behavior seems to be unique in this family. Indeed, below 3.2 K it also displays a quasi-AF cycloidal, incommensurate magnetism, but ferroelectricity, and therefore multiferroicity, occurs only in presence of external magnetic field. Hence, the magnetic phase diagram of BCGO is quite complex [26] and it has been proposed that this material could host skyrmions [27].

On the other hand, $Ba_2MnGe_2O_7$ (BMGO) appears to be a 2D antiferromagnetic system [12,18].

It is clear that the physical properties of the insulating oxides $Ba_2TGe_2O_7$ ($T$=Co, Cu, Mn) mainly depend on the nature of the transition metal ion and along the series there is complete variation of electronic configuration, spin state, polarization and d-p hybridization as well as the cell parameters [13,23]. Due to the substantially local nature of some proposed mechanisms, we expect interesting ferroelectric/multiferroic properties could emerge in mixed melilite oxides. For example the Mn doping in BCGO should alter the spiral magnetic ordering and thus the magnetic phase diagram.

In the present study, we discuss solid state reaction synthesis and structural analysis of polycrystalline samples of $Ba_2TGe_2O_7$ with T=Cu and Mn.

$Ba_2Cu_{1-x}Mn_xGe_2O_7$ (BCMGO) samples have been synthesized, with $x$ varying in the whole range (0–1), and the evolution of structural properties has been systematically studied.

## 2. Experimental procedures

### 2.1. Synthesis

Polycrystalline samples (2 g) of $Ba_2Cu_{1-x}Mn_xGe_2O_7$, with $x$=0, 0.1, 0.25, 0.5, 0.75, 0.9 and 1, were prepared by standard solid state reaction. As starting materials, $BaCO_3$ (Sigma Aldrich 99.999%), CuO (MV Laboratories 99.9999%), $MnCO_3$ (99.99% Alfa Aesar) and $GeO_2$ (Alfa Aesar, 99.99%) were used. These starting materials were weighed out in a stoichiometric ratio and well mixed in an agate mortar. The $Ba_2Cu_{1-x}Mn_xGe_2O_7$ mixtures, pressed into pellets, were placed in an alumina crucible and heated at 880 °C, 950 °C and 980 °C for 15 h each, with intermediate grindings. For $x \geq 0.75$ an additional step at 1050 °C again for 15 h was also performed.

### 2.2. Characterization

Wide-angle X-ray diffraction (WAXD) patterns were obtained by an automatic Bruker D8 Advance diffractometer, in reflection, at 35 kV and 40 mA, using the nickel filtered Cu-Kα radiation. The data were collected by step-scanning in the angle range of $10° \leq 2\theta \leq 65°$ at a step size of 0.02°. The morphology of the samples was inspected by scanning electron microscopy (SEM) (LEO, model EVO 50), and the compositional homogeneity of synthesized pellets was checked by energy dispersive spectroscopy (EDS).

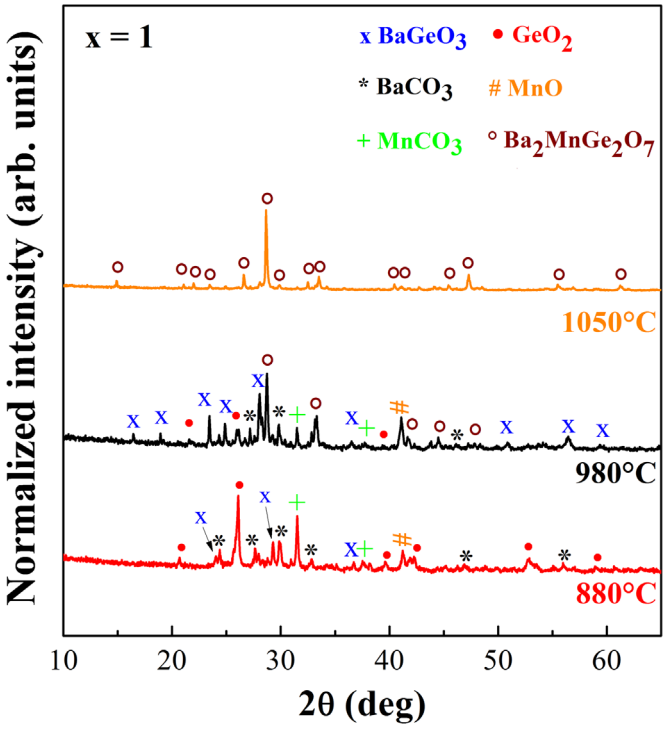


**Fig. 1.** Comparison of normalized XRD patterns of BMGO samples processed at different temperatures. For the sake of clarity the patterns have been shifted. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article).

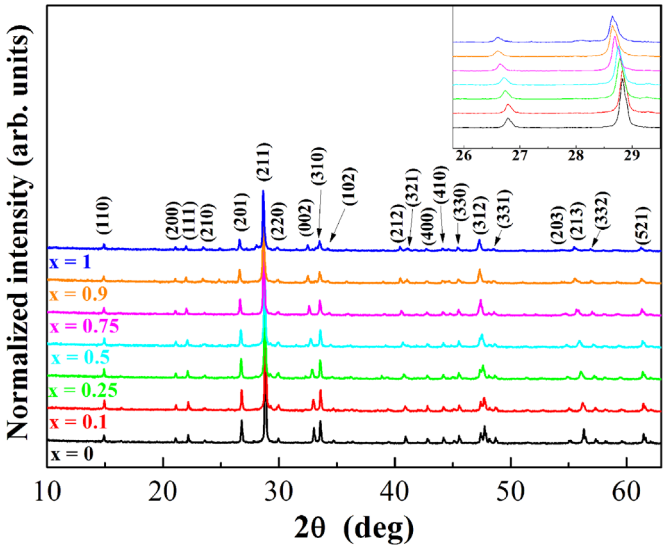


**Fig. 2.** XRD patterns of $Ba_2Cu_{1-x}Mn_xGe_2O_7$ compounds ($x$=0, 0.1, 0.25, 0.5, 0.75, 0.9, 1). In the upper panel a zoom of XRD data shows the systematic shift of the peaks.

## 3. Results and discussion

The synthesis of the BTGOs ($T$=Cu, Mn), despite the structural analogies of these oxides, proved to be surprisingly different case by case.

Heating temperature is found to be a crucial parameter for this kind of process. Fig. 1 shows the XRD patterns of pure BMGO samples processed at different temperatures: 880 °C, 980 °C and 1050 °C. The sample heated at the lowest temperature is not a single phase and its color is dark green, due to the presence of a little amount of MnO formed in situ from the decomposition of its carbonate. The use of $MnCO_3$ was chosen instead of the others Mn oxides ($Mn_2O_3$ or $MnO_2$), differently from what have been reported in previous works [28,29]. Employing $MnCO_3$ the oxidation state of the manganese must not change during the synthesis process.

Indeed, at the lowest temperature, the BMGO phase is almost absent, whereas in addition to unreacted $GeO_2$, $MnCO_3$ and $BaCO_3$, $BaGeO_3$ and MnO form. The persistence of the manganese carbonate at this temperature, much higher than its decomposition temperature, is unexpected. However, it is possible that inside the pellets, $CO_2$ can not flee out and thus accumulate preventing the