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Thermal expansion of Ti-substituted barium hexaferrite

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Thermal expansion measurements in the range of 20–500 °C were carried out on both polycrystalline and single crystalline samples of the hexagonal magnetoplumbite ferrite with composition BaTiFe$_{11}$O$_{19}$. The continuous scanning of the thermal expansion reveals the existence of a $\lambda$-type anomaly near the Curie temperature. In contrast to the usual observed anisotropic behavior for magnetoplumbite hexaferrites, the averaged thermal expansion coefficient for the $a$ direction is larger than for the $c$ direction, i.e., $12.8 \times 10^{-6}$ and $9.5 \times 10^{-6} \degree C^{-1}$, respectively.

Hexagonal ferrites MFe$_{12}$O$_{19}$ (M=Ba, Sr, or Pb) with the magnetoplumbite structure are widely used as permanent magnet materials due to the rather good energy product–cost ratio but there is also an increasing interest in using these materials as magnetic and magneto-optic recording media, as well as in microwave devices. Up until now the magnetic properties of these materials related to permanent magnet applications have been mainly tailored by the microstructure and not by chemical substitutions.

However, chemical substitutions are more suitable for improving the performance of these materials for magnetic recording media. Recent studies on Ti-substituted BaFe$_{12}$O$_{19}$ have shown that Ti substitution strongly affects the magnetic properties.$^{1–3}$ For instance, an enhancement of the magnetic anisotropy was found for small concentrations of Ti in the system BaFe$_{12-x}$Ti$_x$O$_{19}$ ($x=0.2$), whereas for higher concentrations (Ti~1.0) the anisotropy decreases with progressive Ti substitution.

In a number of cases, the hexagonal ferrites have to be grown as thin films to be used in the above mentioned applications. The coefficient of thermal expansion is an important physical parameter in the growth of films, in order to ensure the suitability of the substrate employed.$^{4}$ In this paper we report the results of the continuous scanning of the thermal expansion on Ti-substituted barium ferrite with composition BaFe$_{11}$TiO$_{19}$. Keeping in mind the anisotropy of the hexagonal structure, measurements on single crystalline specimens in both parallel and perpendicular directions to the $c$ axis were performed, as well as on a polycrystalline sample.

Polycrystalline bars were prepared by a ceramic technique which includes several preheating and ball milling stages and finally isostatically pressing followed by sintering at 1350 °C in 10$^{-3}$ atm oxygen. X-ray diffraction measurements confirm that the material is a single phase magnetoplumbite with lattice parameters $a=5.885 \pm 0.001$ Å and $c=23.290 \pm 0.005$ Å.

Single crystals of BaFe$_{11}$TiO$_{19}$ were prepared by a recrystallization process of the polycrystalline bars based on a floating zone technique using an arc-image furnace.$^5$ In contrast to pure BaFe$_{12}$O$_{19}$, the ferrite BaFe$_{11}$TiO$_{19}$ melts congruently, which enables us to grow large single crystals without additional flux in the molten zone.$^3$ The lattice parameters of the single crystals turned out to be within experimental error equal to the polycrystalline parameters. From the as-grown single crystalline ingots, rectangular bars, $2 \times 2 \times 20$ (resp. 7) mm, were cut along the $a$ (resp. $c$) directions, and used as samples for the thermal expansion measurements.

Thermal expansion measurements have been carried out on both polycrystalline and single crystalline samples in the temperature range of 20–500 °C using a dilatometer based on a differential transformer as the displacement recording system. In order to prevent oxidation of the samples and hence avoid changes in the defect content, the measuring process was performed in an inert N$_2$ atmosphere. For each sample the measurement has been carried out several times in order to ensure the reliability of the results.

In Fig. 1 the thermal expansion traces determined in the $c$ and $a$ directions as well as the results for the polycrystalline samples are plotted. As can be seen, the thermal expansion is not linear, which is primarily caused by the magnetic contribution to the thermal expansion. In Fig. 2, the temperature dependence of the thermal expansion coefficients is shown, which clearly reveals the $\lambda$ anomaly, with a maximum value of the expansion coefficient near the Curie temperature (325 °C). The thermal expansion coefficients were calculated using the approach given in Ref. 6 from the derivation of the experimental curves of Fig. 1.

Similar anomalous temperature dependences of the thermal expansion coefficients were already reported for unsubstituted isotropic polycrystalline BaFe$_{12}$O$_{19}$ (Ref. 7) and for magnetically oriented polycrystalline SrFe$_{12}$O$_{19}$ in the direction of orientation and perpendicular to it.$^8$ The measurements on the oriented SrFe$_{12}$O$_{19}$ are also indicative of the anisotropic thermal expansion in the $a$ and $c$ directions, with a larger expansion in the $c$ direction of about 20%. Compa-
rable results concerning the anisotropy and the \( \lambda \) anomaly were reported for the temperature dependence of the lattice parameters of unsubstituted \( \text{BaFe}_{12}\text{O}_{19} \) with a slightly larger expansion in the \( c \) direction of about 4% over a total temperature range of 20–600 °C.\(^9\)

More recently,\(^4\) a larger anisotropy of about 22% was reported for \( \text{BaFe}_{12}\text{O}_{19} \), but from the experimental data no temperature dependence of expansion coefficient could be revealed, which must be due to the resolution of the experimental technique used by these authors. The thermal expansion coefficients along the \( a \) and \( c \) directions were reported to be \( 10.0 \times 10^{-6} \text{ (%) C}^{-1} \), and \( 12.2 \times 10^{-6} \), respectively.\(^4\) In contrast with the available data in literature on \( M \) hexaferrites,\(^4,7–9\) our results for \( \text{BaFe}_{11}\text{TiO}_{19} \) indicate just a lower thermal expansion in the \( c \) direction. For the thermal expansion coefficient averaged over the temperature range of 20–500 °C values of \( 12.8 \times 10^{-6} \) and \( 9.5 \times 10^{-6} \) were found for the \( a \) and \( c \) direction, respectively. Compared with pure \( \text{BaFe}_{12}\text{O}_{19} \), the composition of our investigated hexaferrite is not so different that one could expect a drastic change in the lattice thermal expansion. Indeed, the data for \( \text{BaFe}_{12}\text{O}_{19} \) above the Curie temperature given in Ref. 9 may be considered as the lattice thermal expansion, which show that the lattice thermal expansion contribution in the \( c \) direction is lower than in the \( a \) direction in agreement with our findings. In addition, the consistency of our results is supported by the value obtained for the polycrystalline sample. For a random crystallite orientation in this sample, the longitudinal expansion measured involves the contribution of a third of crystallites whose \( c \) axis is aligned with the measuring direction and two thirds perpendicular to it. The averaged thermal expansion coefficient of \( 12.0 \times 10^{-6} \text{ (%) C}^{-1} \) found for the polycrystalline sample agrees rather well with this model.

The discrepancies in the thermal expansion below the Curie temperature between the present and literature data must then be due to the magnetic contribution to the thermal expansion. The substitution of \( \text{Fe}^{3+} \) by \( \text{Ti}^{4+} \) means also that an equivalent amount of \( \text{Fe}^{2+} \) ions are introduced in the lattice. According to Ref. 10 the \( \text{Ti}^{4+} \) ions occupy preferen-

\[ a(10^6 \text{ °C}^{-1}) \]

\[ \begin{array}{c|c|c}
\text{Temperature (°C)} & \text{a-axis} & \text{c-axis} \\
\hline
20 & a1 & c1 \\
50 & a2 & c2 \\
100 & a3 & c3 \\
200 & a4 & c4 \\
500 & a5 & c5 \\
\end{array} \]

FIG. 1. The temperature dependence of the thermal expansion coefficient of \( \text{BaFe}_{11}\text{TiO}_{19} \) along the \( a \) and \( c \) axis and for an isotropic polycrystalline sample.
film and substrate. The thermal expansion data for the pure M ferrites\(^4\) are not representative for the magneto-optical materials.
