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SYNTHESSES OF AMORPHOUS AND "ORTHORHOMBIC" GIG

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Résumé.- Le GIG (Gadolinium Iron Garnet) amorphe qui ne contient aucun des oxydes ordinaires formant habituellement les verres (B₂O₃, SiO₂ ou P₂O₅) est obtenu par le refroidissement rapide. Le spectre Mössbauer du GIG amorphe présente deux maxima à la température ambiante, tandis qu'à 4,2 K on obtient un sextuplet symétrique correspondant à un champ hyperfin de 460 kOe. 

Abstract.- Amorphous GIG (Gadolinium Iron Garnet) whose constituent contains none of the usual glass-forming oxides such as B₂O₃, SiO₂ or P₂O₅, was obtained by rapid quenching. The Mössbauer spectrum of the amorphous GIG at room temperature was a doublet, while the spectrum at 4.2 K was a symmetrical six-finger pattern due to a hyperfine field, 460 kOe.

1. Introduction.- Recently magnetic behaviors of amorphous alloys or oxide glasses have been examined /1/. However, there is only little informations on the amorphous state of magnetic materials whose main constituent is such a magnetic oxide as FeO, Fe₃O₄, or Fe₂O₃. The purpose of the present study is to prepare amorphous GIG without the usual glass forming oxide such as B₂O₃, SiO₂ or P₂O₅ and examine magnetic properties. The crystallization process of amorphous GIG was examined by DTA, X-ray and magnetic balance measurements.

2. Sample preparation.- A small piece of the sintered GIG (enriched ⁵⁷Fe) pellet was melted with focused CO₂ gas laser beam. The molten GIG was then rapidly quenched by the piston and anvil method /2,3/. The obtained specimen was a thin black sheet, about 10μm in thickness. X-ray diffraction pattern of the specimen showed diffused halos characteristic of an amorphous state.

3. Results and discussion.- 3.1. Amorphous state of GIG.- The spectrum of amorphous GIG at room temperature (Fig. 1A) exhibits a doublet due to a quadrupole interaction (ΔE=1.0 mm/s) and no sign of magnetic ordering. The spectrum at 4.2 K (Fig. 2) is a symmetrical six fingers pattern due to a hyperfine field (H₁=460 kOe). The broadening of Mössbauer spectrum at 4.2 K seems to be caused by a random orientation of the magnetic and EFG principal axes. No significant difference was found between the Mössbauer spectra at 77 K and room temperature. The magnetic ordering temperature of amorphous GIG was between 4.2 K and 77 K, the temperature being very much lower than that of cubic GIG (564 K) /4/.

Magnetization of amorphous GIG was also measured at the temperature range 77 K to 1100 K in helium gas atmosphere.

![Image of Mössbauer spectra measured at various temperatures]

On heating, the magnetization of amorphous GIG was considerably smaller than that of cubic GIG. The inverse susceptibility of amorphous GIG obeyed a Curie-Weiss law with an asymptotic Curie temperature (θ=-170 K).

3.2. Crystallization process of amorphous GIG.- The DTA measurements were carried out at a heating rate...
of 10 K/min. from room temperature to 1573 K under a flow of argon gas or air.

An exothermic peak due to crystallization was observed at 915 K (in argon gas) and 1005 K (in air), respectively.

X-ray diffraction pattern of sample treated in air above the exothermic peak was cubic GIG and heat treated in argon gas was orthorhombic, GdFeO$_3$ type structure, respectively. The lattice constants of the orthorhombic phase are a little smaller than those of the compound GdFeO$_3$. This compound, orthorhombic GIG, was turned to cubic GIG when heated at 1473 K in air. The relation of cubic, amorphous and orthorhombic GIG at 1473 K is illustrated in figure 3. The magnetization of orthorhombic GIG exhibited a ferrimagnetic behavior ($T_c=850 K$).

The deficiency of oxygen seems to have an important role in stabilizing the metastable orthorhombic phase. The ferrous ion was detected by chemical analysis, but there was no sign of the ferrous ion in amorphous and orthorhombic GIG through Mössbauer measurement at room temperature. It seems that the electrons of iron atoms move quickly between ferric and ferrous ions like hopping electrons in magnetite above Verwey ordering temperature.

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