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Comparison of the magnetic properties of $Mn_3Fe_2Si_3O_{12}$ as a crystalline garnet and as a glass

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ABSTRACT

The crystalline garnet $Mn_3Fe_2Si_3O_{12}$ and an amorphous phase of the same nominal composition are synthesized at high pressure. The magnetic properties of the two forms are reported. Both phases order antiferromagnetically. The crystalline phase exhibits a Curie-Weiss theta of −37.2 K, with a sharp ordering transition at 12 K. The glassy phase exhibits a larger antiferromagnetic Curie-Weiss theta, of −89.7 K, with a broad ordering transition observed at 2.5 K. The amorphous phase shows a much higher degree of magnetic frustration than the crystalline phase; it exhibits spin-glass behavior and is determined to have an actual composition of $Mn_3Fe_2Si_3O_{13}$.

1. Introduction

A geometrically frustrated magnet is a material whose structural geometry inhibits long-range magnetic ordering [1]. The archetypical examples are materials whose unpaired electrons interact antiferromagnetically and are on the corners of a triangular lattice, but other geometries can also lead to frustration of antiferromagnetically coupled spins. Random arrangements of spins in a solid can also lead to the inhibition of long range magnetic ordering due to the distribution of magnetic interactions present. In both cases, magnetic ordering often does not emerge until significantly below the Weiss temperature. For crystalline solids, one of the interactions often dominates and a long range ordered state is obtained at low temperatures, while in amorphous solids, a "spin glass" is often observed at low temperatures. Magnetically frustrated phases are of significant scientific interest, as long-range magnetic ordering is among the most common electronic ground states, and hindering it allows for the observation of a number of unusual and interesting properties [1–5].

The garnet crystal structure, which can be generalized as belonging to the form $A_3B_2C_3O_{12}$, has long served as an interesting materials platform. Garnets often easily form solid solutions, and a wide variety of atoms can fit on the *A*, *B*, and *C* sites, leading to an enormous number of possible combinations [6]. One particularly fruitful area of research has been the study of garnets containing magnetic atoms. These garnets can exhibit a wide variety of unusual properties, with examples of geometrically frustrated magnetism [7,8], ferrimagnetism [9], spin glass [7], and spin liquid [2] reported. Geometric magnetic frustration can be found in garnets when the magnetic atoms decorate the *A* sublattice, as that lattice is made of corner sharing triangles [6].

While many garnets of interest occur in nature, many others are uncommon. In addition, many garnets form solid solutions of variable composition. One such example is the garnet calderite ($Mn_3Fe_2Si_3O_{12}$), which occurs naturally in solid solution with the garnet spessartine ($Mn_3Al_2Si_3O_{12}$); the pure Fe case has yet to be found in nature with no Al present [10,11]. As the formation conditions for calderite are of interest in minerology, there have been multiple publications on the synthesis and structure of this material [11–14], although a study of its magnetic properties has apparently not been previously reported. As the $Mn_3Fe_2Si_3O_{12}$ garnet contains two different magnetic atoms (i.e. Mn^{2+} and Fe^{3+}) in distinct structural positions (i.e. the *A* and *B* sites in the garnet), we can expect potentially interesting magnetic properties due to a balance of magnetic interactions. Extending our previous work on the crystalline and amorphous forms of the spessartine garnet $Mn_3Al_2Si_3O_{12}$, which has one magnetic species present [15], we have been able obtain both crystalline and amorphous phases for the Mn-Fe-Si-O garnet system. We report here the basic magnetic properties of the calderite garnet, as well as the synthesis and basic magnetic properties of a previously unreported amorphous phase of the same nominal composition.

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2. Experimental

2.1. Synthesis

Crystalline and amorphous forms of nominal composition $Mn_3Fe_2Si_3O_{12}$ were synthesized at a pressure of 6 GPa using a Rockland Research Corp. cubic multi-anvil cell. The amorphous phase was synthesized by grinding stoichiometric amounts of Fe_2O_3 (99.85%, Alfa Aesar), SiO_2 (99.8%, Alfa Aesar), and MnO_2 (99.8%, Fisher) with an agate mortar and pestle. The mixture was loaded into a boron nitride (BN) crucible and placed in a pyrophillite sample cube with a graphite furnace, which was pressurized to 6 GPa. The sample was then heated to 1100 °C for 30 min, and quenched to room temperature. Small amounts of impurities were found to form at the sample-crucible boundary; these were mechanically removed and do not influence our measurements. The resulting sample was in the form of a hard, glossy pellet with a dark yellow-tinted brown color.

The crystalline garnet $Mn_3Fe_2Si_3O_{12}$ was synthesized according to the procedure reported by Lattard and Schreyer [11]. A stoichiometric mixture of Fe_2O_3 (99.85%, Alfa Aesar), SiO_2 (99.8%, Alfa Aesar), and Mn_2O_3 (99.99%, Cerac) was placed into a sealed gold crucible. The gold crucible was then placed within a larger BN crucible, and the space between them was packed with a mixture of Fe_2O_3 and Fe_3O_4 to act as an oxygen buffer. The crucible was placed in a sample cube and pressurized to 6 GPa. It was then heated to 700 °C for 72 h, before being quenched to room temperature. The resulting sample was an inhomogeneous mixture of the silicate garnet and a number of metal-oxide impurities. These impurities were removed by heating the sample in concentrated hydrochloric acid for 2 h, and then washing with water. The resulting polycrystalline powder was a light yellow color, appearing almost white when ground.

2.2. Characterization

Room-temperature powder X-ray diffraction (PXRD) measurements were taken using a Bruker D8 Advance Eco diffractometer with a LynxEye-XE detector using Cu *Kα* radiation ($\lambda = 1.5418$ Å). Preliminary phase identification was performed using the Bruker EVA program. Zero-background measurements were taken on a polished Si wafer sample holder. A Rietveld refinement of the crystalline garnet was performed using the FullProf Suite. Magnetization measurements were taken with a Quantum Design Physical Property Measurement System (PPMS) Dynacool in the vibrating sample magnetometer configuration. The field-dependent magnetization for both forms was measured at 2 K. DC magnetic susceptibility measurements were taken between 1.8 K and 300 K in an applied field of 10,000 Oe, and the resulting data was fit using the Curie-Weiss Law. A background correction was made to the raw susceptibility data by taking an identical measurement on an empty sample holder with an empty space of the same volume as the sample. Thermogravimetric analysis was carried out using a TA Instruments SDT Q600, under a flowing atmosphere of 5% H_2 and 95% argon (Airgas).

3. Results and discussion

The X-Ray diffraction pattern of the crystalline garnet $Mn_3Fe_2Si_3O_{12}$ was found to closely match previously reported patterns [13,16]. A small amount of impurity can be observed, which is believed to be coesite, a high-pressure polymorph of SiO_2. A Rietveld refinement on the sample was employed to determine a lattice constant *a* of 11.82239(2) Å, in good agreement with the published value of 11.8288 Å [13,16]. Other resulting structural parameters can be seen in Table 1. The XRD pattern of the glassy phase of nominal composition $Mn_3Fe_2Si_3O_{12}$ on a single crystal miscut silicon zero-background sample holder shows a large, broad hump, with no peaks corresponding to the crystalline garnet phase visible. One small, relatively broad peak can be observed near 27°, which appears to be a polymorph of SiO_2 and does not correspond to any known potential transition-metal-containing impurity phases. The results of the Rietveld refinement and the pattern of the glassy phase can be observed in Fig. 1.

Table 1
Results of Rietveld refinement of the crystalline form of $Mn_3Fe_2Si_3O_{12}$ at ambient temperature, space group *Ia-3d* (No. 230), lattice parameter $a = 11.82239(2)$ Å. R_f factor = 7.30, $R_p = 9.71$, $R_{wp} = 12.4$, $\chi^2 = 1.28$.

Atom	Wyckoff site	*x*	*y*	*z*	B_{iso}
O^{2-}	*96 h*	0.04249(50)	0.05455(42)	0.65636(75)	2.71(15)
Fe^{3+}	*16a*	0	0	0	3.63(13)
Mn^{2+}	*24c*	.125	0	.25	3.16(9)
Si^{4+}	*24d*	.375	0	.25	2.06(15)

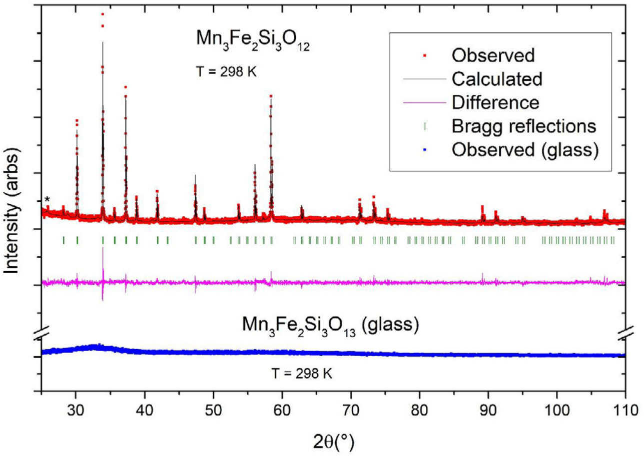

Fig. 1. Rietveld refinement of the crystalline phase of $Mn_3Fe_2Si_3O_{12}$ (red) for 2 θ between 25° and 110°. The pattern of the glassy phase is below, in blue. The small peak indicated with an asterisk corresponds to coesite (SiO_2). The region between 5° and 25° is obstructed by a large air scattering signal and has been removed from this image.

The temperature-dependent magnetic susceptibility and field dependent magnetization of the crystalline form of $Mn_3Fe_2Si_3O_{12}$ can be seen in Fig. 2. The temperature-dependent susceptibility shows a clear magnetic transition, with a sharply-defined local maximum peak, at 12 K. The high-temperature region of the inverse susceptibility (200 K–300 K) was fit to the Curie-Weiss law, $\chi - \chi_0 = C/(T - \theta_W)$, where χ is the magnetic susceptibility, χ_0 is a temperature-independent contribution, C is the Curie Constant, and θ_W is the Weiss Temperature. Inverse susceptibility was fit with a temperature-independent contribution χ_0 of -0.001 emu mol^{-1}. The resulting fit produces a Curie constant (C) of 21.4 and a Weiss temperature (θ_W) of -37.2 K (Table 2), suggesting that the observed local maximum in the susceptibility is an antiferromagnetic ordering transition. $Mn_3Fe_2Si_3O_{12}$ therefore displays a small frustration factor ($f = \theta_W/T_N$) of approximately 3, significantly less than the value of 10 which is frequently employed as a guideline to indicate strongly frustrated magnetism [1]. As there are 5 magnetic ions per formula unit, the effective magnetic moment per ion, μ_{eff}, was determined by the relationship $\mu_{eff} = \sqrt{8C/5}$, and was thus found to be 5.9 μ_B/ion, extremely close to the average of the spin-only values for the free ions (Fe^{3+} and Mn^{2+}; 5.92 μ_B/ion). It can be clearly observed that below the antiferromagnetic transition, as the temperature decreases, the susceptibility increases once more. This low temperature upturn is attributed to a very small number of paramagnetic impurities in the garnet. The susceptibility vs applied field at 2 K shows a slight curvature below 20,000 Oe but is essentially linear for all higher fields, with no signs of saturation.

The same measurements were performed on a sample of the amorphous phase. These are presented in Fig. 3. Unlike the crystalline