NUCLEAR RESPONSE AND PHASE TRANSFORMATION
MELT GROWN, SbI₃-DOPED HgI₂*

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ABSTRACT

Slow solidification of 1.5 wt.% SbI₃-doped HgI₂ yielded a large-grained polycrystalline boule which in thin section exhibited transparent areas. When these areas were contacted with aquadag, a nuclear radiation counter was produced which showed severe polarization effects. Slow solidification of undoped HgI₂ had no transparent areas. Detectors fabricated from sliced sections of that boule gave no response to nuclear radiation. In a crystallographic and a thermodynamic study of SbI₃-doped HgI₂, it was found that an orange-colored high-temperature phase, which is crystallographically identical to the known yellow phase, appeared in all SbI₃-doped HgI₂ samples.

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1. INTRODUCTION

Mercuric iodide single crystals which are used for the fabrication of nuclear radiation detectors operating at room temperature are grown mainly from the vapor phase^{1,2} and occasionally from solution.³

Detectors fabricated from vapor grown HgI_2 crystals usually give very good nuclear radiation spectra. Detectors fabricated from platelets⁴ are limited by their small active size ($2 \times 2 \times 0.4 \text{ mm}^3$) and irregular shape. Large crystals can be grown only by the temperature oscillation method or by solution growth. Both methods, however, are time-consuming, requiring a period of about one month to grow a single crystal of 100g. Growth from the melt, which could produce large crystals ($20 \times 20 \times 10 \text{ mm}^3$) in a much shorter time, is considered to be impossible.

since HgI_2 undergoes a destructive phase transformation^{5,6} when cooled from the yellow orthorhombic phase to the red tetragonal phase at about 130°C. The red to yellow phase transformation on the other hand is nondestructive, and the transparent red crystals transform to transparent yellow crystals. This, of course, is not helpful for the crystal growth of the room-temperature red phase.

The phase transition temperature is sensitive to small changes in HgI_2 stoichiometry, to impurities, to powder particle size,⁵ and to internal stresses built into the grown material. All known dopants of HgI_2 such as Cl and Ag^{7,8} give rise to a very sharp red to yellow transformation. However, upon heating SbI_3 -doped HgI_2 , a red to orange color change was visually observed. The already known orange phase that has been obtained from the vapor⁹ and solution¹⁰ has tetragonal symmetry and a superlattice structure with lattice constants $a = 8.776\text{\AA}$ and $c = 24.723\text{\AA}$.¹¹

In order to understand the feasibility of the melt growth of HgI_2 doped with SbI_3 , samples with various concentrations of SbI_3 were prepared and crystals from the melt were grown by slow cooling. The nuclear radiation response and the thermodynamics of the phase transformation were studied by visual observation, differential thermal analysis, and x-ray powder diffraction.

2. MATERIAL PREPARATION AND CRYSTAL GROWTH

Baker commercial reagent grade HgI_2 was purified by repeated sublimations.¹² Various amounts of The British Drug House 99% pure SbI_3 were mixed with the purified HgI_2 in amounts of 0.5, 1.0, 1.5 and 2.0 wt.%, heated above the SbI_3 melting point and rapidly cooled to room temperature under conditions of uniaxial solidification. The concentration of SbI_3 in the samples was verified by emission spectroscopy. Some contamination of the order of several ppm, consisting mainly of Si, B, Cu, Mg and Al, was found in the molten powders.

1.5 wt.% SbI_3 -doped HgI_2 was molten in a 20-mm-diameter tipped pyrex glass ampoule and uniaxially solidified by slow cooling at a rate of 2°C/h . The boule thus obtained was polycrystalline but had transparent regions. Several thin sections of thicknesses between 300 and 700 microns were solution sawn and polished. Aquadag contacts were applied to the transparent regions over an area of 4 mm^2 .

3. NUCLEAR RESPONSE

Detectors having dimensions of $10 \times 10 \times 0.5\text{ mm}^2$ with a contact area of 4 mm^2 were fabricated from 1.5 wt.% SbI_3 -doped and undoped melt-grown HgI_2 . They were tested for their nuclear response with a system consisting of an HV-power supply, a charge-sensitive preamplifier, a linear amplifier, and a multichannel analyzer. The SbI_3 -doped, melt-grown HgI_2 detectors were biased at 30 V. They showed no spectral resolution but did detect the 60 keV radiation of ^{241}Am (see Fig. 1) and the 122 keV radiation of ^{57}Co . The counting rate within the energy window containing 90% of the counts was measured as a function of time. The count rate decreased by a factor of 10 in one hour and remained stable afterwards, as shown in Fig. 2. This indicates a strong polarization effect in 1.5 wt.% SbI_3 -doped HgI_2 grown from the melt as compared to undoped vapor-grown HgI_2 ¹⁴.

An attempt to fabricate detectors from undoped HgI_2 grown by slow solidification from the melt was unsuccessful. The detectors showed no nuclear response when exposed to gamma radiation even when biased at 2000 V.

4. PHASE-TRANSFORMATION STUDY

It was found that upon heating SbI_3 -doped HgI_2 an orange-colored phase appeared instead of the expected yellow phase. The appearance of this orange phase was investigated kinetically and crystallographically.

5. KINETICS

The solid state and solid-to-liquid phase transitions were measured in the following way. Samples were sieved to obtain a uniform particle size between 100 and 150 mesh and thus to avoid the particle size dependence of the phase transition^{4,5}. They were then introduced into a modified capillary melting point apparatus.⁴ The solid state transition temperature was established by observing the color change of the powder samples from red to yellow, while the apparatus was heated at a rate of $0.2^\circ\text{C}/\text{min}$. This heating rate was found to be the most sensitive for phase transition observations. The temperature at which 50% by volume of the material has transformed was taken as the solid state transition temperature. The melting point was measured in a similar way; the appearance of the first liquid droplets was recorded and the shrinkage of the solid phase during melting was plotted as a function of temperature. This is represented in an S-curve in Figure 3a.

Measurements of undoped HgI_2 and HgI_2 doped with dopants such as Ag and Cl showed a sharp red to yellow transition at about 130°C . However, HgI_2 doped with 0.5 to 2.0 wt.% SbI_3 behaved completely differently upon slow heating ($0.2^\circ\text{C}/\text{min}$) from room temperature to the melting point. The red color of HgI_2 changes gradually above 130°C to a reddish-orange color which can clearly be distinguished from the red HgI_2 . All material changes back to deep red at around 230°C just below the melting point. The melting points evaluated from the S-curves decreased monotonically as the SbI_3 concentration increased from 0.5 to 2.0 wt.% SbI_3 , as shown in Fig. 3b.

Since the red to orange transition temperature cannot be obtained by visual observation, the transformation was followed by differential thermal analysis (DTA). SbI_3 -doped HgI_2 samples showed a broad endothermal peak compared to undoped HgI_2 .

To determine the transition temperature of SbI_3 -doped HgI_2 , undoped HgI_2 was used as a reference instead of the standard Al_2O_3 reference (Fig. 4a and 4b). By this method the transformation of the undoped HgI_2 reference will apparently appear as an exothermal peak. As can be seen in Fig. 4b, the transitions in the doped samples occur at a higher temperature, and the heat of transformation is considerably smaller than in undoped HgI_2 . This may indicate a less destructive transformation of the yellow to red phase in SbI_3 -doped HgI_2 crystals, which could explain the nuclear radiation response capability of SbI_3 -doped HgI_2 and the lack of response of undoped HgI_2 grown from the melt by slow solidification.

6. CRYSTALLOGRAPHY

X-ray diffraction analysis was carried out on powder samples using a GE Debye-Scherrer camera with Ni-filtered Cuka radiation. The powders were prepared by gently crushing polycrystalline samples in a mortar, sieving them through a 325 mesh grid and sealing them in glass capillaries of 0.3 mm in diameter under vacuum (50 microns of Hg). A small heating stage was built for the GE camera, consisting of a nichrome filament closely attached to the irradiated capillary. The exposure time of each run was approximately 6 hours. The experimental diffraction data were compared with calculated data from known HgI_2 standards using a computer code for (hkl)-indexing¹³. The x-ray analysis results summarized in Table 1 indicate that the orange phase of HgI_2 doped with 1.5 wt.% SbI_3 is crystallographically identical to the yellow phase, or consists of a mixture of the red and yellow phases at the transition temperature. The tetragonal phase of orange HgI_2 with a super-structure as observed by Schwarzenbach¹¹ or the orange cubic phase as observed by Jeffrey and Vlasse¹⁰ could not be found. The room temperature diffraction studies of samples doped with 0.5 to 2.0 wt.% SbI_3 showed no change in the tetragonal unit cell dimensions within the error of measurement (see Fig. 5).

7. CONCLUSIONS

The present study showed for the first time the possibility that SbI_3 -doped HgI_2 melt-grown crystals may be used as gamma radiation counters at higher energies (about 100 keV). At present, the detector crystals still show a strong polarization effect. The fact that doping HgI_2 with SbI_3 produces an orange-colored phase at elevated temperatures is interesting and should be studied further. Despite the fact that this orange phase is crystallographically identical to the known yellow phase, the phase transition seems to be less destructive when the orange colored phase is present. This assumption is supported by observations that the heat of transformation in SbI_3 -doped HgI_2 is by a factor of 10 less than in undoped HgI_2 , and that undoped melt-grown HgI_2 crystals which do not exhibit an orange phase could never be fabricated into nuclear detectors.

8. ACKNOWLEDGMENTS

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Table 1. Comparison between undoped commercial "Baker" HgI_2 with doped (1.5% SbI_3) purified HgI_2 .

Temperature	Room Temp.		Transition		Above Transition	
Material	Baker 0 wt% SbI_3	1.5 wt% SbI_3	Baker 0 wt% SbI_3	1.5 wt% SbI_3	Baker 0 wt% SbI_3	1.5 wt% SbI_3
Color	Red	Red	Red + Yellow	Red + Orange	Yellow	Orange
Symetry	Tetragonal		Tetragonal + Orthorhombic		Orthorhombic	
Lattice parameter(Å)	a = 4.37 c = 12.44		Mixture		a = 4.70 b = 7.43 c = 13.87	

FIGURE CAPTIONS

- Figure 1. Nuclear response of an HgI_2 detector produced from a 1.5 wt.% SbI_3 -doped crystal grown from the melt.
- Figure 2. Counting rate vs. time of the detector described in Figure 1.
- Figure 3. Melting percent vs. temperature represented on a typical "S" phase transformation curve.
- (a) Actual "S" curves
 - (b) The 50% melting point read from the "S" curve as a function wt.% SbI_3 in HgI_2 .
- Figure 4. Typical DTA curves of HgI_2 .
- (a) HgI_2 vs. Al_2O_3 standard of various SbI_3 concentrations
 - (b) HgI_2 :1.5% SbI_3 vs. HgI_2 :0% SbI_3
- Figure 5. Variation of the unit cell dimensions of HgI_2 with the amount of doping of SbI_3 .
- 0 "a" axis
 - 0 "c" axis

Figure 1

S-206-TP

Figure 2

S-206-TP

Figure 3

S-206-TP

Figure 4

S-206-TP

Figure 5

S-206-TP