

Figure 2. Response of the 532-nm second harmonic signal intensity $I^{2\omega}$ of a Disperse Orange 1-epoxy film to curing time, temperature, and electric poling field. The time ordinate gives total accumulated curing time while the arrows indicate the time of removal of the 4.8×10^4 V/cm poling field. Not shown: The temperature was returned to 88 °C and the poling field reapplied after each experimental sequence.

in more fluid examples (e.g., Figure 2a,b), the relatively rapid response at higher cross-linking levels (Figure 2c,d) indicates significant residual orientational mobility (at least over relatively small angular excursions and at 88 °C—vide infra). For lightly cross-linked samples, removal of the poling field results in a precipitous drop in $I^{2\omega}$, followed by a leveling-off (Figures 2a,b). As the matrix cross-linking process progresses, the magnitude of the room-temperature zero-field decline steadily decreases, and $I^{2\omega}$ at the leveling-off point correspondingly increases. An attractive explanation for this behavior, which is in accord with the bimodal $d_{33}(t)$ data (vide supra), invokes a decreasing component of the free-volume distribution greater than the critical threshold for chromophore reorientation as the degree of matrix cross-linking increases. That $I^{2\omega}$ in Figure 2d responds rapidly to the temperature drop but not to the removal of the poling field can be explained by the closer temperature proximity of the former process to the matrix T_g (ca. 70–75 °C).

These results demonstrate that polymeric frequency-doubling guest-host materials with improved temporal stability can be formed by orienting/immobilizing NLO chromophores within chemically cross-linkable matrices. Moreover, the fluid character of the non-cross-linked precursor solution suggests the possibility of novel processing/fabrication approaches. Beyond the realm of NLO materials, it is evident that such SHG studies also provide valuable information on free-volume and motional characteristics in cross-linkable polymers that complements information accessible via photoisomerization,^{4,13} electrochromism,¹⁶ and other probes.^{4c,7} Further studies of chemically based NLO chromophore immobilization processes are under way.

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Silver Substitution in $\text{Pb}_2\text{Sr}_2\text{Y}_{1-y}\text{Ca}_y\text{Cu}_3\text{O}_8$ ($y = 0, 0.25$)

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The position of Ag directly below Cu in group IB of the periodic table suggests that silver chemistry may provide a route to novel, high-temperature superconductors analogous to the now famous cuprate superconductors. In fact, some 20 years before the discovery of the superconducting cuprates the highly oxidized silver compounds $\text{Ag}^+[\text{Ag}_6\text{O}_8]\text{X}^-$ ($\text{X}^- = \text{NO}_3^-, \text{F}^-, \text{BF}_4^-$) were shown to be superconducting with transition temperatures of 1.04, 0.3, and 0.15 K, respectively.¹ However, few silver oxides are known because of thermal instability with respect to elemental silver. Compounds with Ag either as a ternary cation as in AgNbO_3 or as the active cation would be a source of potentially interesting materials. No cuprates with Ag as a ternary cation have been reported, and substitution of Ag for Cu in $\text{Ba}_2\text{YCu}_3\text{O}_7$ resulted in replacement of no more than 1.5 at. % of Cu by Ag.^{3,4}

This communication reports substantial Ag substitution for Cu in $\text{Pb}_2\text{Sr}_2(\text{Y,Ca})\text{Cu}_3\text{O}_8$, a class of cuprates with T_c 's as high as 70 K, recently discovered by Cava et al.⁴ The same series of cuprates was found independently by Subramanian et al.⁵ The structure of the prototype cuprate $\text{Pb}_2\text{Sr}_2\text{YCu}_3\text{O}_8$ is shown in Figure 1; it contains layers of corner-shared square-pyramidal $[\text{CuO}_5]$ units (Cu(2)) similar to those in $\text{Ba}_2\text{YCu}_3\text{O}_7$ separated by a bilayer of edge-shared square-pyramidal $[\text{PbO}_5]$ units in turn separated by linear two-coordinate Cu(1) atoms similar to those in $\text{Ba}_2\text{YCu}_3\text{O}_8$. The average oxidation state of copper in $\text{Pb}_2\text{Sr}_2\text{YCu}_3\text{O}_8$ is $+5/3$, consistent with formal copper oxidation states of +2 in the Cu(2) sheets and +1 for the linearly coordinated Cu(1) atoms. $\text{Pb}_2\text{Sr}_2\text{YCu}_3\text{O}_8$ is a semiconductor; superconducting phases are prepared by partial substitution of divalent ions for Y^{3+} , which results in a compensating oxidation of the Cu(2) sheets leaving the overall oxygen stoichiometry and the formal valence of the Cu(1) layers unchanged. The results described below prove that single-phase materials of composition $\text{Pb}_2\text{Sr}_2\text{YCu}_{3-x}\text{Ag}_x\text{O}_8$ can be prepared for $x \leq 0.55$ and that the silver in these materials occupies the linear Cu(1) sites of the $\text{Pb}_2\text{Sr}_2\text{YCu}_3\text{O}_8$ structure. It will be shown that chemical considerations substantially reduce the amount of silver that can be substituted into the superconducting phases $\text{Pb}_2\text{Sr}_2\text{Y}_{1-y}\text{Ca}_y\text{Cu}_3\text{O}_8$ ($y \leq 0.5$) but that some Cu/Ag substitution can be achieved with little effect on the superconductivity.

The silver-substituted phases $\text{Pb}_2\text{Sr}_2\text{YCu}_{3-x}\text{Ag}_x\text{O}_8$ ($0 \leq x \leq 0.55$) were prepared as follows: stoichiometric quantities of SrCO_3 , Y_2O_3 , CuO, and Ag_2O were ground together and heated in air at 840 °C for 24 h with one intermittent

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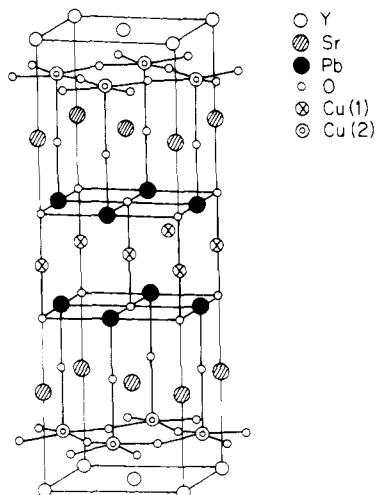


Figure 1. Structure of $\text{Pb}_2\text{Sr}_2\text{YCu}_3\text{O}_8$.

grinding. The resulting precursor mixture was mixed with the stoichiometric amount of PbO , pressed into pellets, heated in air for 1–3 h at 860°C and then quenched in liquid nitrogen. The Ag is present as elemental Ag in the precursor. This procedure yielded polycrystalline products that were found to be single-phase $\text{Pb}_2\text{Sr}_2\text{YCu}_{3-x}\text{Ag}_x\text{O}_8$ by X-ray powder diffraction. The limiting composition for silver substitution in air was $x = 0.55$; more silver-rich compositions afforded a mixture of $\text{Pb}_2\text{Sr}_2\text{YCu}_{2.45}\text{Ag}_{0.55}\text{O}_8$, metallic silver, and a Pb(IV) -containing perovskite with lattice parameters similar to those of SrPbO_3 . Air appears to be a nearly optimal atmosphere in which to prepare the silver-substituted phases; formation of metallic silver is facilitated in more reducing atmospheres with the result that very little silver substitution ($x < 0.2$) could be achieved in 1% O_2/N_2 or 4% O_2/N_2 . On the other hand, significant oxidation of the silver-substituted phases to Pb(IV) -containing perovskites occurs in more O_2 -rich atmospheres at 860°C . Unsuccessful attempts were also made to achieve substitution of Au^+ , Pd^{2+} , or Pt^{2+} (all of which favor linear coordination in oxides) for the Cu(1) in $\text{Pb}_2\text{Sr}_2\text{YCu}_3\text{O}_8$ by reacting PbO with precursor mixtures containing powdered Au, PdO , or PtO_2 in place of some of the CuO . No reaction was observed with gold, whereas the palladium and platinum precursors reacted with PbO to give complex mixtures.

The silver-substituted compounds $\text{Pb}_2\text{Sr}_2\text{YCu}_{3-x}\text{Ag}_x\text{O}_8$ slowly absorb oxygen when heated at 500°C in pure O_2 ; oxygen uptake is accompanied by an expansion of the c axis. For $x = 0.5$, 1.0 equiv of O are absorbed and the unit cell of the product is $a = 5.40 \text{ \AA}$, $b = 5.43 \text{ \AA}$, $c = 16.06 \text{ \AA}$; a small amount of Pb(IV) perovskite is also present in the product. A detailed account of the thermal analysis of $\text{Pb}_2\text{Sr}_2\text{YCu}_{3-x}\text{Ag}_x\text{O}_8$ in different O_2 partial pressures forms part of a separate paper.⁶ The thermal stability of the silver-substituted compounds $\text{Pb}_2\text{Sr}_2\text{YCu}_{3-x}\text{Ag}_x\text{O}_8$ in air is remarkable; among silver oxides it is exceeded only by the thermal stability of the perovskites AgNbO_3 and AgTaO_3 . Comparison of the extent of Ag substitution in this phase with that for $\text{Ba}_2\text{YCu}_{3-x}\text{Ag}_x\text{O}_6$ suggests that the PbO layers facilitate the stability of Ag^+ in this structure. Interestingly, two relatively stable silver plumbates, Ag_2PbO_2 and $\text{Ag}_5\text{Pb}_2\text{O}_6$, have been known for many years.⁷

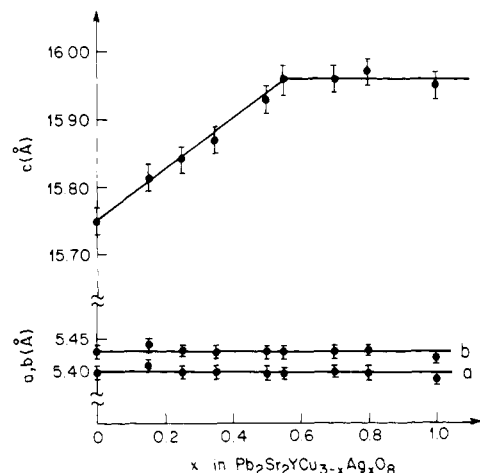


Figure 2. Lattice parameters of $\text{Pb}_2\text{Sr}_2\text{YCu}_{3-x}\text{Ag}_x\text{O}_8$ as a function of x .

The X-ray powder diffraction data for $\text{Pb}_2\text{Sr}_2\text{YCu}_{3-x}\text{Ag}_x\text{O}_8$ ($0 \leq x \leq 0.55$) are summarized in Figure 2. The c lattice parameter increases approximately linearly with x over the whole range of silver substitution with no observable change in a or b . Expansion of the c axis is expected for silver substitution on the Cu(1) sites; the linearly coordinated Ag-O bonds in both Ag_2O and the silver delafossites are $\sim 0.2 \text{ \AA}$ longer than Cu-O bonds in the isostructural copper compounds. The observed intensities of the diffraction peaks in $\text{Pb}_2\text{Sr}_2\text{YCu}_{2.5}\text{Ag}_{0.5}\text{O}_8$ showed small changes from those in $\text{Pb}_2\text{Sr}_2\text{YCu}_3\text{O}_8$ consistent with intensities calculated for substitution on the Cu(1) site.

A number of attempts were made to substitute silver in the superconducting phases $\text{Pb}_2\text{Sr}_2\text{Y}_{1-y}\text{Ca}_y\text{Cu}_3\text{O}_8$ ($y \leq 0.5$). However, as already noted by Cava et al.,⁴ substitution of Ca for Y requires preparation under reduced oxygen partial pressures, typically 1% O_2/N_2 . At higher O_2 pressure formation of Pb(IV) -containing perovskites is seen. As discussed above, only small amounts of silver can be substituted for copper at low O_2 pressure; the limiting composition that could be prepared under 1% O_2/N_2 was $\text{Pb}_2\text{Sr}_2\text{Y}_{0.75}\text{Ca}_{0.25}\text{Cu}_{2.9}\text{Ag}_{0.1}\text{O}_8$. The resistivity of a sintered pellet of $\text{Pb}_2\text{Sr}_2\text{Y}_{0.75}\text{Ca}_{0.25}\text{Cu}_{2.9}\text{Ag}_{0.1}\text{O}_8$ measured as a function of temperature by a four-probe method shows a small negative coefficient of resistivity above 80 K and a broad superconducting transition below 80 K. Zero resistance (within instrumental accuracy) is reached at 15 K. Magnetic flux-exclusion measurements performed on a sintered rod of $\text{Pb}_2\text{Sr}_2\text{Y}_{0.75}\text{Ca}_{0.25}\text{Cu}_{2.9}\text{Ag}_{0.1}\text{O}_8$ cooled to 4.2 K gave a superconducting volume fraction of $\sim 5\%$. The breadth of the superconducting transition, the negative normal-state temperature coefficient, and the low superconducting volume fraction can be attributed to chemical inhomogeneity of the sample; similar behavior is observed in ceramic samples of the other solid-solution superconductors $(\text{La,Sr})_2\text{CuO}_4$ and $\text{Pb}_2\text{Sr}_2\text{Y}_{1-y}\text{Ca}_y\text{Cu}_3\text{O}_8$ ($y \leq 0.5$). The tradeoff between synthesis conditions necessary for Ca substitution and Ag substitution does not allow both sufficient Ca to optimize superconductivity and significant silver substitution.

In summary, we have prepared phases of composition $\text{Pb}_2\text{Sr}_2\text{YCu}_{3-x}\text{Ag}_x\text{O}_8$ for $x \leq 0.55$. These silver oxides exhibit remarkable thermal stability in air, exceeding that of Ag_2O or the silver delafossites. We conclude that the PbO layers in $\text{Pb}_2\text{Sr}_2\text{YCu}_{3-x}\text{Ag}_x\text{O}_8$ play an important part in stabilizing Ag(I) in this structure. Small amounts of silver could also be substituted into the superconducting phase $\text{Pb}_2\text{Sr}_2\text{Y}_{0.75}\text{Ca}_{0.25}\text{Cu}_3\text{O}_8$ with little effect on its su-

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perconducting properties; this implies that the Cu(1) layers in this structure play little role in superconductivity.

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Third-Order Susceptibilities of Soluble Polymers Derived from the Ring-Opening Metathesis Copolymerization of Cyclooctatetraene and 1,5-Cyclooctadiene

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There is currently a substantial research effort devoted to the development of new organic materials with large cubic optical nonlinearities and to gaining insight into the fundamental factors that lead to large optical nonlinearities.¹⁻³ Recent experimental⁴⁻⁶ and theoretical⁷⁻⁹ studies indicate that extended conjugation leads to large cubic susceptibilities. It would be desirable to develop general methodologies¹⁰⁻¹² for the synthesis of new materials that combine the electronic properties arising from extended conjugation and the processability advantages generally associated with polymers. Ring-opening metathesis polymerization represents a promising new route to materials with large third-order optical nonlinearities since inherent in the mechanism of the reaction is the *preservation of the degree of unsaturation present in the monomer*. This is in contrast to many radical, cationic, anionic, and Zie-

gler-Natta polymerizations in which an olefinic monomer will usually lead to a polymer with a fully saturated backbone.

We wish to report some preliminary results on the nonlinear optical properties of a new class of polymers synthesized by the ring-opening metathesis polymerization of highly unsaturated monomers. Mixtures of cyclooctatetraene, 1, and 1,5-cyclooctadiene, 2, have been polymerized by using the tungsten carbene complex 3 as the catalyst¹³ (see Figure 1). The solution polymerization of monomers 1 and 2 in tetrahydrofuran leads to an essentially random copolymer.¹⁴ The monomers contain exclusively cis double bonds and no attempt has been made to isomerize the double bonds in the resulting polymer. The general constitution of the copolymers is also shown in Figure 1 (an all-trans geometrical configuration is shown for simplicity).

The polymerizations of mixtures of 1 and 2, where the mole fraction of 1 was varied from 0.10 to 0.50, were typically performed as described in the following procedure. The monomer mixture (100 μ L, \sim 0.85 mmol) in 400 μ L of a tetrahydrofuran solution containing 8.0 mg (0.01 mmol) of 3 was allowed to react for 6 h. Then 1200 μ L of a tetrahydrofuran solution containing 36 mg (0.42 mmol) of (CH₃)₃CC(O)H, which destroys the catalyst,¹³ and 24 μ L (0.17 mmol) of mesitylene, an internal standard for gas chromatographic studies (vide infra), was added. After quenching, examination of the reaction mixture by gas chromatography allowed us to determine the number of moles of cyclooctatetraene and 1,5-cyclooctadiene incorporated into the polymer.¹⁵

The optical spectra of the copolymer solutions (an example of which is shown in Figure 2) provide insight into the conjugation lengths present. On the basis of previous studies of polyenes¹⁶ and conjugated polymers¹⁷ we would assign the bands at 316, 332, and 344 nm to segments of the polymer with 5 conjugated double bonds, bands at 384, 404, and 432 nm to segments of the polymer with 9 conjugated double bonds, and bands at 432, 464, and 496 nm to segments of the polymer with 13 conjugated double bonds. The segments with 5, 9, and 13 double bonds arise from incorporation of one, two, or three consecutive cyclooctatetraene monomers, respectively, into the polymer. In the copolymers that we have examined the distribution of conjugation lengths is dominated by the 5 double-bond segments with a significant amount of 9 double-bond segments, but there are quite few segments with 13 or more double bonds. From the variation of the solution spectra with monomer composition we can say that there is an *increase in both the percentage of olefinic carbons and the average conjugation length in the polymer as the percentage of cyclooctatetraene in the monomer mixture increases* as was seen in the previously reported copolymer films.¹⁴

Nonlinear optical properties of the polymer mixtures were studied as a function of the composition. The third-order susceptibilities of the copolymer solutions were determined by using wedged-cell third-harmonic generation (THG) techniques.^{18,19} The 1.907- μ m Raman shifted (H₂ gas) output from a Q-switched Nd:YAG laser was used

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