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Magnetorheological finishing (MRF) of potassium dihydrogen phosphate (KDP) crystals: nonaqueous fluids development, optical finish, and laser damage performance at 1064 nm and 532 nm

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ABSTRACT

Over the past year we have been working on specialized MR fluids for polishing KDP crystals. KDP is an extremely difficult material to conventionally polish due to its water solubility, low hardness, and temperature sensitivity. Today, KDP crystals are finished using single-point diamond turning (SPDT) tools and nonaqueous lubricants/coolants. KDP optics fabricated using SPDT, however, are limited to surface corrections due to tool/method characteristics with surface quality driven by microroughness from machine pitch, speed, force, and diamond tool character. MRF polishing offers a means to circumvent many of these issues since it is deterministic which makes the technique practical for surface and transmitted wavefront correction, is low force, and is temperature independent. What is lacking is a usable nonaqueous MR fluid that is chemically and physically compatible with KDP which can be used for polishing and subsequently cleaned from the optical surface. In this study, we will present the fluid parameters important in the design and development of nonaqueous MR fluid formulations capable of polishing KDP and how these parameters affect MRF polishing. We will also discuss requirements peculiar to successful KDP polishing and how they affect optical figure/finish and laser damage performance at 1064 nm and 532 nm.

Keywords: Optical finishing, computer numerical control, magnetorheological finishing, KDP, MRF, nonaqueous MR fluids, carbonyl iron, magnetorheological fluids

1. INTRODUCTION

Optically finished single crystals of KDP comprise a class of specialty optics used in solid-state laser systems as optical frequency conversion and polarization electro-optical switching media. This material, however, presents unique challenges to the processes required to fabricate ultra-precision optical elements, particularly those used in high-fluence environments of Megajoule-class inertial confinement fusion (ICF) laser systems.[1,2,3] KDP crystals are extremely difficult to grow, especially in large sizes of ~60 cm on edge, due to the introduction internal lattice imperfections that affect material performance and optical wavefront characteristics. Furthermore, once high-aspect ratio (40:1, or better) optical plates are harvested from the single crystal boules, polishing is difficult to accomplish using conventional pitch-lapping techniques. KDP optics are very soft (Mohs hardness of 2.5), thermally sensitive, prone to fracture, and scratch easily. KDP has further complication in that it is hygroscopic and extremely water soluble (33g per 100 ml), thus requiring nonaqueous polishing media.[4]

Today, single-point diamond turning (SPDT) is considered state-of-the-art for KDP finishing,[5] and over the years, the process has advanced to the point where it is capable of producing 43 x 43 cm flat single crystal optical plates. Though highly successful, SPDT, by design, is limited to producing a flat surface on each of the KDP optical faces which results in having to select a crystal blank having bulk homogeneity properties adequate for production of an acceptable final optic. Moreover, one essentially has to live with the bulk crystal inhomogeneities that are present in the final optic and the resulting wavefront. The SPDT process is only capable of yielding surfaces with 1.0 to 3.0 nm rms microroughness which leads to an optical surface finish performance disadvantage when compared to other optic types, such as fused silica, where 0.2-0.5 nm rms microroughness is typical. This microroughness is driven by machine pitch, speed, force, and diamond tool character. Mounting fixture and SPDT tool marks can also be problematic in these single crystal optics, particularly when used in high-fluence laser applications since they comprise a set of surface flaws that can damage and limits the optic's usable life. There has also been a resurgence of investigations in conventional lapping[6] and ultra-precision grinding[7] of KDP that attempt to provide alternatives to SPDT to produce super-polished single crystal surfaces. Here, the conventional lapping studies focus upon material removal and surface quality using processes similar to that studied by Fuchs.[8] These techniques, however, have disadvantages that impact single crystal KDP optic performance, namely embedding of abrasives and contamination that are difficult, if not impossible, to remove.

Advanced MRF technology can offer a new and novel means of finishing water-soluble crystals such as KDP with optical properties superior to what is available today. MRF is a deterministic polishing process; that is, the end result can be predicted and repeatedly achieved. Product quality and repeatability is easily attained using MRF while providing a quantum leap in throughput, productivity, yield, and cost effectiveness by replacing the art of optic polishing with science and technology.[9,10] Previous MRF work on KDP conducted by Jacobs, et al,[11] showed that MRF removal functions, or spots, could be made on KDP single crystal surfaces using nonaqueous fluid carriers. The work, however, did not address key aspects of the nonaqueous fluids that are unique to polishing KDP, such as pH, water content, or the interaction of the carrier with the carbonyl iron media and crystal substrate. Further work in this area is absent in the literature, and there has not been a demonstration that MRF polished KDP surfaces could be adequately and consistently polished and subsequently cleaned. Overall, this technological gap had led us to pursue a better understanding of the details of KDP MRF polishing with the objective of formulating a usable nonaqueous MR fluid that is chemically and physically compatible with KDP.

In this study, we will discuss the fluid parameters important in the design and development of nonaqueous MR fluid formulations capable of polishing KDP and how these parameters affect MRF polishing optical figure/finish and subsequent cleaning. In particular, we will touch upon a number of nonaqueous MR fluid characteristics that require attention and control. These characteristics include: 1) carrier liquid type, 2) fluid stabilizer compatibility, 3) intentional or environmental water content, 4) carrier liquid content, and 5) fluid pH. We will also discuss the results of laser damage performance at 1064 nm and 532 nm on MRF polished KDP samples.

2. MR FLUID DESIGN

2.1 Background on aqueous MR fluids

Magnetorheological fluids are generally composed of non-colloidal suspensions of 1-5 μm diameter magnetizable particles in carrier fluids.[12,13] These particles are manufactured via thermal decomposition of iron pentacarbonyl into species known as carbonyl iron powder or spheres[14]. The particles are magnetically polydomain; that is, they possess no overall intrinsic magnetic moment. They, however, attain large magnetic moments when placed into a magnetic field which leads to the alignment of the particles into long columns or chains. This alignment is responsible for the rheological activity of the fluid, namely its yield strength and viscosity. These characteristics make the fluid media amenable to MRF polishing, the details of which can be found elsewhere.[9] Developed and commercially available MRF polishing fluids are aqueous formulations composed of four components:[15,16] 1) magnetizable particles (carbonyl iron spheres), 2) carrier liquid (water), 3) stabilizers required to inhibit oxidation of iron and to prevent particle agglomeration (e.g., glycerol and sodium carbonate), and 4) abrasives (e.g., nano-diamonds or ceria). Typical aqueous formulation recipes consist of ~15 % water, ~77 % carbonyl iron, ~6 % abrasives, and ~1 % stabilizers by weight (Figure 1). Water content is adjusted to about 15% depending upon polishing application to optimize the MRF

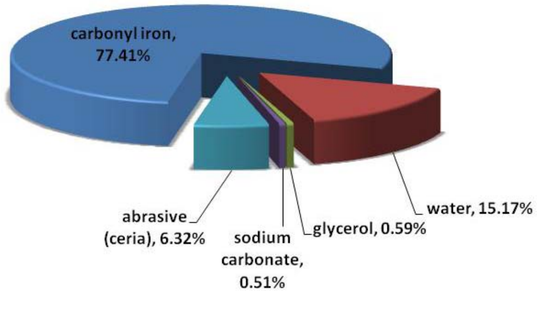


Figure 1: Aqueous MR fluid composition by weight percent. Water content is slightly adjusted to obtain desired viscosity.

operating conditions, such as fluid viscosity and removal function volumetric material removal activity and shape. The carbonyl iron spheres provide the backbone of the MRF removal function, or polishing spot, under the influence of a magnetic field in the MRF polishing zone and the abrasive in the fluid performs polishing. The carbonyl iron spheres are manufactured in a variety of grades and sizes of which the "soft" grade (reduced under hydrogen atmosphere) of 3 μm average particle size is preferable for optical polishing applications. Ceria or nano-diamond abrasives are used in particular formulations to make MRF polishing compatible with a wide array of glass and crystal types. For example, ceria MR fluid works well on fused silica and BK7 substrates while nano-diamond MR fluid is preferred for phosphate glass or crystal and sapphire. The carrier liquid, in this case water, is used due to its compatibility with the glass types being polished. Addition of stabilizers and adjustment of pH to 10 protects the carbonyl iron from severe oxidation (rusting) via reaction with water and air in addition to minimizing, or eliminating, particle agglomeration that can occur at low pH which result in scratching during polishing.

2.2 Nonaqueous MR fluid design considerations

During design of nonaqueous MR fluids for polishing KDP, we considered formulations containing at least four components that are compatible with KDP, the MRF process, and the MRF tool (Figure 2). The components include a nonaqueous carrier liquid, carbonyl iron spheres, a stabilizer, and a chemical buffer. In general, the fluid formulations contain organic carrier liquids and organic and inorganic stabilizers unique to KDP MRF polishing. First, selection of a carrier liquid for KDP MRF polishing requires that the carrier be nonvolatile, or have low volatility, since it is hydrocarbon based. It should also be nonflammable at room temperature with a high flash point, resistant to a potentially corrosive environment, unreactive with the carbonyl iron, KDP, and MRF machine components, have low or no toxicity, viscosity in the range of 10-20 cP, and, lastly, not be capable of dissolving or adversely affecting the optical surface of KDP single crystal optics. Table 1 lists the types of carrier liquid candidates considered during our fluid design.

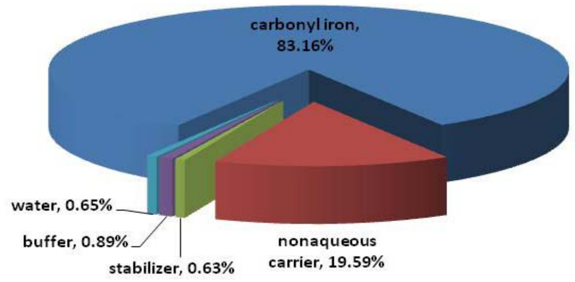
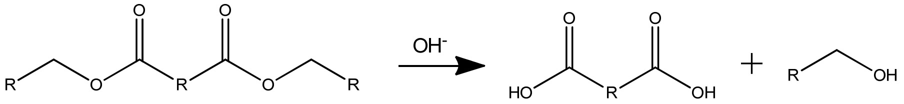


Figure 2: Nonaqueous MR fluid composition by weight. Carrier content is slightly adjusted to attain desired viscosity.

Table 1: Nonaqueous MR fluid carrier liquid candidate types.

Organic carrier liquid candidate type	Design comments and considerations
Hydrocarbons	Used in SPDT. Difficult to clean off of MRF components.
Alcohols	Short chain species are hydrophilic and dissolve/stain KDP. Long chain species are hydrophobic and can be difficult to clean off parts and MRF tool.
esters / diesters **(e.g. dicarboxylic acid esters)**[11]	Low toxicity. React to form acids and alcohols at moderate to high pH. Stain KDP via acid-base reaction. Adversely react with carbonyl iron. Can adversely affect machine seals/components/paint.
halogenated hydrocarbons	Too toxic to consider. Many are highly flammable, and volatile. Can adversely affect machine seals/components/paint.
nitrogen compounds / amines	Volatile and have odor problems. Can be toxic.
polyfunctional compounds **(e.g. alkoxy alcohols)**	Long chain species with hydrophilic and hydrophobic groups/ends. Can be water soluble. Easy to clean off parts and MRF components. Inert in carbonyl iron and stable at moderate to high pH.

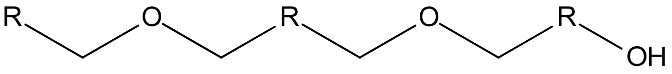
Of the different candidate carrier liquid types considered, dicarboxylic acid esters, long chain alcohols, and long chain alkoxy alcohols possess attributes that potentially make them amenable further investigation. Dicarboxylic acid ester carrier fluids[11], although compatible with KDP in neat form over a short time interval, react with KDP and carbonyl iron. They also undergo reaction at moderate to high pH yielding the dicarboxylic acids and alcohols according to Reaction 1.



1)

Alcoholic products, containing four or less carbons, will cause staining of KDP via dissolution reaction, water absorption, and evaporation. The dicarboxylic acid products are bidentate species that can react with the carbonyl iron creating a coating around the spheres. They can further react with KDP through acid-base reactions. More importantly, the spheres become incompatible with the carrier fluid because of improper stabilization and agglomerate resulting in scratching, pitting, and staining during polishing and optic cleaning. This will be clarified further in the discussion below when we talk about the need to have a proper stabilizer in the nonaqueous MR fluids. Long chain alcohols carrier fluids, like the dicarboxylic acid esters, are compatible with KDP in neat form as long as the organic chain length is four carbons or greater. Shorter carbon length alcohols lead to rapid evaporation and water condensation on the crystal leading to staining during polishing and optic cleanup. There is also a potential of flammability for these species since vapor pressures can be high. Longer carbon chain length alcohols tend to become very hydrophobic which makes optic and MRF tool cleanup difficult. They are, however stable at moderate pH values making them compatible with the carbonyl iron. More work needs to be done in this area to determine the impact of carbon branching and carbon chain length on this carrier fluid type's potential from the polishing, and machine and crystal cleaning perspectives.

Polyfunctional compounds, such as alkoxy alcohols (Equation 2), represent a class of organic compounds that have both hydrophilic and hydrophobic functional groups making them compatible with both hydrocarbon and aqueous solvents. The hydrocarbon chains promote solubility in hydrocarbon solvents. The alkoxy and alcohol functional groups provide solubility in water via hydrogen bonding. As a nonaqueous MR fluid carrier, these compounds have little to no volatility and are inert to reactions with KDP and carbonyl iron. They are also stable in moderately acidic and basic environments. Crystal cleanup after polishing can be readily accomplished by rinsing with the liquid in neat form followed by rinsing with toluene or xylene. They have no effect on the MRF components and the MRF tool can be cleaned using soap and water in a fashion similar to that used in aqueous MR fluid systems.



2)

2.3 Nonaqueous MR fluid stabilizers

Stabilizers are necessary ingredients in MR fluids to minimize interaction between the magnetic particles.[13,14] The carbonyl iron particle surfaces are highly polar and contain several functional groups that can interact through van der Waals forces, electrostatic forces, or combine via chemical reaction when placed into a carrier liquid leading to flocculation or agglomeration. In severe cases, the fluid separates into distinct phases containing large particle aggregates and carrier. For nonaqueous MR systems, the issue is compounded by the fact that the carrier fluids are sufficiently nonpolar and do not protect the carbonyl iron particles from directly contacting and reacting. From the MRF polishing standpoint, this results in an undesirable response in the MRF system ranging from instabilities in the MRF removal function to scratching of optical surfaces. MR stabilizers, or coupling agents, are long chain molecules with polar carboxyl, hydroxyl, or amino functional groups located on one end and nonpolar hydrocarbon groups at the other. Common examples of classical stabilizers are oleic or stearic

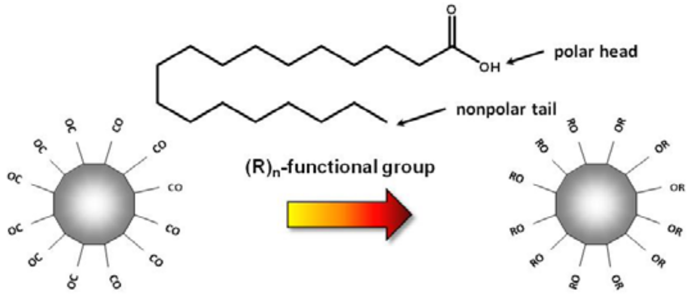


Figure 3: General reaction of polar head group on stabilizer compound, e.g. stearic acid, with carbonyl iron surface forming a protective monolayer. The nonpolar tail resembles the carrier liquid.

acid. Addition of a stabilizer compound to the MR fluid results in chemical or physical bonding between the stabilizer's polar end and the carbonyl iron particle surface forming a tightly bound monolayer around each particle. This monolayer protects the particles from interacting through steric repulsion. Since the long stabilizer chain fragment resembles the polarity of the carrier liquid, the carrier liquid is able to form a solvation boundary around this monolayer further protecting the particles from interaction. In short, MR stabilizers bond with the carbonyl iron particles in the fluid making them compatible with the carrier and neighboring particles. Optimal performance of the stabilized fluid occurs when complete monolayer coverage of each particle is realized. Incomplete coverage results in particle interaction, aggregation, and precipitation. Use of stabilizer in excess impacts the viscosity of the system. A simple geometric model can be used to estimate the amount of stabilizer needed to create a monolayer around the carbonyl iron present in the fluids expressed at a weight ratio, k_{wt}, of carbonyl iron to stabilizer based upon the carbonyl iron particle diameter, d_{ci}, the length of the stabilizer chain, d_{st}, and the densities of the carbonyl iron, ρ_{ci}, and stabilizer, ρ_{st} (Equation 3).

$$k_{wt} = \frac{\rho_{ci} d_{ci}^{3}}{\rho_{st}\left(\left(d_{ci}+2\,d_{st}\right)^{3}-d_{ci}^{3}\right)} \qquad 3)$$

2.4 Water content in nonaqueous MR fluids used for KDP polishing

KDP solubility in water at room temperature is a function of pH; going from 33 g per 100 grams water pH ~5 to a four-fold increase at pH ~8.[4] One of our initial concerns with formulating nonaqueous fluids for KDP MRF polishing was atmospheric absorption, or condensation, of water into the MR fluid which could lead to deleterious effects on polishing and staining on the optic. Since the solubility of KDP in water is so large, environmental water absorption could pose a real challenge to making a successful nonaqueous fluid and could potentially cause issues since the MRF polishing is, by definition, a sub-aperture polishing process. MR fluid carrier residues are always present on the areas of an optic that have been polished and remain there until the entire surface has passed under the MRF removal function. In initial KDP experiments, MRF polishing was performed using anhydrous carrier fluids and we found that the anhydrous fluids cannot support the KDP that was removed from the crystal surface. The KDP removed from the crystal surface precipitates and re-crystallizes in areas within the MRF polishing zone. An example of this phenomenon is shown in Figure 4. The vertical scanning white light interferograms show the topographic nature of the deposits and the MRF sleeking that occurs downstream. The sleeking indicates that the precipitation occurs during polishing while the material is still within the removal function boundary as opposed to later times when the area simply contains fluid residue from previous sub-aperture MRF polishing. Furthermore, the deposits attach to the crystal surface and become part of the crystal making them impossible to remove. Scanning electronic microscopy X-ray analysis performed on the KDP sample confirms the deposits are KDP, K_2HP, or K_3P. It is not surprising that KDP deposits onto the crystal surface when using a fluid for polishing in which it has no solubility. This is peculiar to KDP and stems from the near room temperature, supersaturated solution crystallization process from which it is grown.

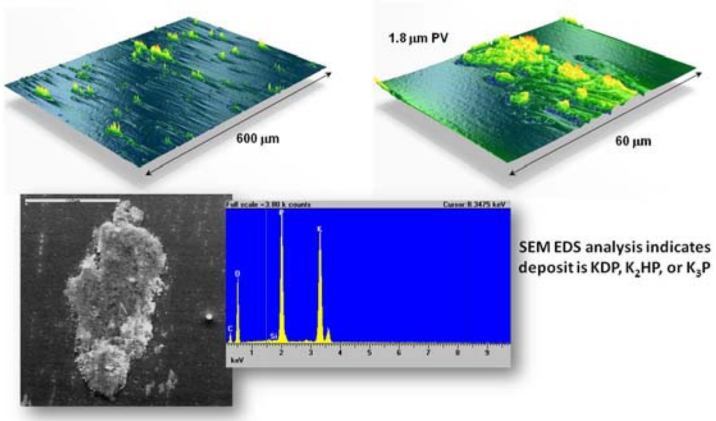


Figure 4: VSI interferogram of re-deposited KDP on crystal surface after MRF polishing with anhydrous MR fluid (top). SED analysis confirms deposits at KDP-like species (bottom).

A small amount of water added to the MF fluid eliminates KDP precipitation and, as such, becomes a crucial component in the nonaqueous MR fluid formulations for KDP polishing. The nonaqueous MR fluid can contain up 10 % water by weight without deteriorating the crystal surface quality and actually enhances controllable material removal, as shown in Figure 5. Water at these low levels is miscible in the alkoxy alcohol carrier fluid and does not concentrate on the KDP surface. Since the fluid has low volatility, there is also little risk of water concentration due to fluid evaporation as one finds if short carbon chain alcohols are used. The large solubility of KDP in water, particularly at moderate pH, makes it possible to keep the MR fluid water content low and still maintain the ability of the fluid to function without promoting precipitation. For example, a nonaqueous MR fluid containing 4 grams of water (~0.6 wt %) per 3 kilograms of carbonyl iron would be capable of supporting 5 grams of KDP. In polishing terms, this amounts to 11.7 cm^3 of KDP that can be removed! For a 43 x 43 cm crystal plate, this equates to 63 μm of material removal which is a factor a 20 greater than that required to perform damage removal and figure correction. If only figure correction is required, the factor approaches 100.

Water in the nonaqueous MR fluid also enhances the peak and volumetric removal rates derived from the MRF removal function. Within the water content operating envelope of 0 to 10 wt % water, the volumetric removal rate linearly increases by about a factor of 4 with peak removal linearly increasing by a factor of 2. These removal rates are similar to the rates obtained on MRF polished fused silica using aqueous MRF fluids and a 50 mm MRF wheel. Beyond 10 wt % water, the MRF removal functions begin to become uncontrollable with increasing nonlinear removal rate behavior and the crystal surfaces begin to sleek and scratch due to significant interaction/dissolution of the KDP and entrapment of carbonyl iron particles at the polishing zone/crystal interface.

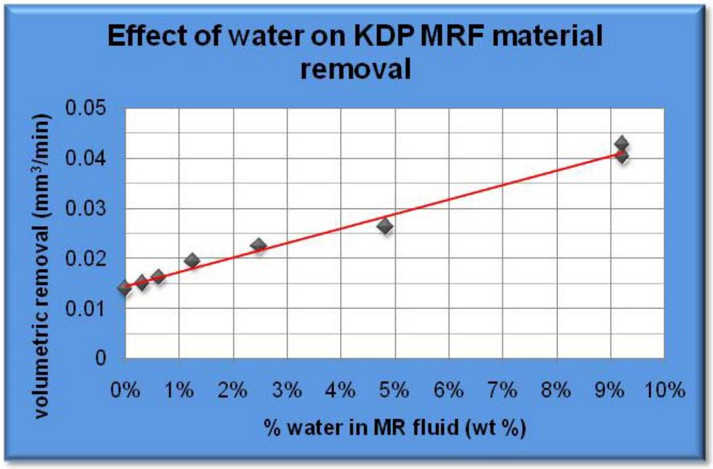


Figure 5: Water content influences the MRF volumetric material removal rate in a controllable and predictable manner within the KDP polishing operating bandwidth.

2.5 Carrier fluid content in nonaqueous MR fluids and its effect on microroughness

The amount of carrier, or liquid content, in the fluid is one of the main variable parameters that is controlled and held constant during the course of a MRF polishing run. The liquid content of the MR fluid largely establishes the plastic viscosity of the fluid system, and thereby, sets the shear stress within the MRF removal function that is responsible for polishing action when an optic is immersed into the magnetically modified MR ribbon moving at the rotational speed of the MRF wheel.[17] In an aqueous MR fluid system, fluid content is controlled by viscosity computed from the flow rate and pressure monitored in the MR fluid by adding water drop-wise to the mixing tank if the viscosity is too high. Evaporation of water from the fluid continuously occurs and is used to increase the viscosity of the fluid if necessary by slowing or stopping water addition. This can be a source of polishing error, particularly during long MRF polishing runs, since the evaporation characteristics of the system change when an optic is immersed into the MR ribbon. During polishing, the increased surface area of the ribbon in the polishing zone and the extraction of water from the ribbon onto the optic can lead to evaporation rate changes that alter the removal function’s properties if the MRF system viscosity feedback is not tightly controlled and quick enough to respond.

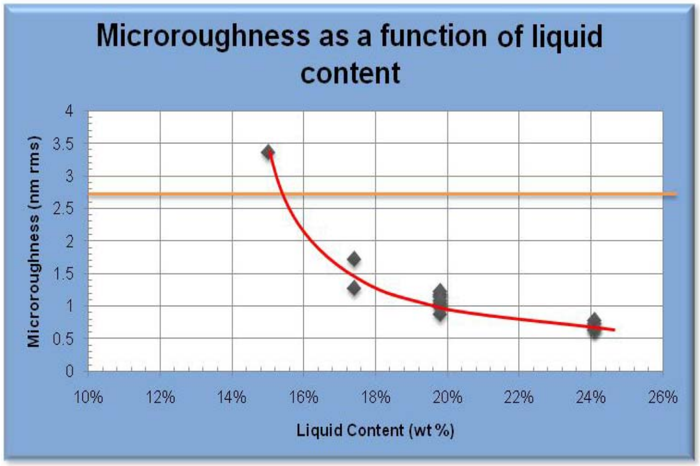


Figure 6: Influence and optimization of the nonaqueous MR fluid carrier content to minimize KDP surface microroughness. The horizontal line at 2.7 nm corresponds to the initial roughness of the SPDT surface being polished.

In contrast, the low volatility of the carrier fluid in a nonaqueous MR fluid system maintains the plastic viscosity of the fluid at the value established by the liquid content used during preparation which results in a very stable environment for polishing. A typical viscosity change on these systems is about 1-3 percent over a three week period. The low volatility of the carrier and the stability in the system is advantageous because viscosity control is not an issue and carrier fluid addition is not necessary. The MR carrier liquid content can be increased, and fluid plastic viscosity decreased, by simply adding carrier fluid to the MRF system mixing tank. Reducing the liquid content, or increasing the viscosity, is more difficult and requires the addition of high viscosity carbonyl iron/carrier liquid mixtures in the appropriate amount.

When used to polish KDP, the nonaqueous MR fluid's carrier liquid content plays a central role in the resulting surface microroughness. At the fluid/crystal interface, the MR fluid in the polishing zone is sheared with respect to fluid core which is moving at the speed of the wheel (unsheared flow). This essentially sets up shear stress responsible for polishing as the material flows through the polishing zone. The depth of the sheared fluid volume is dependent upon the plastic viscosity of the fluid. If the viscosity is too high, the depth of this zone is small and the crystal experiences polishing from the unsheared liquid resulting in increased surface roughness because of interaction with larger carbonyl iron agglomerates that are formed in the magnetically active zone. Increasing the liquid content of the fluid produces a depth increase in the sheared fluid volume which reduces the surface roughness to the point where it is driven by the size distribution of the carbonyl iron particles. This behavior is shown in Figure 6 where at 15 wt % carrier fluid content, the resulting KDP surface microroughness is larger than that of the starting SPDT surface microroughness of 2.72 nm rms. This indicates that the overall fluid viscosity is too high for KDP polishing as large MR particles are contacting the crystal surface due to core impingement. As the carrier fluid content in increased towards 20 wt %, the microroughness significantly improves and asymptotically approaches 0.65 nm rms at ~ 24 wt %. Representative KDP surface interferograms are shown in Figure 7, illustrating the effect of MRF polishing with an optimized carrier fluid content where the surface microroughness is improved to mid- to high- Angstrom rms values, similar to that observed on glasses, such as fused silica, polished with aqueous MR fluids. The interferograms show that the SPDT lines present on the initial KDP surface are removed during MRF polishing and replaced by much shallower MRF lines arising from the unidirectional flow of the MR fluid in the polishing zone.

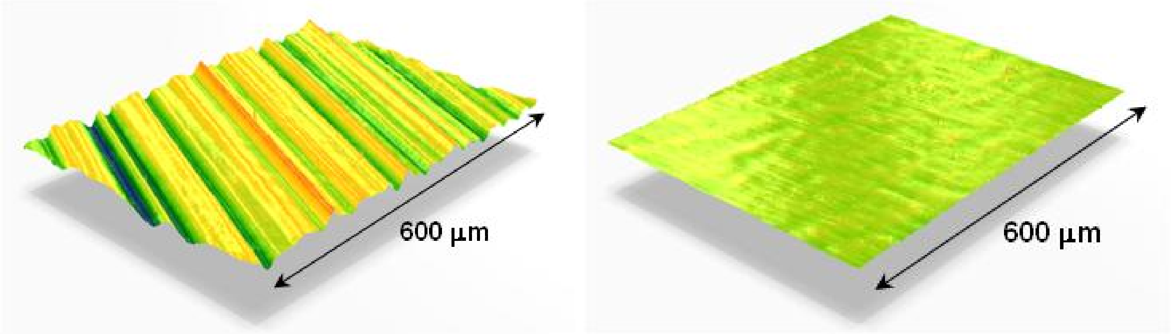


Figure 7: White light micro-phase-measuring interferograms of a KDP surface before and after MRF polishing. Left: SPDT KDP surface with a microroughness of 2.72 nm rms before MRF polishing. Right: MRF polished KDP surface with a microroughness of 0.65 nm, rms.

2.6 Nonaqueous MR fluid pH operating range

Fluid pH needs to be controlled in both aqueous and nonaqueous MR fluids when used for optic polishing. First, the fluid itself must have its pH maintained in an operating range to eliminate or minimize reaction of the carbonyl iron particles with the carrier fluid and the abrasives used, if present. Furthermore, the operating pH must be such that the carrier liquid does not deteriorate over time from acid-base reaction with species present in the polishing media. All polishing media possess some form of conjugate acid-base characteristics due to the fact that the species present in the system contain hydrolyzed or oxidized surface groups created during preparation and/or exposure to the environment (Figure 8). These groups undergo

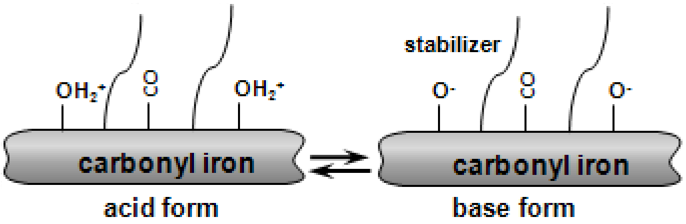


Figure 8: Acid and base forms of the carbonyl iron particle surface in an MR fluid. The acid form contains a net positive charge due to protonation of the hydrolyzed or oxidized surface groups. The base form contains a net negative charge due to stripping of protons from the particle's surface.

acid-base reaction depending upon fluid pH leading to a net surface charge, or zeta potential, on the particles in the media. In acid form, the surface of the particles possesses a net positive charge due to the protonation of the hydrolyzed or oxidized surface groups and solvation by the carrier. In base form, the particle surfaces have a net negative charge due to removal of protons by the basic environment. In MRF polishing, the fluid pH must be biased towards the basic form for two reasons. First, the carbonyl iron particles undergo oxidation reactions (rust) at low pH (pH < 6) yielding ferrous and ferric species that lead to particle agglomeration and settling. The large particle masses cause unacceptable surface quality during MRF polishing, namely scratches and pits. Second, a high pH environment promotes and maintains particle ionization, or negative zeta potential, resulting in electrostatic repulsion between particles that eliminates irreversible fluid agglomeration and scratching during polishing. For our nonaqueous MR fluids, the conjugate acid-base behavior of the particle surfaces can be described by a simple single-equilibrium model with a pK_a of 6.7 as determined by titration of the fluid with standardized base (Figure 9). The plot displays the titration data and the amount of acid and base forms present as a function of pH. At pH 6.7, a 50:50 mix of acid and base forms are present in the fluid and by pH 8.5, nearly all of the species are converted to base form. The reaction is reversible within a pH range of 6.5-12.5 as determined by acid back titration. Furthermore, the reaction involves surface modification of the carbonyl iron particles as evidenced by the amount of species titrated compared to the total amount present (4 millimoles titrated versus 0.5 moles carbonyl iron present). Overall, the nonaqueous MR fluid is stable above pH 6.5.

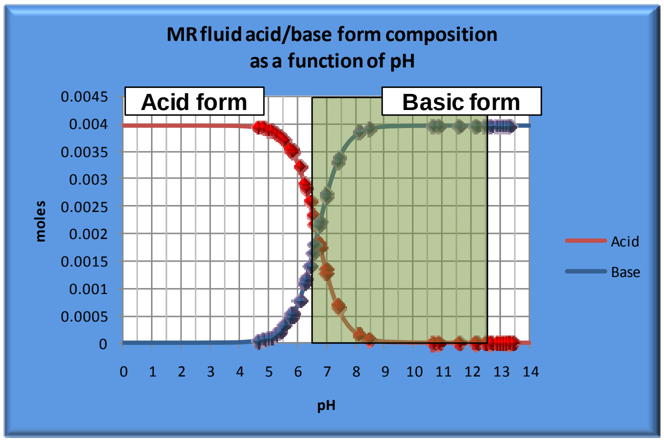


Figure 9: Nonaqueous MR fluids exist in conjugate acid-base forms that must be controlled to attain fluid stability during polishing. The basic form of the fluid is stable within a pH range of 6.5-12.5.

Another aspect of nonaqueous MR fluid pH that is peculiar to KDP crystal polishing and must be considered is the solubility of KDP, or to be more exact, the solubility of the predominant conjugate acid-base species present in the MR fluid at a particular pH. In solution, KDP forms conjugate acid-base pairs that are variations of phosphoric acid species depending upon the pH environment present as shown in Figure 10.

$$H_3PO_4 \rightleftarrows H_2PO_4^- \rightleftarrows HPO_4^{-2} \rightleftarrows PO_4^{-3}$$

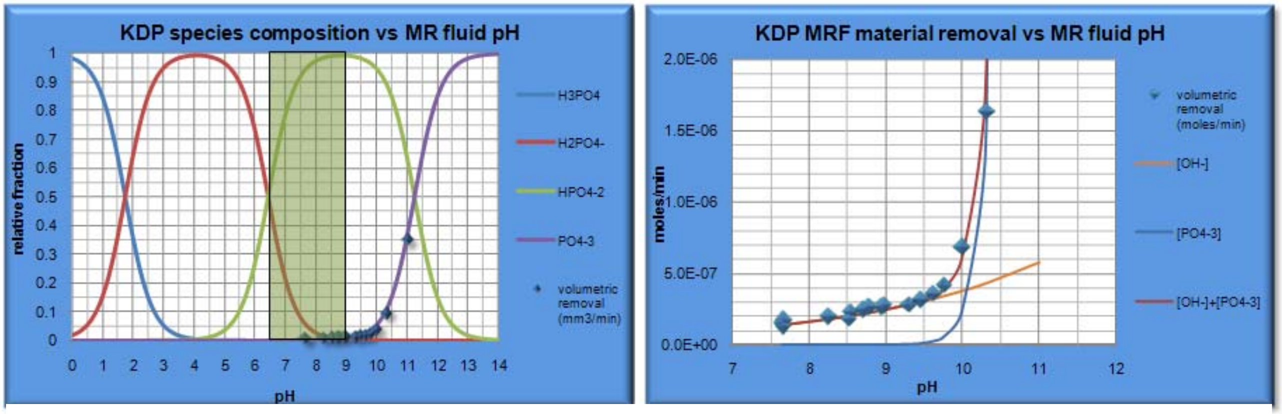


Figure 10: Dissolved KDP species composition as a function of the pH environment. Left: the KDP species relative fraction plot shows that the predominant species present in the usable pH range for MRF polishing is the hydrogen phosphate anion, HPO_4^{-2}. Right: at pH values above 9.5, MRF material removal on the crystal surface dramatically increases due to the formation of PO_4^{-3} in the polishing zone. Usable pH range is limited to 6.5-9.0.

At pH values above 6.5 where the nonaqueous MR fluid is stable, the predominant species present in the MRF polishing zone is HPO_4^{-2} or PO_4^{-3} as illustrated by the KDP species relative fraction plot. During tests to determine the usable pH range that can be used for MRF polishing, we found that material removal is controllable in the range pH 6.5-9.5 with volumetric and peak removal rates increasing almost linearly with pH. At pH above 9.5, however, KDP material removal dramatically increases and the removal functions become uncontrollable. This is due to the formation of significant quantities of PO_4^{-3} at the polishing interface. In fact, at pH values above 9.0, KDP dissolution at the polishing interface surface is too large and causes adhesion of MR fluid to crystal surface resulting in scratching during optic cleaning. Overall, the usable pH range for MRF polishing of KDP is restricted by the MR fluid stability and KDP species present. The usable pH range for KDP MRF polishing is pH 6.5-9.0.

Since KDP is also inherently acidic with a solution pH of 4.3, the MR fluid pH will change under use. Consequently, the removal function characteristics change over time since KDP material removal is pH dependent (Figure 10). To eliminate the effects of pH change due to amount of KDP added to the MR fluid over time, a buffer can be added to maintain fluid pH at a specified value. KDP and potassium hydroxide are suitable buffering agents[18] used to adjust the pH of the MR fluid. The function of these species as buffering agents is to drive the fluid to a certain pH state and prevent a change in this pH. The advantage of using these species in the nonaqueous MR fluid lies in the fact that they contain ions common to those already present during polishing. We selected a buffer pH target of pH 8 to add to the fluid to center the working pH within the usable envelope.

3. KDP POLISHING AND LASER DAMAGE TEST RESULTS

Beyond the design and optimization of nonaqueous MR fluids for MRF polishing of KDP, we performed polishing tests on two 50 x 50 x 10 mm KDP specimens that were previously finished using SPDT. The before and after MRF polishing surface interferograms are presented in Figure 11. The interferograms on the left show the incoming surface figure resulting from SPDT, one with a large peak-to-valley (P-V) of 1.02 μm and the other with a small P-V of 0.327 μm. The small spots within the interferogram apertures are from non-uniform tape adhesion on the rear surfaces of the KDP crystals. Vinyl protective tape is used on the rear surface to eliminate reflection from this surface in the surface interferogram. After single pass MRF polishing of the KDP crystal surfaces, the surface figure is improved by about 5

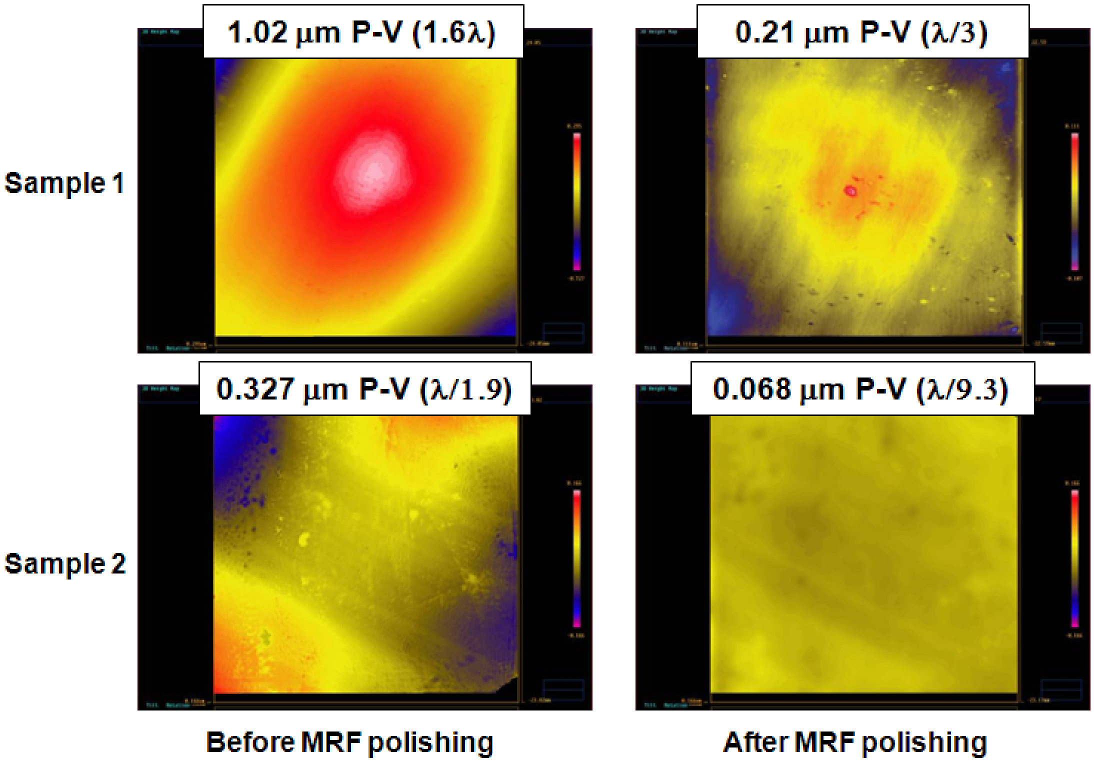


Figure 11: Surface interferograms of KDP samples before and after MRF polishing using nonaqueous MR fluids. Single pass MRF polishing improved surface figure by 5 times in both cases.

times, to 0.21 mm P-V and 0.68 mm P-V. This result is typical of the surface figure improvements made on a per pass basis using deterministic MRF polishing. Overall, the success of these polishing tests combined with the improvements in surface roughness made (Figure 7) shows promise for using MRF as a technique to final finish KDP crystals with improved optical figure and finish.

Laser damage tests in the infrared, 1064 nm, 10-ns equivalent, and in the visible, 532 nm, 7.5-ns equivalent, were conducted on several MRF polished KDP specimens to determine the influence of MRF polishing on damage performance versus that obtained using SPDT. Our basic goal for these tests is to obtain damage performance data indicating that the MRF polished surfaces are, at least, equivalent to damage performance obtained using SPDT with any improvements considered to be advantageous. In addition to a control sample that was SPDT finished only, the damage test samples included specimens that were MRF polished using carbonyl iron based fluids containing a) nonaqueous carrier fluid only (anhydrous), b) carrier fluid with water, c) carrier fluid, water, and stabilizer at neutral pH, and a final fluid containing d) carrier fluid, water, stabilizer, and a buffer set to control pH at pH 8. The results of these tests are listed in Table 2.

Table 2: Infrared and visible laser damage test results for SPDT and MRF polished KDP specimens.

Finish	Water	Surface damage threshold (J/cm²) @ 10 ns, 1064 nm	Surface damage threshold (J/cm²) @ 7.5 ns, 532 nm
SPDT (control)	No	20.1	12.0
MRF / carrier only	No	45.6	20.6
MRF / carrier only	Yes	51.1	20.6
MRF / stabilizer neutral	Yes	45.6	20.6
MRF / pH stable	Yes	98.5	25.3

The damage test results for all the MRF polished samples indicate that MRF polishing improves laser induced damage performance compared to SPDT by a factor of a 2.0-4.9 times in the infrared and by 1.6-2.1 times in the visible. Furthermore, optimization of the nonaqueous MR fluid, via addition of water, stabilizer, and pH shows a distinct increase in performance relative to the uncontrolled and unoptimized fluid formulations.

4. SUMMARY AND CONCLUSIONS

Successful polishing of KDP crystal surfaces using MRF techniques requires specifically tailored nonaqueous MR fluids compatible with both the magnetically active environment and the physical and chemical properties peculiar to KDP. Compatible nonaqueous carrier liquids that form the basis of these fluids must be able to support dissolved KDP and/or water to keep the KDP removed from the crystal surface during polishing from re-depositing back onto the crystal surface. Appropriate stabilizers must be used in the fluids to protect the carbonyl iron and the KDP crystal from reactions leading to fluid instability and particle agglomeration that produce poor surface finish from artifacts such as polishing induced scratches and digs. The fluid must also be maintained between pH values of 6.5-9.0 to eliminate surface oxidation, particle agglomeration, and uncontrollable KDP dissolution via acid-base reaction where significant quantities of PO_4^{-3} are produced. Nonaqueous MR fluid performance can be optimized to produce mid-Angstrom level microroughness on KDP surfaces by adjusting the carrier liquid content. Single pass MRF polishing tests conducted on 50 x 50 mm KDP crystal specimens show a factor of 5 improvement in surface figure indicating that the MRF polishing techniques can be successfully applied to final finish KDP crystals with improved optical figure and finish particularly when combined with improvements made in surface microroughness. Lastly, laser damage test results on MRF polished KDP specimens show a 2.0-4.9 times improvement in performance in the infrared and 1.6-2.1 times in the visible versus current SPDT finishing technology. **This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.**

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